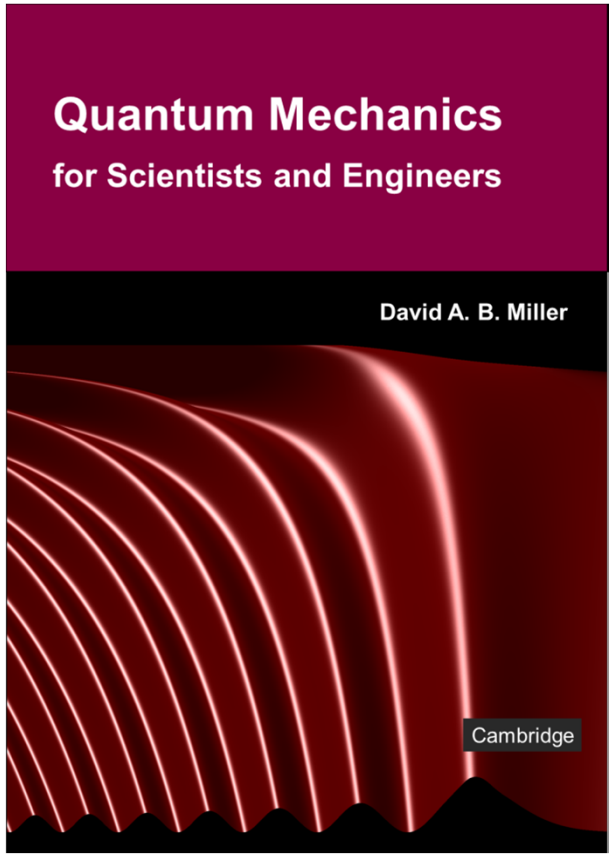
9.1 Tight binding and variational models

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

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

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

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

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

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

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

We can rewrite this using $\int_0^1 \sin\pi\xi\left(\xi - 1/2\right)\sin 2\pi\xi d\xi = -\frac{8}{9\pi^2}$

the known unperturbed eigenenergies

and the orthogonality of the sine functions

Example of the variational method

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

To find the minimum

we take the derivative with respect to a_{var}

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

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

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

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

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 $\left\langle E\left(a_{\text{var}}\right)\right\rangle$

is $\left\langle E\left(0.175\right)\right\rangle \simeq 0.906$

which compares with

0.904 from the finite basis subset method and

0.9025 from the perturbation calculation