

Perturbation theory

Quantum mechanical systems may be exposed to perturbations including external electric fields, magnetic fields, or electromagnetic radiation. Due to such perturbations, the quantum system considered here is stimulated and, as a consequence, changes its state. This change of state may include changes in the shape of wave functions, state energies, and occupation probability of states. This is what perturbation theory is all about. Perturbation theory is one of the most important methods for obtaining approximate solutions to Schrödinger's equation.

10.1 First-order time-independent perturbation theory

This section covers first-order perturbation calculation of a stationary, non-degenerate quantum state. Suppose a quantum mechanical system whose eigenstate energies and wave functions are known. Suppose that the unperturbed system is described by the hamiltonian operator H^0 , the eigenstate energies E_n^0 , and the wave functions ψ_n^0 . Then the Schrödinger equation of the unperturbed system is given by

$$H^0 \psi_n^0 = E_n^0 \psi_n^0. \quad (10.1)$$

Here, the superscript 0 is used for energies, wave functions and the hamiltonian operator of the *unperturbed* system. If the system is subjected to a small perturbation, then perturbation theory allows one to determine the modifications of the eigenstate energies, wave functions, and occupation probabilities. It may seem that these are very special circumstances; however, it will become clear, that perturbation theory is of great practical importance.

The hamiltonian operator of a perturbed system is given by

$$H = H^0 + \lambda H' \quad (10.2)$$

where H^0 is the hamiltonian operator of the unperturbed system and H' is called the *perturbation term* in the hamiltonian. The parameter λ allows us to turn the perturbation on ($\lambda = 1$) and off ($\lambda = 0$). The parameter λ further indicates the smallness of the perturbation. That is, the system described by the hamiltonian H has experienced only a *small* perturbation when compared to the unperturbed system. The parameter λ can have the value of unity, ($\lambda = 1$), without loss of general validity of the perturbation theory. The Schrödinger equation of the perturbed system is given by

$$H \psi_n = (H^0 + \lambda H') \psi_n = E_n \psi_n. \quad (10.3)$$

It is evident that the perturbed system merges with the unperturbed system if λ approaches zero, *i. e.*

$$\lim_{\lambda \rightarrow 0} E_n = E_n^0 \quad (10.4)$$

and

$$\lim_{\lambda \rightarrow 0} \psi_n = \psi_n^0. \quad (10.5)$$

To obtain a solution of the perturbed problem, an expansion of E_n and ψ_n in a power series in λ is employed

$$E_n = E_n^0 + \lambda E_n' + \lambda^2 E_n'' + \dots \quad (10.6)$$

$$\psi_n = \psi_n^0 + \lambda \psi_n' + \lambda^2 \psi_n'' + \dots \quad (10.7)$$

where $E_n' = dE_n/d\lambda$ and $\psi_n' = d\psi_n/d\lambda$. The first three terms of this power series are illustrated in **Fig. 10.1**, where the unperturbed values of E_n and ψ_n are displayed together with their first-order correction term ($\lambda E_n'$ and $\lambda \psi_n'$) and their second-order correction term ($\lambda^2 E_n''$ and $\lambda^2 \psi_n''$). It is the goal of *first-order* perturbation theory to find the values of E_n' and ψ_n' . Correspondingly, it is the aim of *second-order* perturbation theory to find the values of E_n'' and ψ_n'' .

