8.2 Approximation methods

Slides: Video 8.2.1 Approximation methods – introduction

Text reference: Quantum Mechanics for Scientists and Engineers

Chapter 6 introduction
Approximation methods

Quantum mechanics for scientists and engineers

David Miller
8.2 Approximation methods

Slides: Video 8.2.2 Potential well with field

Text reference: Quantum Mechanics for Scientists and Engineers

Section 6.1
Approximation methods

Potential well with field

Quantum mechanics for scientists and engineers

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Potential well with field

We are considering an electron in a potential well with infinitely high walls and with an applied electric field $E$. Without field, the electron is confined within the potential well $E_1$. With field, the applied field $eE$ extends the potential well by $eEL_z$. The diagram illustrates the change in the potential well due to the applied field.
Construction of Hamiltonian

The energy of an electron in an electric field $E$ simply increases linearly with distance.

A positive electric field in the positive $z$ direction pushes the electron in the negative $z$ direction with a force of magnitude $eE$.

So the potential energy of the electron increases in the positive $z$ direction with the form $eEZ$. 
Construction of the Hamiltonian

We choose the potential to be zero in the middle of the well.

Hence, within the well, the potential energy is

\[ V(z) = eE\left(z - \frac{L_z}{2}\right) \]

and the Hamiltonian becomes

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + eE\left(z - \frac{L_z}{2}\right) \]
Construction of the Hamiltonian

We can usefully define dimensionless units

A convenient unit of energy is the confinement energy of the first state of the original infinitely deep well

\[ E_1^\infty = \frac{\hbar^2}{2m} \left( \frac{\pi}{L_z} \right)^2 \]

and in those units the eigenenergy of the \( n \)th state will be

\[ \eta_n = \frac{E_n}{E_1^\infty} \]
Construction of the Hamiltonian

A convenient unit of field $E_o$

gives one energy unit of potential change
from one side of the well to the other

\[ E_o = \frac{E_1}{eL_z} \]

So, the (dimensionless) field will be

\[ f = \frac{E}{E_o} \]

A convenient distance unit is the thickness $L_z$
so the dimensionless distance will be

\[ \xi = \frac{z}{L_z} \]
Construction of the Hamiltonian

From the original Hamiltonian

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + eE(z - L_z / 2) \]

dividing by \( E_1^\infty \) and using dimensionless units gives

\[ \hat{H} = -\frac{1}{\pi^2} \frac{d^2}{d\xi^2} + f(\xi - 1/2) \]

and a time-independent Schrödinger equation

\[ \hat{H} \phi(\xi) = \eta \phi(\xi) \]
Construction of the Hamiltonian

For the “unperturbed” problem without field we write the “unperturbed” Hamiltonian within the well as

\[ \hat{H}_o = -\frac{1}{\pi^2} \frac{d^2}{d\xi^2} \]

The normalized solutions of the corresponding Schrödinger equation

\[ \hat{H}_o \psi_n = \varepsilon_n \psi_n \]

are then

\[ \psi_n(\xi) = \sqrt{2} \sin(n\pi \xi) \]
8.2 Approximation methods

Slides: Video 8.2.4 Use of finite matrices

Text reference: Quantum Mechanics for Scientists and Engineers

Section 6.2
Approximation methods

Use of finite matrices

Quantum mechanics for scientists and engineers

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Finite matrix method for an electron in a well with field

We will need to construct the matrix of the Hamiltonian for this problem.

The matrix elements are

\[ H_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle \]

\[ = -\frac{1}{\pi^2} \int_0^1 \psi_i^*(\xi) \frac{d^2}{d\xi^2} \psi_j(\xi) d\xi + \int_0^1 \psi_i^*(\xi)(\xi - 1/2) \psi_j(\xi) d\xi \]

In this particular case, because the wavefunctions are real, the complex conjugation makes no difference.
Finite matrix method for an electron in a well with field

In the integral

\[
H_{ij} = -\frac{1}{\pi^2} \int_0^1 \psi_i^*(\xi) \frac{d^2}{d\xi^2} \psi_j(\xi) d\xi + \int_0^1 \psi_i^*(\xi)(\xi - 1/2) \psi_j(\xi) d\xi
\]

if we choose the energy eigenfunctions of the “unperturbed” problem to form our basis set

\[
\psi_n(\xi) = \sqrt{2} \sin(n\pi \xi)
\]

we can easily perform the derivative analytically

The resulting integrations can be solved analytically also or they can just be performed numerically
For our explicit example here, we consider a field of 3 dimensionless units, i.e., $f = 3$ with the first three energy eigenfunctions of the "unperturbed" problem as our finite basis subset then, evaluating the matrix elements $H_{ij}$ gives the Hamiltonian matrix

$$
\hat{H} = \begin{bmatrix}
1 & -0.54 & 0 \\
-0.54 & 4 & -0.584 \\
0 & -0.584 & 9
\end{bmatrix}
$$

which is Hermitian, as expected
Finite matrix method for an electron in a well with field

Now we numerically find the eigenvalues of this matrix

\[ \eta_1 = 0.904, \quad \eta_2 = 4.028, \quad \eta_3 = 9.068 \]

which are close to the “unperturbed” (zero field) values which would be 1, 4, and 9, respectively

We see also that the lowest energy eigenvalue has reduced from its unperturbed value

These can be compared with the results from the exact (“Airy function”) solutions

\[ \epsilon_1 \approx 0.90419, \quad \epsilon_2 \approx 4.0275, \quad \epsilon_3 \approx 9.0173 \]
Finite matrix method for an electron in a well with field

The corresponding eigenvectors are solved numerically as

\[
\begin{pmatrix}
0.985 \\
0.174 \\
0.013
\end{pmatrix}
\begin{pmatrix}
\phi_1 \\
\phi_2 \\
\phi_3
\end{pmatrix}
\begin{pmatrix}
-0.175 \\
0.978 \\
0.115
\end{pmatrix}
\begin{pmatrix}
0.007 \\
-0.115 \\
0.993
\end{pmatrix}
\]

Note these are normalized with the sum of the squares of the elements of the vectors each adding to 1

So, explicitly, the first eigenfunction is

\[
\phi_1 (\xi) = 0.985\sqrt{2} \sin(\pi \xi) + 0.174\sqrt{2} \sin(2\pi \xi) + 0.013\sqrt{2} \sin(3\pi \xi)
\]
Calculated wavefunction

Here is a comparison of
- Unperturbed - i.e., no field
- Perturbed - 3 units of field

(finite basis method)

The electron wavefunction has
moved to the left with field

Adding more elements to the
finite basis

makes negligible change to
the calculated eigenvalue
For probability density, we compare:
- Unperturbed - i.e., no field
- Perturbed - 3 units of field (finite basis method)

The electron probability density has moved to the left with field.