1 Solutions to Chapter 1 Exercises

1.1

Exercise 1.1.1 According to the prescription of the text, we assume that the solutions in the two regions take the form

$$\Psi_1(x) = A_1 \sin(Kx) + B_1 \cos(Kx) \ , \tag{1.1.1}$$

and

$$\Psi_2(x) = A_2 e^{\kappa x} + B_2 e^{-\kappa x} \ . \tag{1.1.2}$$

There is no need to write down the solution for $\Psi_3(x)$, since the complete solution is either symmetric, in which case the derivative of $\Psi_2(x)$ vanishes at $x = 0$, or antisymmetric, therefore, $\Psi_2(x)$ itself vanishes at $x = 0$.

The boundary conditions of the problem are

$$\Psi_1\left(x = -a - \frac{b}{2}\right) = 0 \longrightarrow A_1 \sin\left(K\left(-a - \frac{b}{2}\right)\right) + B_1 \cos\left(K\left(-a - \frac{b}{2}\right)\right) = 0 \ . \tag{1.1.3}$$

$$\Psi_1\left(x = -\frac{b}{2}\right) = \Psi_2\left(x = -\frac{b}{2}\right) \longrightarrow A_1 \sin\left(K\left(-\frac{b}{2}\right)\right) + B_1 \cos\left(K\left(-\frac{b}{2}\right)\right) = A_2 e^{-\kappa\frac{b}{2}} + B_2 e^{\kappa\frac{b}{2}} \tag{1.1.4}$$

$$\left.\frac{\Psi_1}{dx}\right|_{x=-\frac{b}{2}} = \left.\frac{\Psi_2}{dx}\right|_{x=-\frac{b}{2}} \longrightarrow A_1 K \cos\left(K\left(-\frac{b}{2}\right)\right) - B_1 K \sin\left(K\left(-\frac{b}{2}\right)\right) = A_2 \kappa e^{\kappa\frac{b}{2}} - B_2 \kappa e^{-\kappa\frac{b}{2}} \ , \tag{1.1.5}$$

and finally,

$$\Psi_2(x = 0) = 0 \longrightarrow A_2 + B_2 = 0 \tag{1.1.6}$$

i.e., $A_2 = -B_2$ for the antisymmetric case, or

$$\left.\frac{\Psi_2}{dx}\right|_{x=0} = 0 \longrightarrow A_2\kappa - B_2\kappa = 0 \ , \tag{1.1.7}$$

i.e., $A_2 = B_2$ for the symmetric case. Regarding the amplitudes A_1, B_1, A_2 and B_2 as the unknowns, we get a homogeneous set of four linear equations, which means that in order to

have a solution, the determinant of the corresponding matrix must vanish. From this condition, we arrive at the equation

$$\kappa \sin aK \cosh \frac{\kappa b}{2} + K \cos aK \sinh \frac{\kappa b}{2} = 0 \tag{1.1.8}$$

for the antisymmetric case, and

$$\kappa \sin aK \sinh \frac{\kappa b}{2} + K \cos aK \cosh \frac{\kappa b}{2} = 0 \tag{1.1.9}$$

for the symmetric one. Dividing by $\cos aK$ and $\cosh \frac{b\kappa}{2}$, or $\sinh \frac{b\kappa}{2}$, respectively, we get

$$\frac{\tan aK}{K} = -\frac{\tanh \frac{b\kappa}{2}}{\kappa} \tag{1.1.10}$$

$$\frac{\tan aK}{K} = -\frac{\coth \frac{b\kappa}{2}}{\kappa} \tag{1.1.11}$$

for the antisymmetric and symmetric case, respectively.

We have an additional equation, which links K and κ. Namely,

$$\frac{\hbar^2 K^2}{2m} = E \tag{1.1.12}$$

$$\frac{\hbar^2 \kappa^2}{2m} = U_0 - E \ , \tag{1.1.13}$$

i.e.,

$$\kappa = \sqrt{\frac{2mU_0}{\hbar^2} - K^2} \ . \tag{1.1.14}$$

Then the two equations above, Eqs. (1.1.10-1.1.11), lead to two equations for K, where a, b and $2mU_0/\hbar^2$ play the role of parameters. Let us note that in Eq. (1.1.14), κ becomes imaginary, when $\hbar^2 K^2/2m > U_0$. This means that in that case, we have real sine and cosine solutions in the barrier, which is a simple consequence of the fact that the particle's energy is larger than the "confining" potential, i.e., the particle is not bound in that region.