Substitution of Eqs. (10.6) and (10.7) into the perturbed Schrödinger equation (Eq. 10.3) yields

$$\begin{aligned} & \lambda^0 (H^0 \psi_n^0 - E_n^0 \psi_n^0) \\ & + \lambda^1 (H^0 \psi_n' + H' \psi_n^0 - E_n^0 \psi_n' - E_n' \psi_n^0) \\ & + \lambda^2 (H^0 \psi_n'' + H' \psi_n' - E_n^0 \psi_n'' - E_n' \psi_n' - E_n'' \psi_n^0) \\ & + \lambda^3 (\dots) \\ & + \lambda^4 (\dots) \\ & + \dots = 0. \end{aligned} \quad (10.8)$$

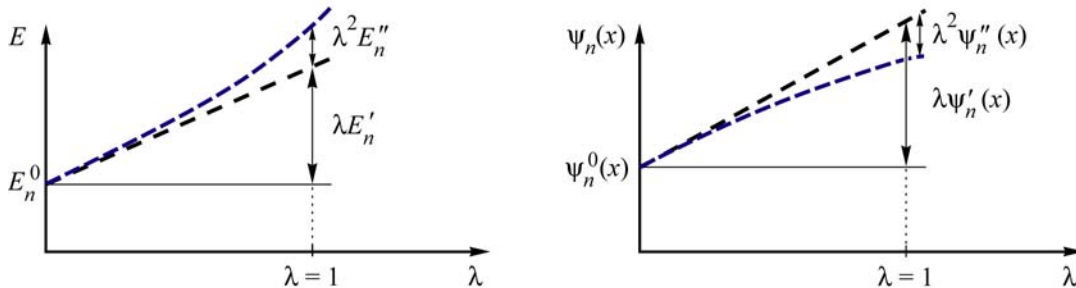


Fig. 10.1. Illustration of first-order and second-order corrections terms to the unperturbed energy E_n^0 and to the amplitude of the unperturbed wavefunction ψ_n^0 at a particular position x . The parameter λ is a parameter that controls the magnitude of the perturbation; $\lambda = 0$ corresponds to "no perturbation".

If the perturbation is neglected ($\lambda = 0$), one obtains the original eigenvalues E_n^0 and eigenfunctions ψ_n^0 . We next consider the case $\lambda \neq 0$. The sum in Eq. (10.8) equals zero, only if each summand is zero, that is

$$\text{0th order terms: } \boxed{H^0 \psi_n^0 = E_n^0 \psi_n^0} \quad (10.9)$$

$$\text{1st order terms: } \boxed{H^0 \psi_n' + H' \psi_n^0 = E_n^0 \psi_n' + E_n' \psi_n^0} \quad (10.10)$$

$$\text{2nd order terms: } \boxed{H^0 \psi_n'' + H' \psi_n' = E_n^0 \psi_n'' + E_n' \psi_n' + E_n'' \psi_n^0} \quad (10.11)$$

The first of these three equations is the unperturbed Schrödinger equation. The second equation contains only first-order terms and it will be used to derive first-order perturbation results. The third equation contains only first-order and second-order terms and it will be used to derive second-order perturbation results. Note that in the above three equations, H^0 , ψ_n^0 , E_n^0 , and H' are known.

It is the purpose of first-order perturbation theory to find solutions for E_n' and ψ_n' (E_n'' and ψ_n'' will be determined by second-order perturbation theory which is discussed in the subsequent section). Because ψ_n' is an unknown wave function, we will try to *express ψ_n' as a series of a complete set of orthogonal eigenfunctions*

$$\boxed{\psi_n' = \sum_j a_j \psi_j^0} \quad (10.12)$$

The wave functions ψ_j^0 represent the complete orthonormal set of wave functions of the system. Nearly any wave function can be synthesized from this orthonormal set. The particular wave function ψ_n is one specific wave function of the complete set. In order to determine the perturbed wave function ψ_n' , the coefficients a_j must be determined. Substitution of Eq. (10.12) into Eq. (10.10) yields

$$H^0 \sum_j a_j \psi_j^0 + H' \psi_n^0 = E_n^0 \sum_j a_j \psi_j^0 + E_n' \psi_n^0. \quad (10.13)$$

Using

$$H^0 \sum_j a_j \psi_j^0 = \sum_j a_j E_j^0 \psi_j^0 \quad (10.14)$$

one obtains

$$\sum_j a_j E_j^0 \psi_j^0 + H' \psi_n^0 = E_n^0 \sum_j a_j \psi_j^0 + E_n' \psi_n^0. \quad (10.15)$$

