

9.1 Tight binding and variational models

Slides: Video 9.1.1 Tight binding model

Text reference: Quantum Mechanics for Scientists and Engineers

Section 6.5





Tight binding and variational models



Tight binding model

Quantum mechanics for scientists and engineers

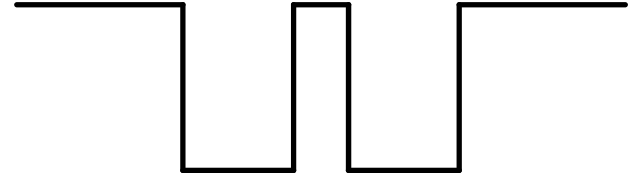
David Miller

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

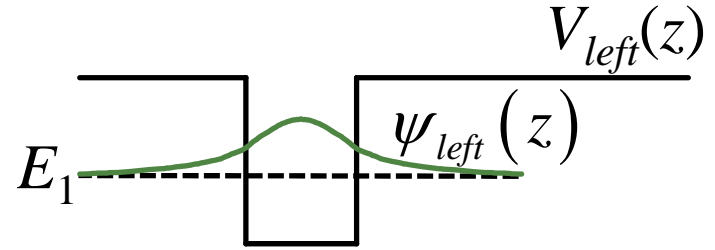
If we had the “left” potential well
present on its own

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

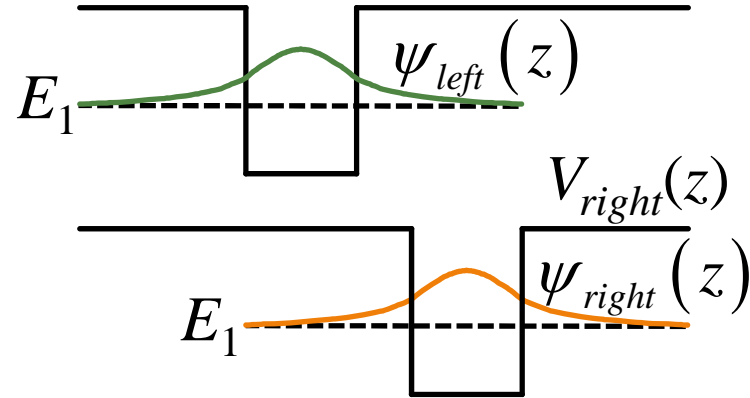
with potential $V_{right}(z)$

we would have the wavefunction solution $\psi_{right}(z)$

which is the same as $\psi_{left}(z)$

except shifted to the right

and it would have the same energy E_1



Coupled potential wells

The actual potential is $V(z)$

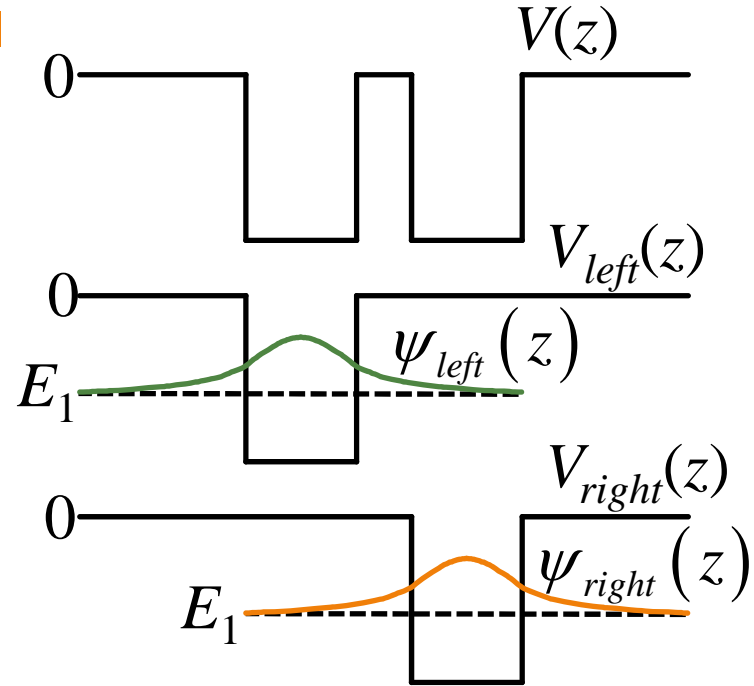
which we could call a coupled potential well