The attached Mathematica code contains the derivation and the graphical solutions of the two equations above. A typical case is shown in Fig. 1.1, where $a = 1$, $2mU_0/\hbar^2 = 100$, and $b = 0.1$, or $b = 0.02$. We plotted only $K > 0$, since the equations are invariant under the transformation $K \leftrightarrow -K$. By trying various values for b, we notice that as we increase b, the energy of the symmetric solution drops rapidly, while that of the antisymmetric is more or less constant. In particular, when $b \to 0$, the right hand side of Eq. (1.1.11) tends to $-\infty$, which means that the first solution will be at $K = \pi/2$. At the same time, the right hand side of Eq. (1.1.10) tends to 0, i.e., all solutions of that equation will be at integer multiples of π. This immediately answers the second question of the problem, because the wave number of the symmetric solution is exactly half of that of the asymmetric solution. Also, if we keep the thickness of the barrier constant, and increase the potential, the two solutions separate more and more.

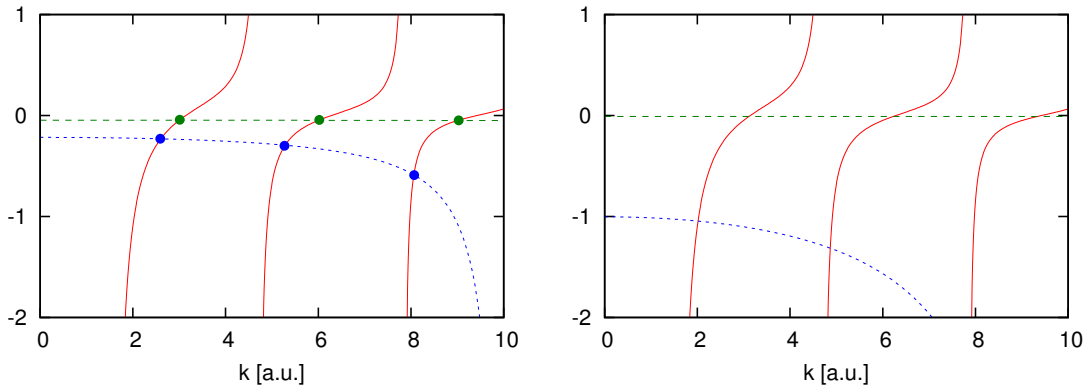

Fig. 1.1 The functions in Eqs. (1.1.10)-(1.1.11) of Exercise 1.1.1 for $a = 1$, $b = 0.1$, and $2mU_0/\hbar^2 = 100$ on the left hand side, and for $a = 1$, $b = 0.02$, and $2mU_0/\hbar^2 = 100$ on the right hand side. The common left hand side of the equations is shown in solid red; the long-dashed green is the right hand side of Eq. (1.1.10) for the asymmetric solution; while the short-dashed blue line is the right hand side of Eq. (1.1.11) for the symmetric solution.

Next, we calculate the first roots of Eqs.(1.1.10)-(1.1.11) as a function of the barrier width, b. We see from Fig. 1.1 that both of these roots are in the interval $[\pi/2, \pi]$, and no other roots are to be found there. This means that we can use this interval for bracketing the solutions. The results are shown in Fig. 1.2. We can notice that for $b \to 0$, we indeed have a factor of 2 in the values of the wave number, while for $b \to \infty$, the two energies will virtually be the same. This behavior can be understood, if we notice that as $b \to \infty$, the overlap of the wavefunctions in the central region goes to zero, so the solutions become decoupled.