Consider next a wave function ψ_m^0 which is the m th wave function of the orthonormal set of wave functions ψ_j^0 given in Eq. (10.12). Pre-multiplication of Eq. (10.15) with ψ_m^{0*} , and integration over position space yields

$$a_m E_m^0 + \langle \psi_m^0 | H' | \psi_n^0 \rangle = a_m E_n^0 + E_n' \delta_{mn}. \quad (10.16)$$

Here, we have used the orthogonality of the set ψ_j^0 , that is $\langle \psi_m^0 | \psi_j^0 \rangle = 0$ for $m \neq j$ and

$\langle \psi_m^0 | \psi_j^0 \rangle = 1$ for $m = j$. This can be expressed by the Kronecker delta $\langle \psi_m^0 | \psi_j^0 \rangle = \delta_{mj}$ or $\langle \psi_m^0 | \psi_n^0 \rangle = \delta_{mn}$. In Eq. (10.16), it is either $m = n$ or $m \neq n$. One obtains for

$$m = n: \quad E'_n = \langle \psi_n^0 | H' | \psi_n^0 \rangle \quad (10.17)$$

which is the *first-order correction term* to the energy. Hence, the energy of the n th state of a system, subjected to the perturbation hamiltonian H' , calculated by first-order perturbation theory, is given by

$$E_n = E_n^0 + \lambda \langle \psi_n^0 | H' | \psi_n^0 \rangle \quad (10.18)$$

Furthermore, one obtains for

$$m \neq n: \quad a_m = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \quad (10.19)$$

This equation can be used to calculate all a_m , except the value of $a_{m=n}$. The value of $a_{m=n}$ can be calculated by requiring that the first-order corrected wave function is normalized, *i. e.* $\langle \psi_n^0 + \lambda \psi'_n | \psi_n^0 + \lambda \psi'_n \rangle = 1$. This condition yields for

$$m = n: \quad \int_{-\infty}^{\infty} \left(\psi_n^0 + \lambda \sum_m a_m \psi_m^0 \right)^* \left(\psi_n^0 + \lambda \sum_m a_m \psi_m^0 \right) dx = 1 + \lambda a_m + \lambda a_m^* + \lambda^2 \sum_m a_m a_m^* = 1 \quad (10.20)$$

A simple solution of this equation is $a_m = a_m^* = a_n = a_n^* = 0$. Hence, the wave function of the n th state of a system, subjected to the perturbation hamiltonian H' , calculated by first-order perturbation theory, is given by

$$\psi_n = \psi_n^0 + \lambda \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0 \quad (10.21)$$

The sum in this equation is carried out for all values of m *except* the value $m = n$. This equation shows, that the wave functions of all other (unperturbed) states have to be known, to calculate the perturbed wave function of the n th state. The influence of other wave functions decreases, as the energy-separation increases, since $E_n^0 - E_m^0$ is in the denominator of the expression.

10.2 Second-order time-independent perturbation theory

The energy and the wave function of a perturbed state can be expressed in terms of the expansion of Eqs. (10.6) and (10.7). It is the aim of the *second-order* perturbation calculation to find formulas for E_n'' and ψ_n'' . In analogy to the first-order calculation, ψ_n'' is expressed in terms of the complete set of orthonormal wave functions of the unperturbed system, *i. e.*

$$\boxed{\psi_n'' = \sum_j b_j \psi_j^0} \quad (10.22)$$

Inserting Eq. (10.22) and Eq. (10.12) into Eq. (10.11) yields

$$\sum_j b_j E_j^0 \psi_j^0 + H' \sum_j a_j \psi_j^0 = \sum_j b_j E_n^0 \psi_j^0 + \sum_j a_j E_n' \psi_j^0 + E_n'' \psi_n^0. \quad (10.23)$$