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

so we can say

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

simplifying the algebra



Coupled potential wells

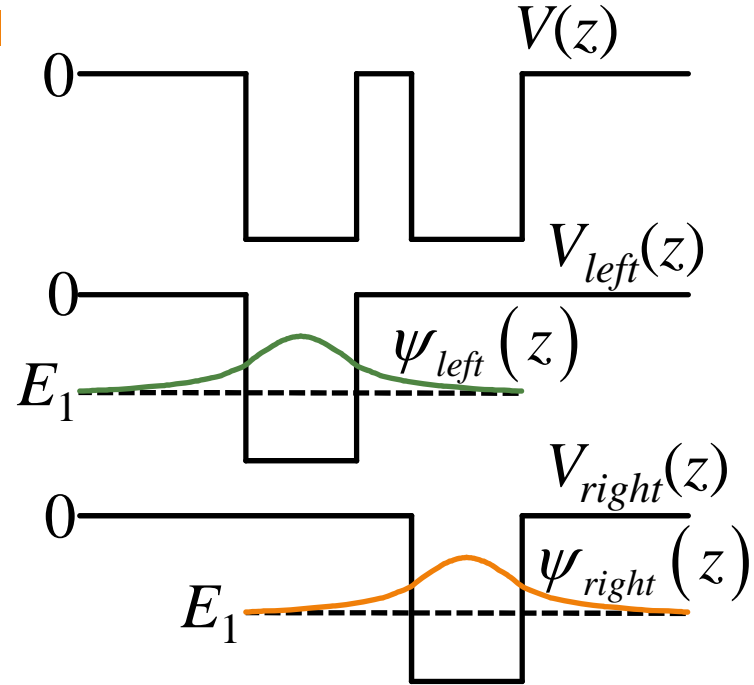
With our choice of energy origin
the Hamiltonian for this system is

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

We now solve using the finite basis
subset model

choosing the wavefunctions in the
isolated wells

$\psi_{\text{left}}(z)$ and $\psi_{\text{right}}(z)$
for our basis wavefunctions



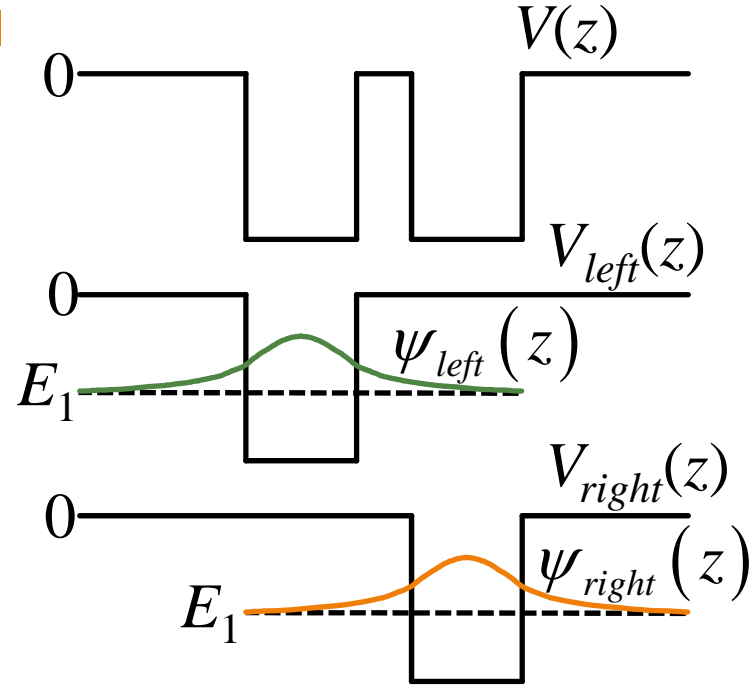
Coupled potential wells

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

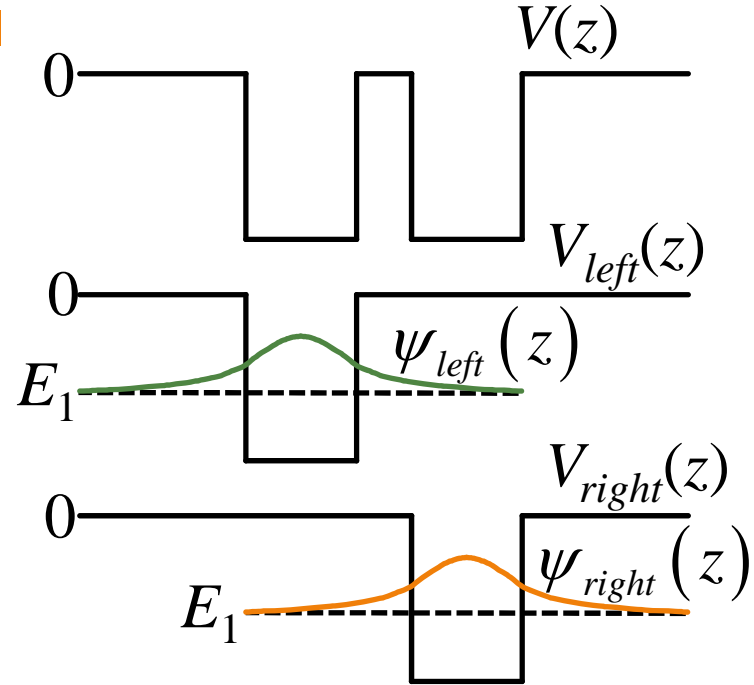
Hence the wavefunction can be written approximately in the form