Once we have the value of K, we can solve for A_1, B_1, A_2 and B_2, which give the wavefunctions. Two typical solutions are shown in Fig. 1.3, for $a = 1$, $2mU_0/\hbar^2 = 100$, and $b = 0.1$, or $b = 0.3$.

Mathematica code:

```
(* ========= Matrix describing the antisymmetric configuration ======== *)
MatAnti := {{Sin[k*(-a - b/2)], Cos[k*(-a - b/2)], 0, 0}, {Sin[-k*b/2],
Cos[-k*b/2], -Exp[-kappa*b/2], -Exp[kappa*b/2]}, {k*Cos[-k*b/2], -k*
Sin[-k*b/2], -kappa*Exp[kappa*b/2], kappa*Exp[-kappa*b/2]}, {0, 0, 1,
1}}
MatrixForm[MatAnti]
DetMat = Det[MatAnti]
DetMat2 = FullSimplify[DetMat]

(* ========== Matrix describing the symmetric configuration ========== *)
MatSim := {{Sin[k*(-a - b/2)], Cos[k*(-a - b/2)], 0, 0}, {Sin[-k*b/2],
Cos[-k*b/2], -Exp[-kappa*b/2], -Exp[kappa*b/2]}, {k*Cos[-k*b/2], -k*
Sin[-k*b/2], kappa*Exp[kappa*b/2], -kappa*Exp[-kappa*b/2]}, {0, 0,
kappa, -kappa}}
MatrixForm[MatSim]
```

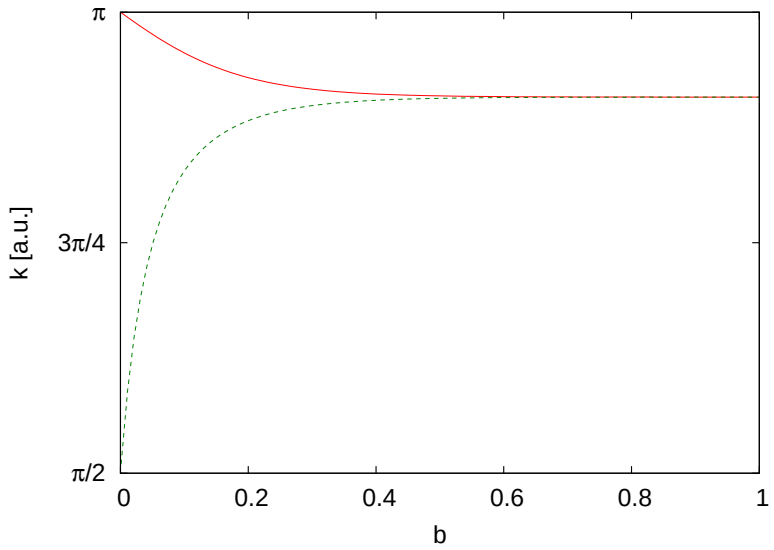

Fig. 1.2 The first roots of Eqs. (1.1.10)-(1.1.11) of Exercise 1.1.1 as a function of b, for $a = 1$, and $2mU_0/\hbar^2 = 100$. The solid red line belongs to the antisymmetric solution, while the dashed green line to the symmetric case.