Similar to the previous section, we consider one specific wave function ψ_m^0 of the complete orthonormal set of wave functions of the unperturbed system. Pre-multiplication with ψ_m^{0*} , integration over all configuration space, and recalling that $\langle \psi_m^0 | \psi_j^0 \rangle = \delta_{mj}$ yields

$$b_m E_m^0 + \sum_j a_j \langle \psi_m^0 | H' | \psi_j^0 \rangle = b_m E_n^0 + E_n' a_m + E_n'' \delta_{nm}. \quad (10.24)$$

In this equation, it is either $m = n$ or $m \neq n$. With $m = n$, one obtains the *second-order correction term* to the energy

$$m = n: \quad E_n'' = \sum_j a_j \langle \psi_n^0 | H' | \psi_j^0 \rangle - E_n' a_n \quad (10.25)$$

$$= \sum_{j \neq n} a_j \langle \psi_n^0 | H' | \psi_j^0 \rangle + a_n \langle \psi_n^0 | H' | \psi_n^0 \rangle - E_n' a_n. \quad (10.26)$$

In Eq. (10.25), the sum is carried out for all values of j , whereas in Eq. (10.26), the sum is carried out for all values of j except the value $j = n$. Using the result of first-order perturbation theory for E_n' (see Eq. 10.17), then the last two terms of Eq. (10.26) cancel. Using the first-order perturbation result for a_j (Eq. 10.19), one obtains

$$\boxed{E_n'' = \sum_{j \neq n} \frac{|\langle \psi_n^0 | H' | \psi_j^0 \rangle|^2}{E_n^0 - E_j^0}} \quad (10.27)$$

which is the second-order correction to the energy of the n th state of a system subjected to the perturbation hamiltonian H' . Note that the second-order term given in the above equation increases drastically if two energy-levels are closely spaced, *i. e.* for small $E_n^0 - E_j^0$. The second-order correction term becomes large for a small separation of two energy levels. It is therefore frequently said that energy levels *repel each other*. States energetically distant from the state of interest may be neglected in practical calculations.

For $m \neq n$ in Eq. (10.24), using that $a_n = 0$, and with Eqs. (10.17) and (10.19), one obtains

$$m \neq n: \quad b_m = \sum_{j \neq n} \frac{\langle \psi_j^0 | H' | \psi_n^0 \rangle \langle \psi_m^0 | H' | \psi_j^0 \rangle}{(E_n^0 - E_j^0)(E_n^0 - E_m^0)} - \frac{\langle \psi_n^0 | H' | \psi_n^0 \rangle \langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)^2}. \quad (10.28)$$

Finally $b_m = b_n$ ($m = n$) must be determined, which can again be achieved with the normalization condition.

$$m=n: \left\langle \psi_n^0 + \lambda \sum_j a_j \psi_j^0 + \lambda^2 \sum_j b_j \psi_j^0 \left| \psi_n^0 + \lambda \sum_j a_j \psi_j^0 + \lambda^2 \sum_j b_j \psi_j^0 \right. \right\rangle = 1. \quad (10.29)$$

Evaluation of this integral yields the value of $b_{m=n} = b_n$

$$b_n = -\frac{1}{2} \sum_j |a_j|^2 = -\frac{1}{2} \sum_{j \neq n} \frac{\left| \langle \psi_j^0 | H' | \psi_n^0 \rangle \right|^2}{(E_n^0 - E_j^0)^2}. \quad (10.30)$$

Using these values of b_m , the second-order correction term of the wave function (see Eq. 10.22) is given by

$$\psi_n'' = \sum_{m \neq n} \left\{ \left[\sum_{j \neq n} \frac{\langle \psi_j^0 | H' | \psi_n^0 \rangle \langle \psi_m^0 | H' | \psi_j^0 \rangle}{(E_n^0 - E_j^0)(E_n^0 - E_m^0)} - \frac{\langle \psi_n^0 | H' | \psi_n^0 \rangle \langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)^2} \right] \psi_m^0 - \frac{\left| \langle \psi_m^0 | H' | \psi_n^0 \rangle \right|^2}{2(E_n^0 - E_m^0)^2} \psi_n^0 \right\} \quad (10.31)$$

