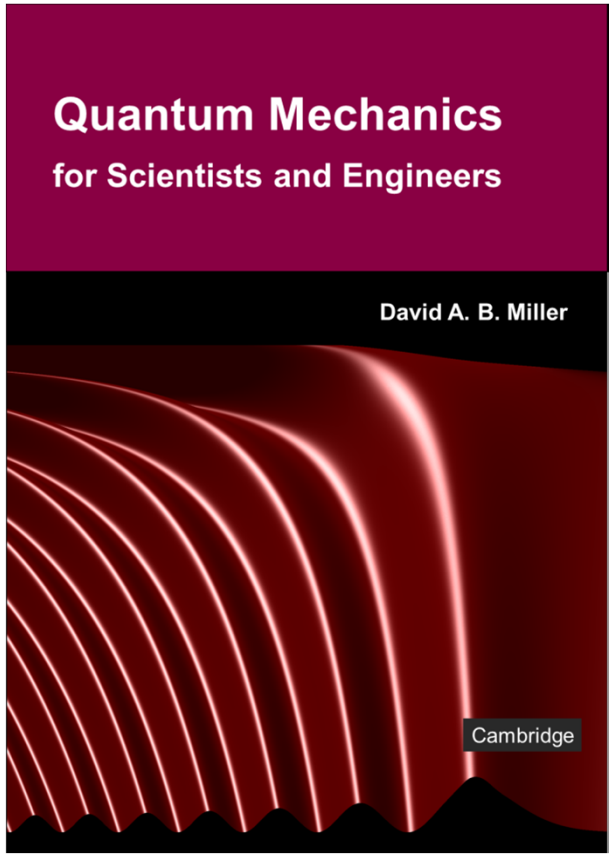
8.2 Approximation methods

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

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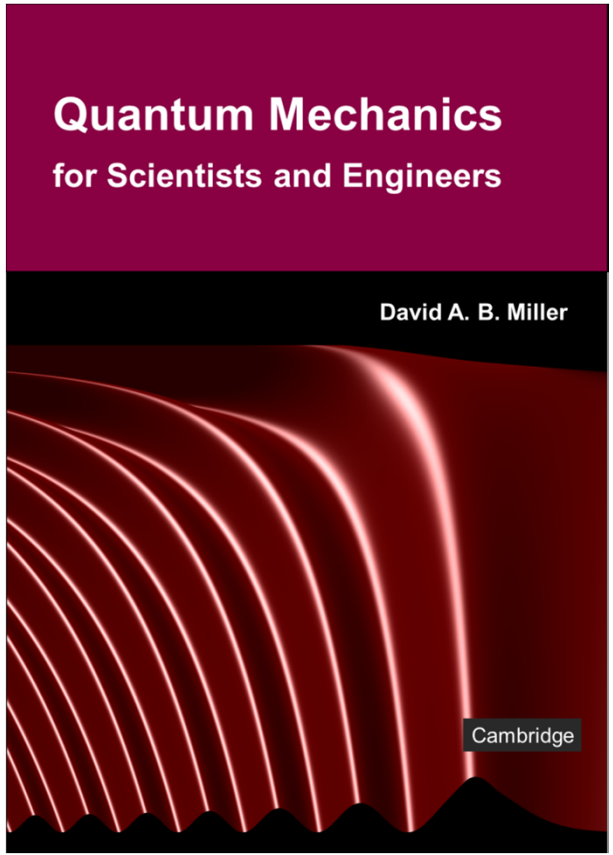
8.2 Approximation methods