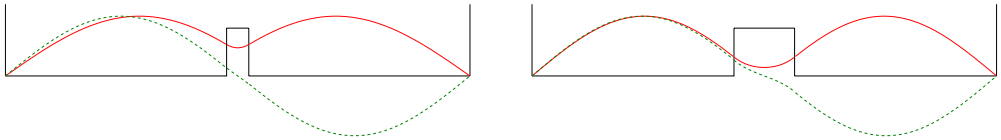

Fig. 1.3 The symmetric (solid red line) and antisymmetric (dashed green line) wave functions for Exercise 1.1.1 for $a = 1$, $b = 0.1$, and $2mU_0/\hbar^2 = 100$ on the left hand side, while $a = 1$, $b = 0.3$, and $2mU_0/\hbar^2 = 100$ on the right hand side.

```
DetMat = Det[MatSim]
DetMat3 = FullSimplify[DetMat]

(* ================= Here we plot the two solutions ================== *)
Plot[{DetMat3 /. {kappa -> Sqrt[20 - k^2], a -> 1, b -> 0.1},
DetMat2 /. {kappa -> Sqrt[20 - k^2], a -> 1, b -> 0.1}}, {k, 0, 4},
PlotStyle -> {RGBColor[1, 0, 0],
RGBColor[0, 1, 0]}]
(* ==== Red is the symmetric, green is the antisymmetric solution.
   Also, this is the case    of strong coupling, for b=0.01 ==== *)

(* ==== Now, we try to find the solutions
   Note that we need to use eps,
   in order to avoid a run-away solution ===== *)

eps = .1
```

```
Ksym = k /. FindRoot[DetMat3 /. {
    kappa -> Sqrt[20 - k^2], a -> 1, b -> 0.1} ,
{k, eps, 4}]
Kanti = k /. FindRoot[DetMat2 /. {kappa -> Sqrt[
          20 - k^2], a -> 1, b -> 0.1} ,
{k, eps, 4}]

(* === We fix a=1, b=0.1, 2mV/hbar^2=20 here === *)
a = 1;
b = .1;
kappa1 = Sqrt[20 - Ksym^2] ;
Bs = (-Sin[Ksym*b/2] + Tan[Ksym*(a + b/2)]*Cos[Ksym*b/
    2])/(Exp[-kappa1*(b/2)] + Exp[kappa1*(b/2)]) ;
ps1 = Plot[Sin[Ksym*x] + Tan[Ksym*(a + b/2)]*Cos[Ksym*x], {
      x, -a - b/2, -b/2}, PlotStyle -> RGBColor[1, 0, 0]] ;
ps2 = Plot[Bs*(Exp[kappa1*(x)] + Exp[-
    kappa1*(x)]), {x, -b/2, b/2}, PlotStyle -> RGBColor[1, 0, 0]]
ps3 = Plot[-Sin[Ksym*x] + Tan[Ksym*(a + b/2)]*
      Cos[Ksym*x], {x, b/2, a + b/2}, PlotStyle -> RGBColor[1, 0, 0]] ;

        Show[ps1, ps2, ps3]


(* ===== The antisymmetric solutions can be obtained in a similar way ===== *)

a = 1;
b = .1;
kappa2 = Sqrt[20 - Kanti^2] ;
Ba = (-Sin[Kanti*b/2] + Tan[Kanti*(a + b/2)]*
Cos[Kanti*b/2])/(Exp[-kappa2*(b/2)] - Exp[kappa2*(b/2)]) ;
pa1 = Plot[Sin[Kanti*x] + Tan[Kanti*(a + b/2)]*Cos[Kanti*x], {
      x, -a - b/2, -b/2}, PlotStyle -> RGBColor[0, 1, 0]] ;
pa2 = Plot[Ba*(Exp[kappa2*(x)] -
 Exp[-kappa2*(x)]), {x, -b/2, b/2}, PlotStyle -> RGBColor[0, 1, 0]]
pa3 = Plot[Sin[Kanti*x] - Tan[Kanti*(a + b/2)]*Cos[Kanti*x], {x, b/2,
          a + b/2}, PlotStyle -> RGBColor[0, 1, 0]] ;
Show[{pa1, pa2, pa3}]
```

Exercise 1.1.2 a) Assuming that the coupling term is negative, we write the matrix of the Hamiltonian,

$$H = \begin{pmatrix} E_1 & -U_{12} \\ -U_{12} & E_2 \end{pmatrix} \tag{1.1.15}$$

which has the eigenvectors

$$\begin{aligned} |v_1\rangle &= \left(1, \frac{\sqrt{4U_{12}^2 + (E_1 - E_2)^2} + E_2 - E_1}{2U_{12}}\right) \\ |v_2\rangle &= \left(1, \frac{-\sqrt{4U_{12}^2 + (E_1 - E_2)^2} + E_2 - E_1}{2U_{12}}\right) \end{aligned} \tag{1.1.16}$$

with the eigenvalues

$$\tilde{E}_1 = \frac{E_1 + E_2}{2} - \sqrt{\left(\frac{E_1 - E_2}{2}\right)^2 + U_{12}^2}$$
$$\tilde{E}_2 = \frac{E_1 + E_2}{2} + \sqrt{\left(\frac{E_1 - E_2}{2}\right)^2 + U_{12}^2} \ . \tag{1.1.17}$$