The second order correction terms for the energy and the wave function have now been obtained. For convenience, the results of first-order and of second-order perturbation theory for the energy and wave function of the n th state are summarized:

First- and second-order correction to the energy of the n th state:

$$E_n = E_n^0 + \lambda \langle \psi_n^0 | H' | \psi_n^0 \rangle + \lambda^2 \sum_{j \neq n} \frac{\left| \langle \psi_n^0 | H' | \psi_j^0 \rangle \right|^2}{E_n^0 - E_j^0} \quad (10.32)$$

First- and second-order correction to the wave function of the n th state:

$$\psi_n = \psi_n^0 + \lambda \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0 + \lambda^2 \sum_{m \neq n} \left\{ \left[\sum_{j \neq n} \frac{\langle \psi_j^0 | H' | \psi_n^0 \rangle \langle \psi_m^0 | H' | \psi_j^0 \rangle}{(E_n^0 - E_j^0)(E_n^0 - E_m^0)} - \frac{\langle \psi_n^0 | H' | \psi_n^0 \rangle \langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)^2} \right] \psi_m^0 - \frac{\left| \langle \psi_m^0 | H' | \psi_n^0 \rangle \right|^2}{2(E_n^0 - E_m^0)^2} \psi_n^0 \right\} \quad (10.33)$$

10.3 Example for first-order perturbation calculation

A simple example for a first-order perturbation calculation is illustrated in **Fig. 10.2**. The *unperturbed* potential is a square-shaped quantum well. The lowest eigenstate energy $E_{n=0}^0$ and wave function $\psi_{n=0}^0$ are shown as well. The system is now subjected to a potential perturbation, and it is the purpose of this example to calculate the perturbed ground-state energy

$E_{n=0} = E_{n=0}^0 + \lambda E_n'$. The perturbation used in this example is a potential energy perturbation given by

$$U_p(x) = 0 \quad (x < b) \quad (10.34)$$

$$U_p(x) = -U_0 \quad (b \leq x \leq c) \quad (10.35)$$

$$U_p(x) = 0 \quad (x > c). \quad (10.36)$$

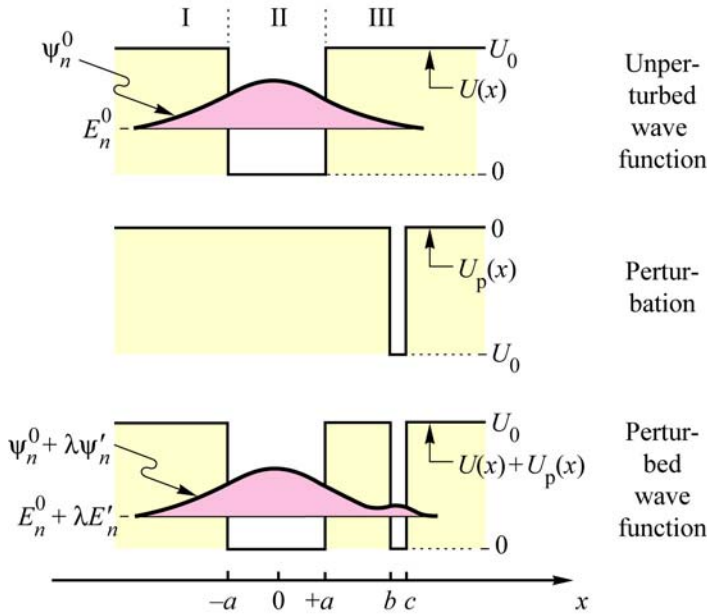


Fig. 10.2. Simple example of an (i) unperturbed wave function, (ii) a small perturbation, and (iii) and resulting perturbed wave function. The first-order correction to the energy due to the perturbation is $\lambda E_n'$. The correction to the wavefunction is $\lambda \psi_n'$.