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

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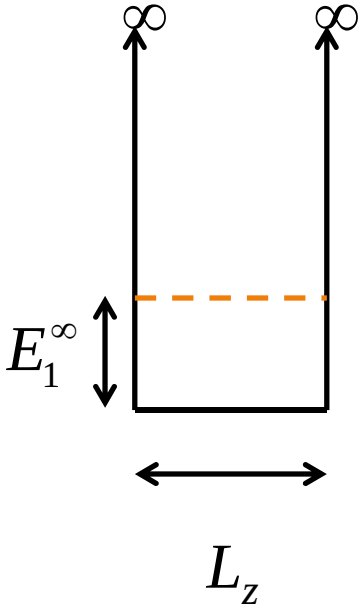
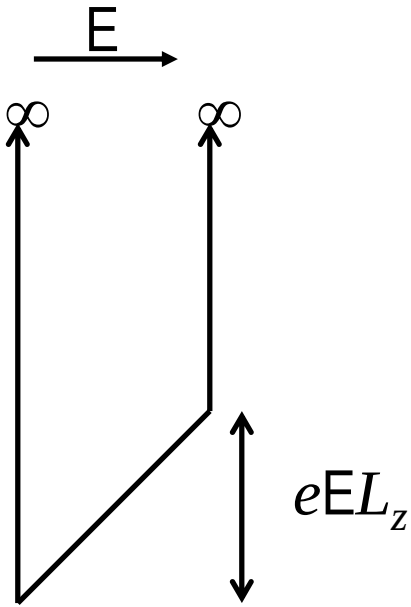
Potential well with field

We are considering
an electron in
a potential well
with infinitely
high walls
and with an
applied
electric field E

without field



with 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

$$V(z) = e\mathsf{E}\left(z - L_z/2\right)$$

and the Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + e\mathsf{E}\left(z - L_z/2\right)$$

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 nth 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

$$\mathrm{E}_o = \frac{E_1^{\infty}}{eL_z}$$

So, the (dimensionless) field will be

$$\mathrm{f} = \mathrm{E} / \mathrm{E}_o$$

A convenient distance unit is the thickness L_z

so the dimensionless distance will be

$$\xi = z / L_z$$

Construction of the Hamiltonian

From the original Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + e\mathsf{E}\left(z - L_z/2\right)$$

dividing by E_1^{∞} and using dimensionless units gives

$$\hat{H} = -\frac{1}{\pi^2}\frac{d^2}{d\xi^2} + \mathsf{f}\left(\xi - 1/2\right)$$

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

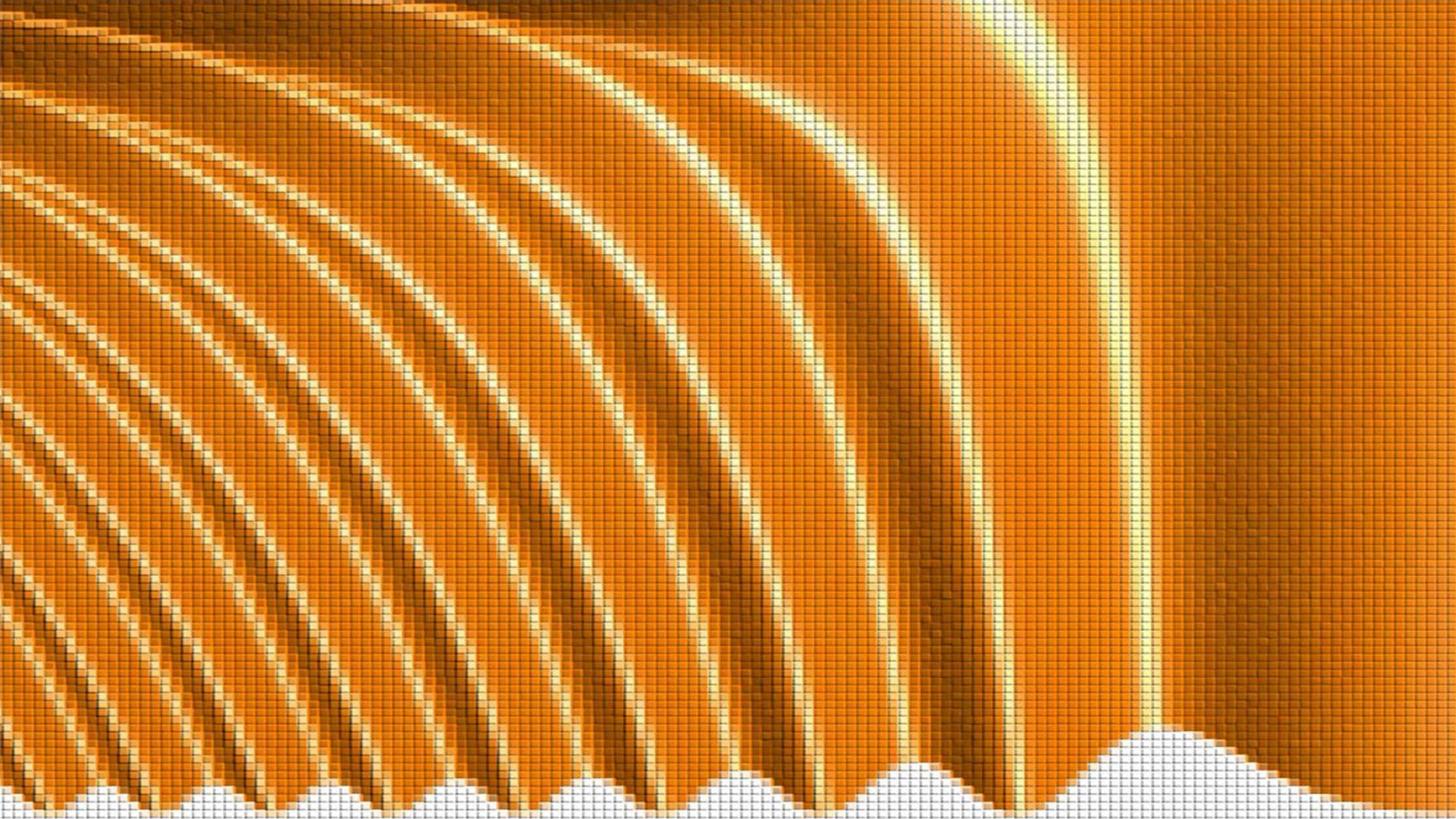
$$\hat{H}_o = -\frac{1}{\pi^2}\frac{d^2}{d\xi^2}$$