In the case of two identical atoms, i.e., $E_1 = E_2$, the two eigenvectors reduce to

$$|v_1\rangle = (1, 1)$$
$$|v_2\rangle = (1, -1) \ , \tag{1.1.18}$$

while the eigenvalues become

$$\tilde{E}_1 = E_1 - U_{12}$$
$$\tilde{E}_2 = E_1 + U_{12}. \tag{1.1.19}$$

Therefore, the magnitudes of the coefficients of the second vector are the same, but the signs are opposite, while the coefficients of the first vector are equal. Since the new wave function should still be normalized, i.e.,

$$1 = \langle v|v\rangle = \left(c_1^*\langle\psi_1| \pm c_1^*\langle\psi_2|\right)\left(c_1|\psi_1\rangle \pm c_1|\psi_2\rangle\right) = |c_1|^2 \underbrace{\langle\psi_1|\psi_1\rangle}_{=1} + |c_1|^2 \underbrace{\langle\psi_2|\psi_2\rangle}_{=1} = 2|c_1|^2 \ , \tag{1.1.20}$$

the magnitude of $c_1 = 1/\sqrt{2}$ and c_2 is $1/\sqrt{2}$. Note that we made use of the fact that the overlap between different wave functions is small, i.e., $|\psi_1\rangle$ and $|\psi_2\rangle$ are nearly orthogonal. Since for $c_1 = c_2$ the energy is lowered, $c_1 = c_2$ corresponds to the bonding state, while $c_1 = -c_2$, raising the energy, gives the antibonding configuration.

b) When there is substantial overlap between the atomic wave functions, we have to start from scratch, to use (1.1.10) from the book, which we write as (for negative coupling $-U_{12}$)

$$c_1 E_1 - c_2 U_{12} = c_1 E + c_2 E\langle\psi_1|\psi_2\rangle$$
$$-c_2 U_{12} - c_2 E_2 = c_2 E + c_1 E\langle\psi_2|\psi_1\rangle \tag{1.1.21}$$

or

$$\begin{pmatrix} E_1 & -U_{12} - E\langle\psi_1|\psi_2\rangle \\ -U_{12} - E\langle\psi_1|\psi_2\rangle^* & E_2 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \tag{1.1.22}$$

There is therefore a correction to the coupling (overlap) energy, proportional to

$$I_{12} = \langle\psi_1|\psi_2\rangle. \tag{1.1.23}$$

The first-order correction for the case of identical atoms can be obtained by setting $E = E_1 = E_2$ inside the matrix.

In addition, there is a correction to the normalization of the wave functions. For the case of identical atoms, the eigenstates are still of the form

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\psi_1\rangle \pm |\psi_2\rangle) \ , \tag{1.1.24}$$

i.e.,

$$\langle\Psi|\Psi\rangle = \frac{1}{\sqrt{2}}\left(\langle\psi_1| \pm \langle\psi_2|\right)\frac{1}{\sqrt{2}}\left(|\psi_1\rangle \pm |\psi_2\rangle\right) = \frac{1}{2}(2 \pm \langle\psi_1|\phi_2\rangle \pm \langle\psi_2|\psi_1\rangle) \tag{1.1.25}$$

$$= 1 \pm \mathsf{Re}\ I_{12} \tag{1.1.26}$$

where I_{12} is the overlap integral of the two states. Therefore, the energies of the states are, to the next order of approximation,