Since the perturbation is purely a potential energy perturbation, the hamiltonian operator is given by

$$H = H^0 + H' = H^0 + U_p(x). \quad (10.37)$$

The solution of the Schrödinger equation for the unperturbed problem (which is the finite square-well potential) is given by

$$\psi_I(x) = A_1 e^{\kappa x} \quad (10.38)$$

$$\psi_{II}(x) = A_1 \left(\frac{e^{-\kappa a}}{\cos \kappa a} \right) \cos \kappa x \quad (10.39)$$

$$\psi_{III}(x) = A_1 e^{-\kappa x} \quad (10.40)$$

where A_1 is a normalization constant and

$$\kappa = \frac{1}{\hbar} \sqrt{2m(U_0 - E_0^0)} \quad (10.41)$$

$$k = \frac{1}{\hbar} \sqrt{2mE_0^0} \quad (10.42)$$

where $E_{n=0}^0 = E_0^0$ is the lowest eigenstate energy of the unperturbed system.

The change of the lowest eigenstate energy is now calculated by using to Eq. (10.18). Furthermore, we use $\lambda = 1$ and obtain

$$E_0 = E_0^0 + \int_{-\infty}^{\infty} \psi_0^0 U_p(x) \psi_0^0 dx. \quad (10.43)$$

Since $U_p(x) = 0$ outside the interval between b and c , the integration can be limited to this interval

$$E_0 = E_0^0 + \int_b^c (-U_0) A_1^2 e^{-2\kappa x} dx = E_0^0 - \frac{U_0 A_1^2}{2\kappa} (e^{-2\kappa b} - e^{-2\kappa c}). \quad (10.44)$$

The equation reveals that the perturbed energy of the state, E_0 , is lower than the unperturbed value of the energy, E_0^0 . Thus the eigenstate energy decreases upon perturbation.

Exercise: Quantum well electroabsorption. The band diagram of a quantum well structure is shown in **Fig. 10.3**. Consider an electron with effective mass m^* in a symmetric quantum well with thickness L_{QW} , clad by infinitely high barriers. Assume that the center of the quantum well is located at the origin of the coordinate system, *i. e.* at $x = 0$. The quantum well is now subjected to a constant electric field \mathcal{E} , so that the potential energy created by the electric field is given by $U(x) = e \mathcal{E} x$. Upon application of an electric field, the quantum well potential is perturbed. The perturbation hamiltonian for a constant electric field is given by

$$H' = -e \mathcal{E} x. \quad (10.45)$$

- What is the energy of the lowest eigenstate in the well for $\mathcal{E} = 0$?
- Calculate the change in lowest eigenstate energy due to the electric field using first-order perturbation theory and show that first-order perturbation theory yields *no* change in the energy of the ground state.
- Calculate the change in lowest eigenstate energy due to the electric field using second-order perturbation theory. Use reasonable approximations and explain them. Show that second order perturbation theory yields a *decrease* in the ground-state energy.
- Show that the energy between the highest valence band state and the lowest conduction band state (*i. e.* the absorption edge) decreases upon application of an electric field.

The concept of shifting the absorption edge by an electric field is used in electroabsorption quantum-well modulators. In these modulators, quantum wells are placed in the depletion region of a reverse-biased pn junction. Such electroabsorption modulators can be modulated at a much higher bit rate than would be possible by direct current modulation of a semiconductor laser. The speed advantage is due to the much smaller depletion capacitance of the reverse-biased

modulator junction as compared to the diffusion capacitance of the forward-biased laser junction.