The normalized solutions of the corresponding Schrödinger equation

$$\hat{H}_o\psi_n = \varepsilon_n\psi_n$$

are then

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

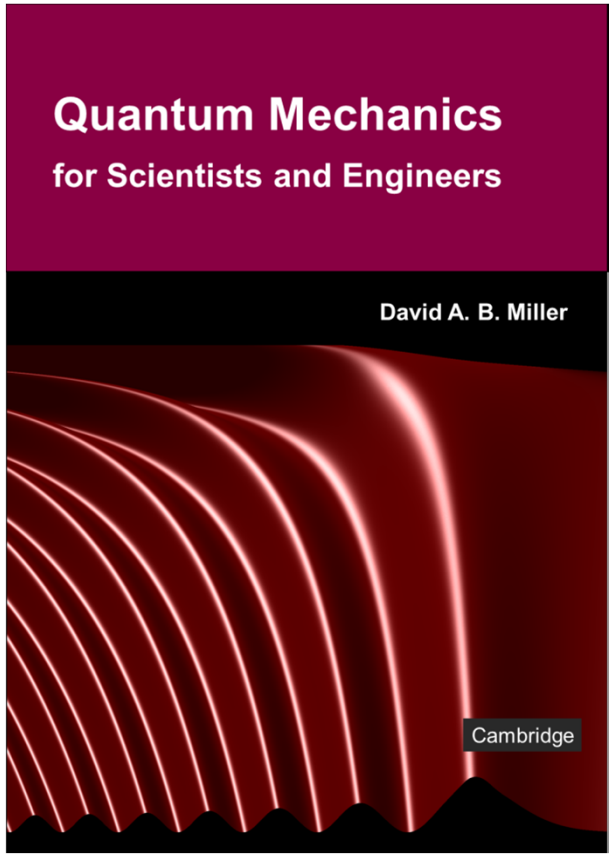


8.2 Approximation methods

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

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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

$$H_{ij} \equiv \left\langle \psi_i \middle| \hat{H} \middle| \psi_j \right\rangle$$

$$= -\frac{1}{\pi^2}\int_0^1 \psi_i^*(\xi)\frac{d^2}{d\xi^2}\psi_j(\xi)\,d\xi + \mathrm{f}\int_0^1 \psi_i^*(\xi)(\xi - 1/2)\psi_j(\xi)\,d\xi$$