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

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

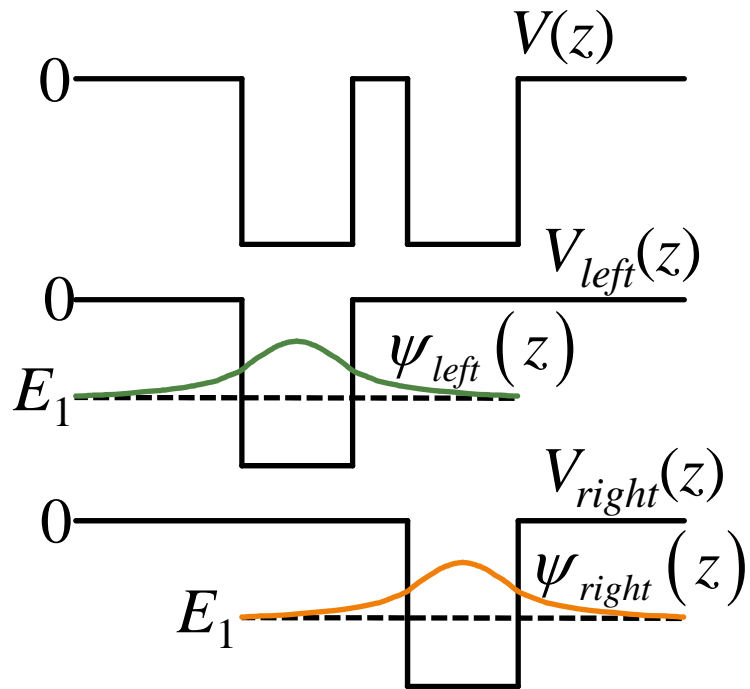
In this matrix form

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

we have, first,

$$H_{11} =$$

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



Coupled potential wells

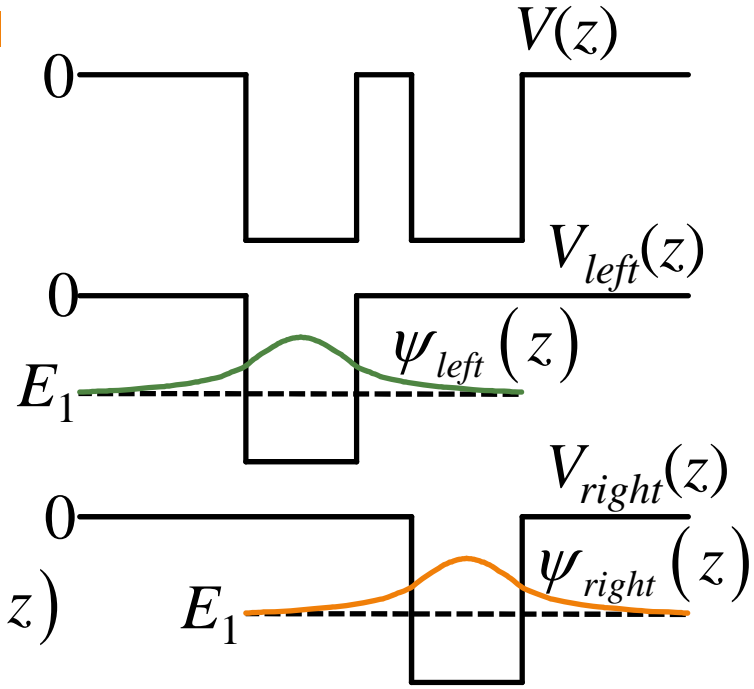
Because we presume the barrier is relatively thick

the amplitude of $\psi_{\text{left}}(z)$
is \sim zero inside the right well
so the integrand

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

is \sim zero inside the right well

Hence the term $\int \psi_{\text{left}}^*(z) V_{\text{right}}(z) \psi_{\text{left}}(z) dz$ can be neglected



