Quantum Mechanics for Scientists and Engineers

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Tight binding and variational models
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Tight binding model
Coupled potential wells

Consider two identical potential wells separated by a finite barrier.
Solid state physicists would call the kind of approach we are going to use here a "tight-binding" calculation.
Coupled potential wells

We imagine two separate “unperturbed” potential wells. If we had the “left” potential well present on its own with potential $V_{\text{left}}(z)$, we would have the first wavefunction solution $\psi_{\text{left}}(z)$ with energy $E_1$, a problem we can solve.
Coupled potential wells

Similarly, if we considered the right potential well on its own with potential $V_{\text{right}}(z)$, we would have the wavefunction solution $\psi_{\text{right}}(z)$ which is the same as $\psi_{\text{left}}(z)$ except shifted to the right and it would have the same energy $E_1$. 
Coupled potential wells

The actual potential is $V(z)$ which we could call a coupled potential well.

Note we have chosen the origin for the potential at the top of the well so we can say

$$V(z) = V_{left}(z) + V_{right}(z)$$

simplifying the algebra.
Coupled potential wells

With our choice of energy origin the Hamiltonian for this system is

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V_{left}(z) + V_{right}(z) \]

We now solve using the finite basis subset model choosing the wavefunctions in the isolated wells

\[ \psi_{left}(z) \text{ and } \psi_{right}(z) \]

for our basis wavefunctions
Coupled potential wells

These two functions are approximately orthogonal if the barrier is reasonably thick. The basis wavefunctions are presumed relatively tightly confined in one well with little “leakage” into the adjacent well hence the term “tight-binding.”
Coupled potential wells

Hence the wavefunction can be written approximately in the form

$$\psi = a\psi_{\text{left}} + b\psi_{\text{right}}$$

We put this in vector form into our finite basis subset approximation of Schrödinger’s equation

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = E \begin{bmatrix} a \\ b \end{bmatrix}$$
Coupled potential wells

In this matrix form

\[
\begin{bmatrix}
H_{11} & H_{12} \\
H_{21} & H_{22}
\end{bmatrix}
\begin{bmatrix}
a \\
b
\end{bmatrix}
= E
\begin{bmatrix}
a \\
b
\end{bmatrix}
\]

we have, first,

\[
H_{11} = 
\int \psi^*_\text{left}(z) \left( \frac{-\hbar^2}{2m} \frac{d^2}{dz^2} + V_{\text{left}}(z) + V_{\text{right}}(z) \right) \psi_{\text{left}}(z) dz
\]
**Coupled potential wells**

Because we presume the barrier is relatively thick, the amplitude of $\psi_{left}(z)$ is $\sim$ zero inside the right well so the integrand

$$\psi_{left}^*(z)\left(\frac{-\hbar^2}{2m}\frac{d^2}{dz^2} + V_{left}(z) + V_{right}(z)\right)\psi_{left}(z)$$

is $\sim$ zero inside the right well.

Hence the term $\int \psi_{left}^*(z)V_{right}(z)\psi_{left}(z) \, dz$ can be neglected.
Coupled potential wells

Hence

\[ H_{11} \approx \int \psi_{left}^* (z) \left( -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V_{left} (z) \right) \psi_{left} (z) \, dz \]

\[ = E_1 \]

We can argue similarly for \( H_{22} \)

Hence

\[ H_{11} = H_{22} \approx E_1 \]
Coupled potential wells

For the same reasons
that \( \psi_{\text{left}}(z) \approx 0 \) in the right well
or that \( \psi_{\text{right}}(z) \approx 0 \) in the left well
when integrating within either well
we neglect all integrations

\[
\begin{align*}
\int \psi^*_{\text{left}}(z) V_{\text{right}} \psi_{\text{right}}(z) \, dz \\
\int \psi^*_{\text{left}}(z) V_{\text{left}} \psi_{\text{right}}(z) \, dz \\
\int \psi^*_{\text{right}}(z) V_{\text{right}} \psi_{\text{left}}(z) \, dz \\
\int \psi^*_{\text{right}}(z) V_{\text{left}} \psi_{\text{left}}(z) \, dz
\end{align*}
\]
Coupled potential wells