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

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

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

Finite matrix method for an electron in a well with field

For our explicit example here,

we consider a field of 3 dimensionless units, i.e., $\mathsf{f} = 3$

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

$$\eta_1 = 0.904,\ \eta_2 = 4.028,\ \eta_3 = 9.068$$

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

$$\varepsilon_1 \simeq 0.90419,\ \varepsilon_2 \simeq 4.0275,\ \varepsilon_3 \simeq 9.0173$$

Finite matrix method for an electron in a well with field

The corresponding eigenvectors are solved numerically as

$$|\phi_1\rangle = \begin{bmatrix} 0.985 \\ 0.174 \\ 0.013 \end{bmatrix} \quad |\phi_2\rangle = \begin{bmatrix} -0.175 \\ 0.978 \\ 0.115 \end{bmatrix} \quad |\phi_3\rangle = \begin{bmatrix} 0.007 \\ -0.115 \\ 0.993 \end{bmatrix}$$

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

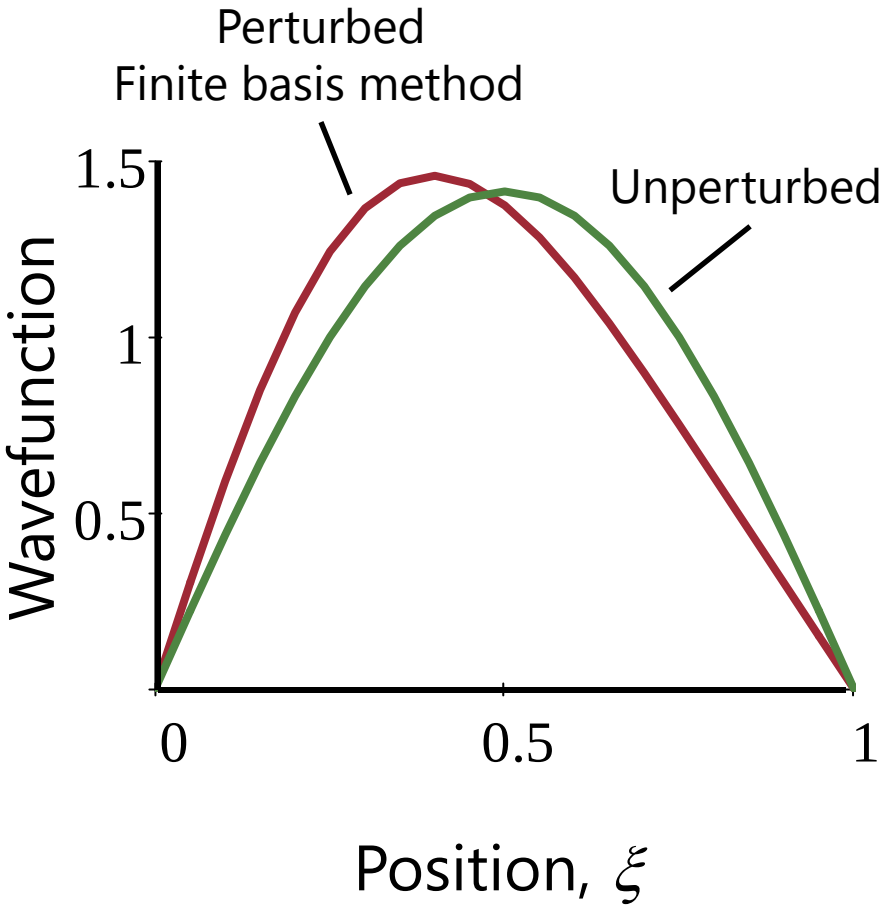
Perturbed - 3 units of field

(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



Calculated probability density

For probability density, we compare

Unperturbed - i.e., no field

Perturbed - 3 units of field

(finite basis method)

The electron probablity density has moved to the left with field