Coupled potential wells

Hence

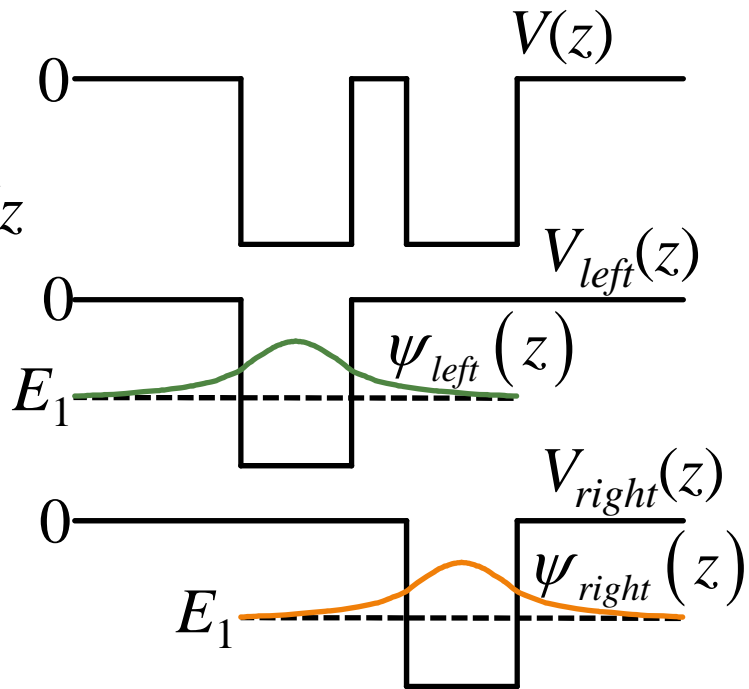
$$H_{11} \approx \int \psi_{left}^*(z) \left(\frac{-\hbar^2}{2m} \frac{d^2}{dz^2} + V_{left}(z) \right) \psi_{left}(z) dz$$

$$= E_1$$

We can argue similarly for H_{22}

Hence

$$H_{11} = H_{22} \cong E_1$$



Coupled potential wells

For the same reasons

that $\psi_{\text{left}}(z) \cong 0$ in the right well

or that $\psi_{\text{right}}(z) \cong 0$ in the left well

when integrating within either well

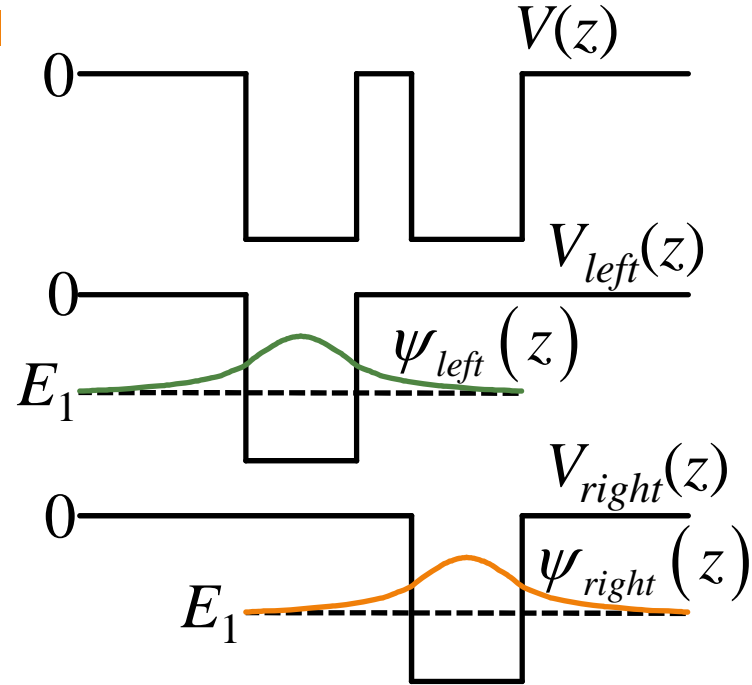
we neglect all integrations

$$\int \psi_{\text{left}}^*(z) V_{\text{right}} \psi_{\text{right}}(z) dz$$

$$\int \psi_{\text{left}}^*(z) V_{\text{left}} \psi_{\text{right}}(z) dz$$

$$\int \psi_{\text{right}}^*(z) V_{\text{right}} \psi_{\text{left}}(z) dz$$

$$\int \psi_{\text{right}}^*(z) V_{\text{left}} \psi_{\text{left}}(z) dz$$



Coupled potential wells

We retain the interaction within the
(middle) barrier

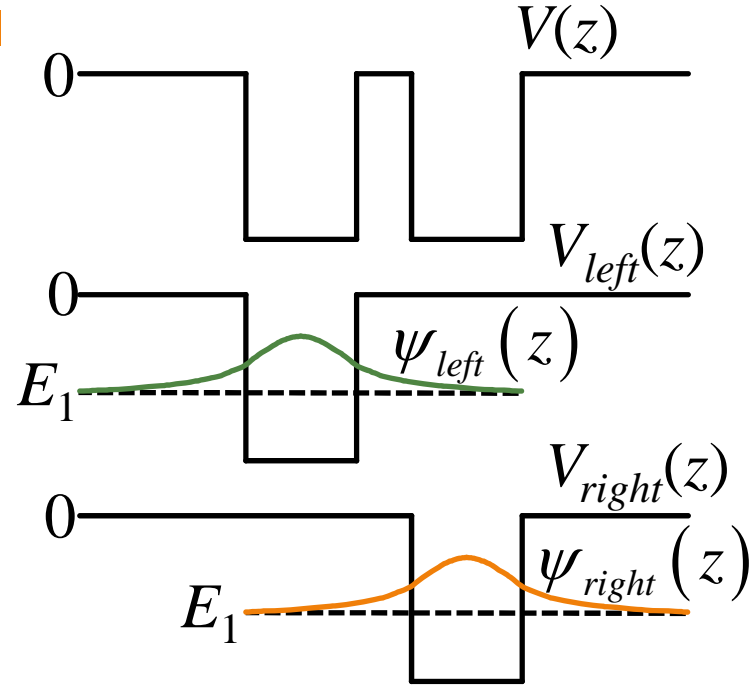
where the wavefunctions, though
small, are presumed not negligible