Results:

(a)

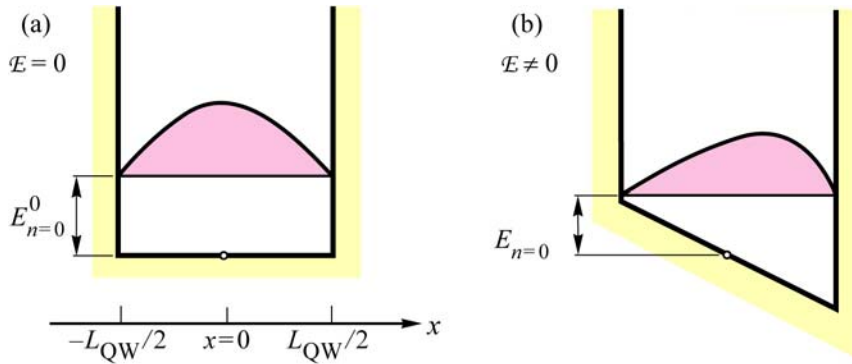


Fig. 10.3. Quantum well structure (a) without and (b) with electric field. The energy of the lowest state changes upon application of field. The change can be calculated by second-order perturbation theory.

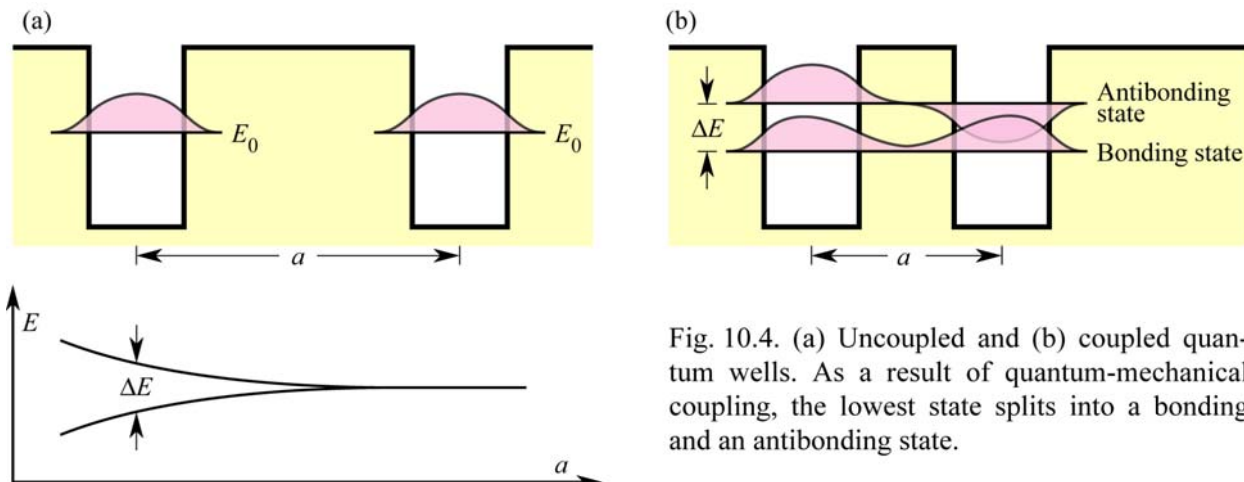


Fig. 10.4. (a) Uncoupled and (b) coupled quantum wells. As a result of quantum-mechanical coupling, the lowest state splits into a bonding and an antibonding state.

Exercise: Coupled quantum wells. If the states of two identical quantum wells (QWs), the state will split into two states, a *bonding state* and an *anti-bonding state*. The energy split ΔE increases as the separation of the QWs decreases. Coupled QWs and the schematic dependence of ΔE on the distance between the two QWs are shown in **Fig. 10.4**. The energy splitting is given by:

$$\Delta E = \tag{10.46}$$

Show the dependence of the ground-state energy levels of two identical atoms as a function of the distance between the two atoms. Explain the difference between the coupling of two QWs and the coupling of two atoms.