We retain the interaction within the (middle) barrier where the wavefunctions, though small, are presumed not negligible but neglect contributions from regions outside the barrier because one or other basis wavefunction is \( \sim \) zero there i.e., we retain a result

\[
\Delta E = \int_{\text{barrier}} \psi_\text{left}^* (z) \left( -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V(z) \right) \psi_\text{right} (z) dz
\]
Coupled potential wells

But inside the barrier, \( V(z) = 0 \)
so we have

\[
\Delta E = \int_{\text{barrier}} \psi_{\text{left}}^*(z) \left( -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \right) \psi_{\text{right}}(z) \, dz
\]

Note: \( \Delta E \) is a negative number here
because the second derivative
of \( \psi_{\text{right}} \) inside the barrier
is \( > 0 \)
Coupled potential wells

With these simplifications

\[
\begin{bmatrix}
H_{11} & H_{12} \\
H_{21} & H_{22}
\end{bmatrix}
\begin{bmatrix}
a \\
b
\end{bmatrix}
= E
\begin{bmatrix}
a \\
b
\end{bmatrix}
\]

becomes

\[
\begin{bmatrix}
E_1 & \Delta E \\
\Delta E^* & E_1
\end{bmatrix}
\begin{bmatrix}
a \\
b
\end{bmatrix}
= E
\begin{bmatrix}
a \\
b
\end{bmatrix}
\]

Note: $\Delta E$ in practice is typically real though we have left the complex conjugate for completeness.
Coupled potential wells

We find the eigenvalues of

\[
\begin{bmatrix}
E_1 & \Delta E \\
\Delta E^* & E_1
\end{bmatrix}
\begin{bmatrix}
a \\
b
\end{bmatrix}
= E
\begin{bmatrix}
a \\
b
\end{bmatrix}
\]

as usual by setting

\[
\det\begin{vmatrix}
E_1 - E & \Delta E \\
\Delta E^* & E_1 - E
\end{vmatrix} = 0
\]

i.e.,

\[
(E_1 - E)^2 - |\Delta E|^2 = E^2 - 2EE_1 + E_1^2 - |\Delta E|^2 = 0
\]

obtaining eigenvalues

\[
E = E_1 \pm |\Delta E|
\]
Coupled potential wells

Within the approximations here, the energy levels are split by the coupling between the wells symmetrically about the original "single-well" energy, $E_1$.

$$ E = E_1 \pm |\Delta E| $$
Coupled potential wells

Substituting eigenvalues \( E = E_1 \pm |\Delta E| \) back into
\[
\begin{bmatrix}
E_1 & \Delta E \\
\Delta E^* & E_1
\end{bmatrix}
\begin{bmatrix}
a \\
b
\end{bmatrix} = E
\begin{bmatrix}
a \\
b
\end{bmatrix}
\]
and solving for \( a \) and \( b \) gives us, after normalization

\[
\psi_a = \frac{1}{\sqrt{2}}(\psi_{\text{left}} - \psi_{\text{right}})
\]

\[
\psi_s = \frac{1}{\sqrt{2}}(\psi_{\text{left}} + \psi_{\text{right}})
\]
Coupled potential wells

The lower energy state is a symmetric linear combination of single-well eigenfunctions. The wavefunction has the same sign in both wells.

The upper energy state is associated with an anti-symmetric combination with opposite sign in the two wells.
Coupled potential wells

We can no longer view the states as corresponding to an electron in the "left" well or an electron in the "right" well.

In both states, the electron is equally in both wells.
Tight binding and variational models

The variational method
Variational method

Consider an arbitrary quantum mechanical state $|\phi\rangle$ of some system

The Hamiltonian of the system is $\hat{H}$ and we want the expectation value of the energy $\langle E \rangle$

Since the Hamiltonian is a Hermitian operator, it has some complete set of eigenfunctions $|\psi_n\rangle$ with associated eigenenergies $E_n$

We may not know what they are but we do know that they exist

(Here, we assume the eigenvalues are not degenerate)
Variational method

We can certainly expand any arbitrary state in the $|\psi_n\rangle$
so we can write as usual, for expansion coefficients $a_i$

$$|\phi\rangle = \sum_i a_i |\psi_i\rangle$$

We presume this is normalized, so $\sum_i |a_i|^2 = 1$

Hence, the expectation value of the energy becomes

$$\langle E \rangle = \langle \phi | \hat{H} | \phi \rangle = \sum_i |a_i|^2 E_i$$