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

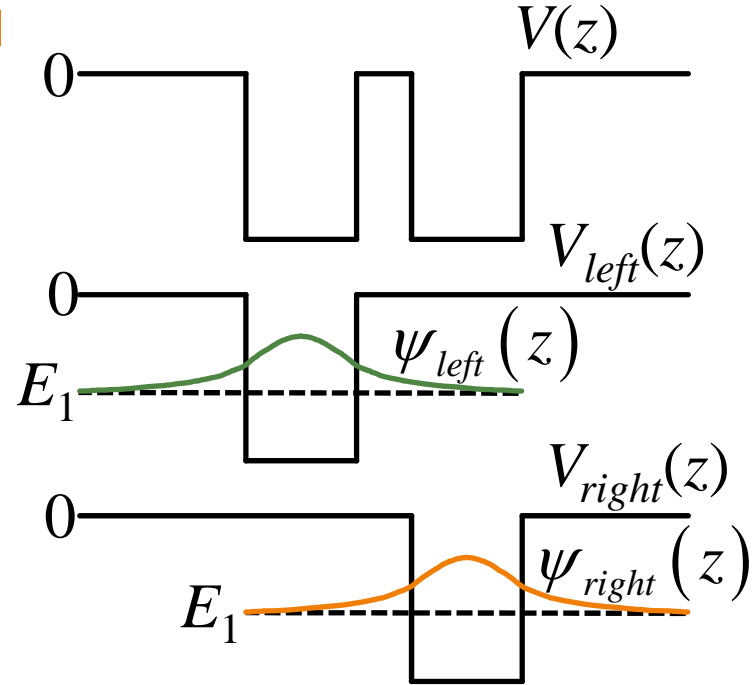
$$\Delta E = \int_{\text{barrier}} \psi_{\text{left}}^*(z) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \right) \psi_{\text{right}}(z) dz$$

Note: ΔE is a negative number here

because the second derivative

of ψ_{right} inside the barrier

is > 0



Coupled potential wells

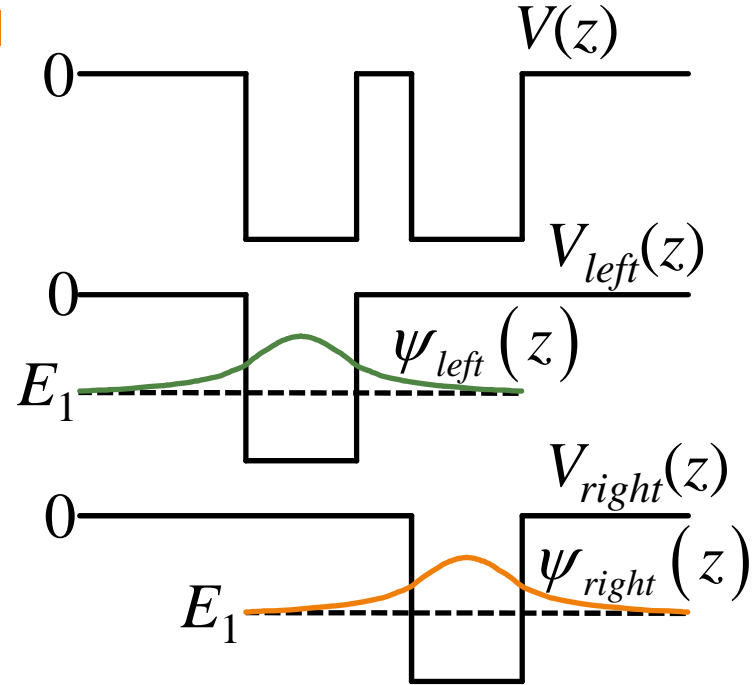
With these simplifications

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

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: ΔE 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

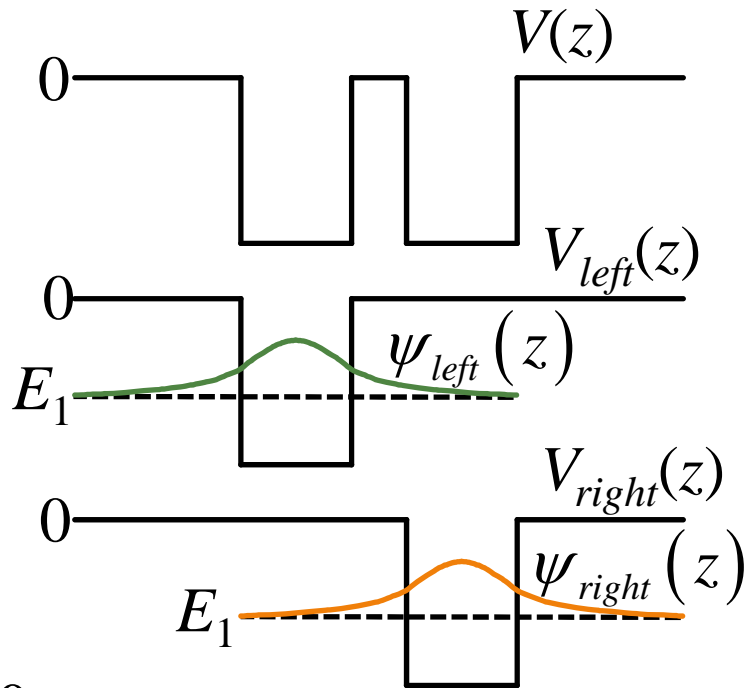
$$\det \begin{vmatrix} E_1 - E & \Delta E \\ \Delta E^* & E_1 - E \end{vmatrix} = 0$$