We also presume we have ordered the eigenfunctions
in order of the eigenvalues, starting with the smallest, $E_1$
Variational method

From $\langle E \rangle = \langle \phi | \hat{H} | \phi \rangle = \sum_i |a_i|^2 E_i$

the smallest possible expectation value of the energy
that we can have for any state is $E_1$

with $a_1 = 1$ and all the other $a_i$ zero

If we made another expansion coefficient $a_j$ finite

then, using the normalization sum $\sum_i |a_i|^2 = 1$

the energy expectation value has to increase

$\langle E \rangle = |a_1|^2 E_1 + |a_j|^2 E_j = \left(1 - |a_j|^2\right) E_1 + |a_j|^2 E_j = E_1 + |a_j|^2 \left(E_j - E_1\right) > E_1$
Example of the variational method

We use our example problem of an electron in an infinitely deep potential well with applied field.

We use as our trial function:

an unknown linear combination of the first two states of the infinitely deep quantum well.

though variational calculations more commonly choose some function unrelated to exact eigenfunctions of any problem.
Example of the variational method

Hence, our trial function is

$$\phi_{\text{trial}}(\xi, a_{\text{var}}) = \frac{\sqrt{2}}{\sqrt{1 + a_{\text{var}}^2}} \left( \sin \pi \xi + a_{\text{var}} \sin 2\pi \xi \right)$$

where $a_{\text{var}}$ is the parameter we vary to minimize the energy expectation value.

Note that we have normalized this wavefunction by dividing by $\sqrt{1 + a_{\text{var}}^2}$.

We must normalize wavefunctions here because we use them to calculate expectation values.
Example of the variational method

The expectation value of the energy then becomes

$$\langle E(a_{\text{var}}) \rangle = \frac{1}{1 + a_{\text{var}}^2} \left[ \int_0^1 \left( \sqrt{2} \sin \pi \xi + a_{\text{var}} \sqrt{2} \sin 2\pi \xi \right) \right. $$

$$ \left. \times \left( -\frac{1}{\pi^2} \frac{\partial^2}{\partial \xi^2} + f(\xi - 1/2) \right) \left( \sqrt{2} \sin \pi \xi + a_{\text{var}} \sqrt{2} \sin 2\pi \xi \right) d\xi \right] $$

We can rewrite this using

$$ \int_0^1 \sin \pi \xi (\xi - 1/2) \sin 2\pi \xi d\xi = -\frac{8}{9\pi^2} $$

the known unperturbed eigenenergies

and the orthogonality of the sine functions
Example of the variational method

We obtain \( \langle E(a_{\text{var}}) \rangle = \frac{1}{1 + a_{\text{var}}^2} \left[ \varepsilon_1 \left( 1 + 4a_{\text{var}}^2 \right) - \frac{32a_{\text{var}}^2 f}{9\pi^2} \right] \)

To find the minimum, we take the derivative with respect to \( a_{\text{var}} \)

\[
\frac{d \langle E(a_{\text{var}}) \rangle}{da_{\text{var}}} = \frac{2}{9\pi^2} \left( \frac{16f a_{\text{var}}^2 + 27\pi^2 a_{\text{var}} - 16f}{(1 + a_{\text{var}}^2)^2} \right)
\]

which is 0 at the roots of the quadratic in the numerator.

The root that gives the lowest value of \( \langle E(a_{\text{var}}) \rangle \) is

\[
a_{\text{var min}} = \left[ -27\pi^2 + \sqrt{\left(27\pi^2\right)^2 + 1024f^2} \right] / 32f
\]
Example of the variational method

For $f = 3$ in our example, we find $a_{\text{var min}} \approx 0.175$

which compares with

0.174 from the finite basis subset method and
0.180 from the perturbation calculation

The corresponding energy expectation value

substituting the value of $a_{\text{var min}}$ back into $\langle E(a_{\text{var}}) \rangle$

is $\langle E(0.175) \rangle \approx 0.906$

which compares with

0.904 from the finite basis subset method and
0.9025 from the perturbation calculation