i.e.,

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

obtaining eigenvalues

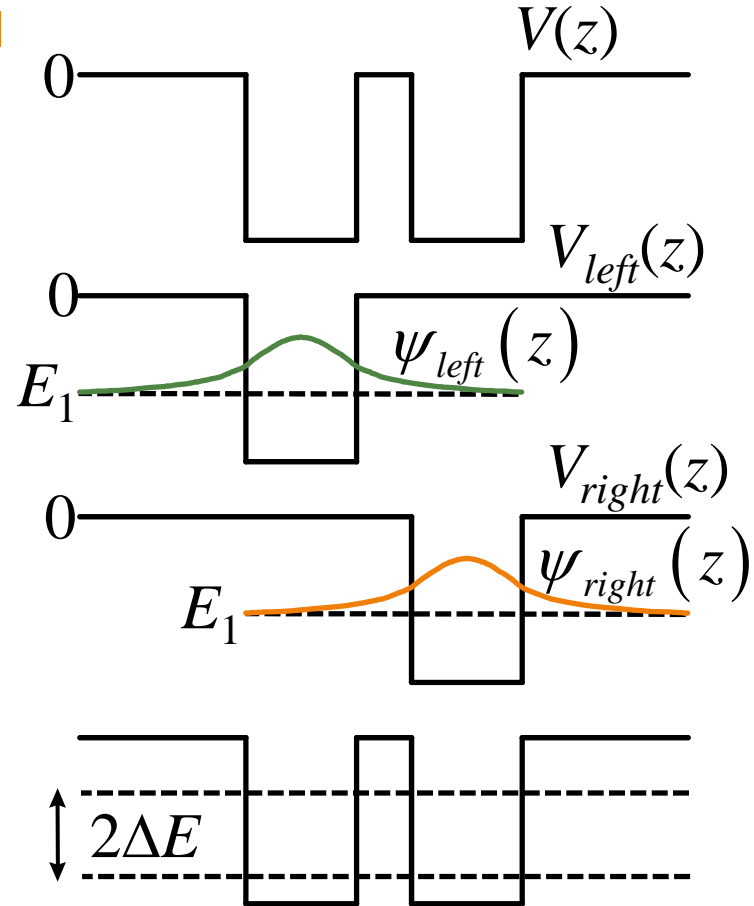
$$E = E_1 \pm |\Delta E|$$



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 $E = E_1 \pm |\Delta E|$

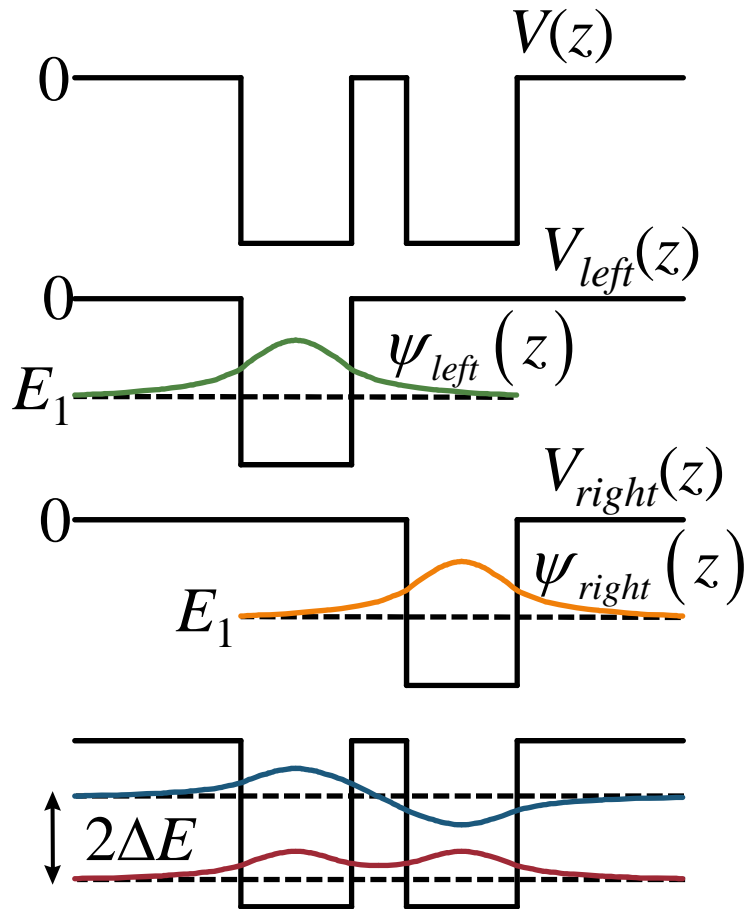
back into
$$\begin{bmatrix} E_1 & \Delta E \\ \Delta E^* & E_1 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = E \begin{bmatrix} a \\ b \end{bmatrix}$$

and solving for a and b

gives us, after normalization

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

$$\psi_s = \frac{1}{\sqrt{2}} (\psi_{\text{left}} + \psi_{\text{right}})$$



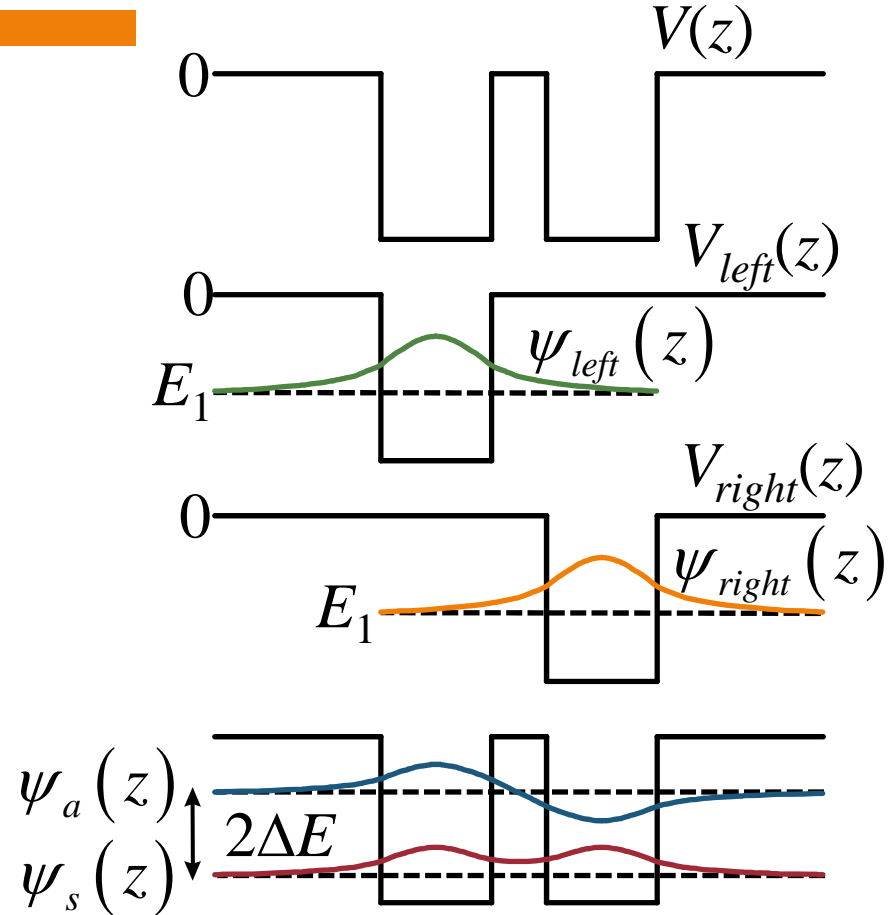
Coupled potential wells

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

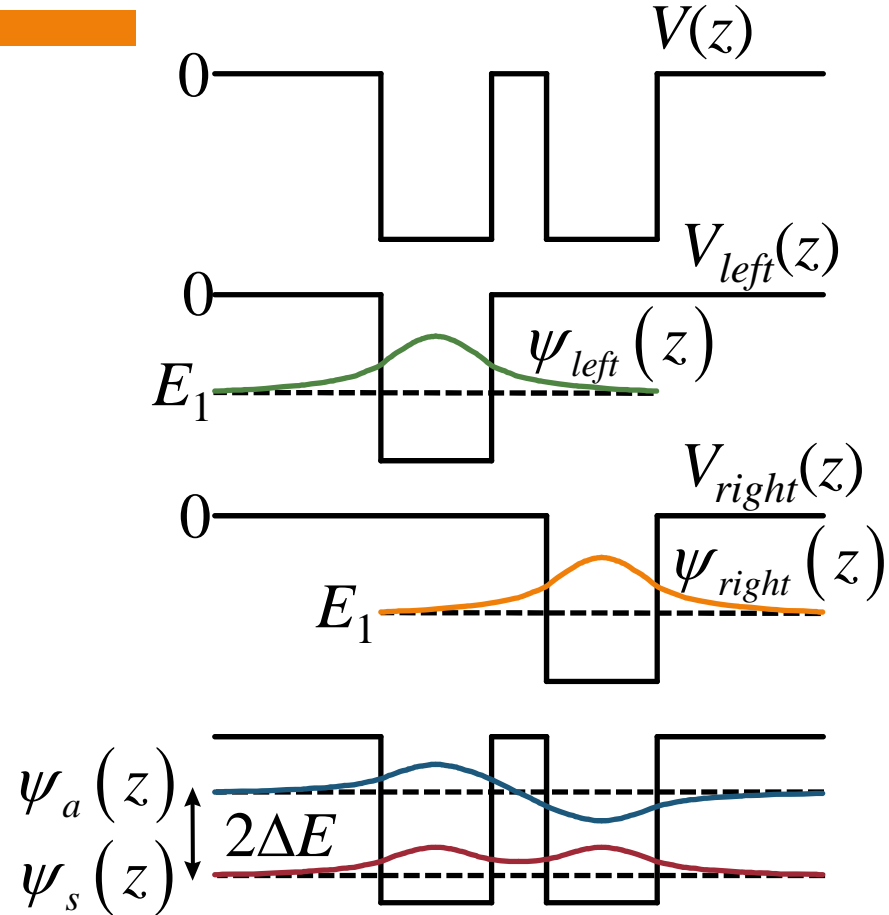


Coupled potential wells

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



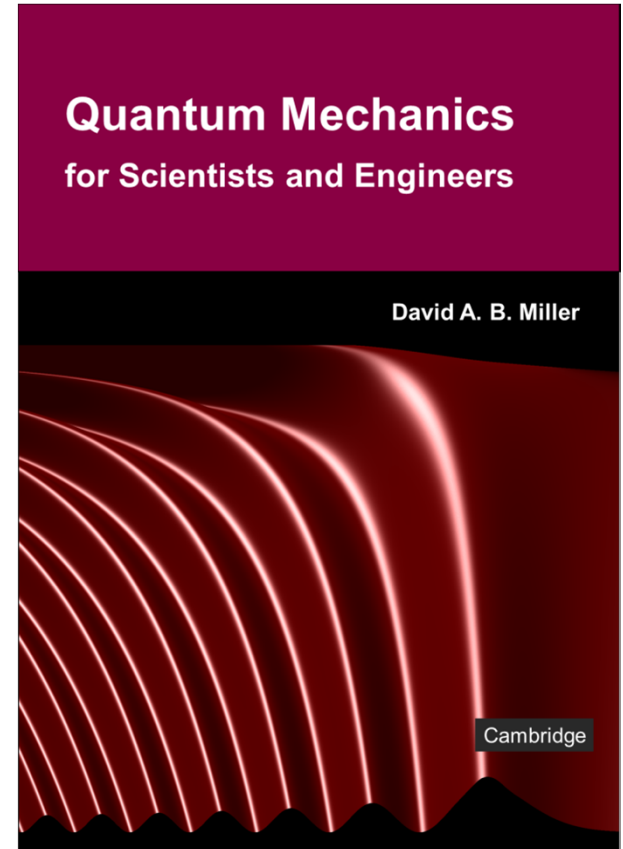


9.1 Tight binding and variational models

Slides: Video 9.1.3 The variational method

Text reference: Quantum Mechanics for Scientists and Engineers

Section 6.6





Tight binding and variational models



The variational method

Quantum mechanics for scientists and engineers

David Miller

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

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

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

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

where a_{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

$$\langle E(a_{\text{var}}) \rangle = \frac{1}{1 + a_{\text{var}}^2} \left[\int_0^1 \left(\sqrt{2} \sin \pi \xi + a_{\text{var}} \sqrt{2} \sin 2\pi \xi \right) \times \left(-\frac{1}{\pi^2} \frac{\partial^2}{\partial \xi^2} + f(\xi - 1/2) \right) \left(\sqrt{2} \sin \pi \xi + a_{\text{var}} \sqrt{2} \sin 2\pi \xi \right) d\xi \right]$$

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

To find the minimum

we take the derivative with respect to a_{var}

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

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

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

Example of the variational method

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

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 $\langle E(0.175) \rangle \simeq 0.906$

which compares with

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