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{E_1 \mp |U_{12} + E_1 I_{12}|}{1 \pm \mathsf{Re}\ I_{12}}\ . \tag{1.1.27}$$

c) In this third part of the problem, we first have to determine the two basis functions. Taking one quantum well, the potential is infinite on one side, while it has height U_0 on the other side. That is, for the lowest-lying state, we can search for the solution as

$$\phi_1(x) = A\sin(kx) \equiv \phi_1^-(x), \qquad 0 < x < a \tag{1.1.28}$$

$$\phi_1(x) = Be^{-\kappa x} \equiv \phi_1^+(x), \qquad x > a \tag{1.1.29}$$

with the boundary conditions

$$\phi_1^-(0) = 0 \tag{1.1.30}$$

$$\phi_1^+(a) = \phi_1^+(a) \tag{1.1.31}$$

$$\left.\frac{d\phi_1^-}{dx}\right|_{x=a} = \left.\frac{d\phi_1^+}{dx}\right|_{x=a}\ . \tag{1.1.32}$$

With the specific choice in Eq. (1.1.28), the boundary condition in Eq.(1.1.30) is automatically satisfied, while the second and third boundary condition leads to the two equations

$$A\sin(ka) = Be^{-\kappa a} \tag{1.1.33}$$

$$Ak\cos(ka) = -B\kappa e^{-\kappa a}\ , \tag{1.1.34}$$

or

$$\frac{\tan(ka)}{k} = -\frac{1}{\kappa}\ . \tag{1.1.35}$$

As in Exercise 1.1.1, we still have

$$\kappa = \sqrt{\frac{2mU_0}{\hbar^2} - k^2}\ . \tag{1.1.36}$$

From the same numerical approach as used in Exercise 1.1, we find for the case $a = 1$, $b = 0.1$ and $2mU_0/\hbar^2 = 100$, that the lowest k that satisfies Eq.(1.1.35) is $k = 2.85$. The reason for choosing this value of U_0 is that this is the one that we thoroughly studied in Exercise 1.1.1.

The values of A and B are fixed by the condition that the wave function is normalized. We impose the normalization condition

$$1 = A^2\int_0^a dx\ \sin^2 kx + B^2\int_a^\infty dx\ e^{-2\kappa x} = \frac{A^2(2ka - \sin 2ka)}{4k} + \frac{B^2e^{-2a\kappa}}{2\kappa}\ . \tag{1.1.37}$$

Using the continuity condition in Eq. (1.1.33), we can rewrite the normalization as

$$1 = \frac{A^2(2ka - \sin 2ka)}{4k} + \frac{A^2 \sin^2 ka}{2\kappa} \ , \tag{1.1.38}$$

i.e.,

$$A = \left(\frac{(2ka - \sin 2ka)}{4k} + \frac{\sin^2 ka}{2\kappa} \right)^{-1/2} \ , \tag{1.1.39}$$

and

$$B = \left(\frac{(2ka - \sin 2ka)}{4k} + \frac{\sin^2 ka}{2\kappa} \right)^{-1/2} e^{\kappa a} \sin ka \ . \tag{1.1.40}$$

This gives us one of the basis functions, $\phi_1(x)$, using these values of A and B in Eqs. (1.1.28)-(1.1.29). We get the other one by centering it on the second well, after reflecting it with respect to $x = 0$, and shifting it to the right by $2a + b$. This gives

$$\phi_2(x) = A \sin[k(-x + 2a + b)], \quad a + b < x < 2a + b \tag{1.1.41}$$

$$\phi_2(x) = Be^{-\kappa(-x+2a+b)}, \quad x < a + b \tag{1.1.42}$$

Having obtained the two basis functions, we can calculate the energy of the system using Eq. (1.1.27). When we do not assume orthogonality, we need the overlap integral I_{12}, which we can calculate noting that while the wavefunctions extend to infinity or minus infinity, their product is non-zero over a finite interval $[0, 2a + b]$ only, because outside this interval one of the wavefunctions is zero. Therefore,

$$\begin{aligned} I_{12} = \int_{-\infty}^{\infty} dx \ \phi_1(x)\phi_2(x) &= \int_0^{2a+b} dx \ \phi_1(x)\phi_2(x) \\ &= 2AB \int_0^a dx \ \sin kx \ e^{\kappa x} e^{-\kappa(2a+b)} + B^2 \int_a^{a+b} dx \ e^{-\kappa x} e^{\kappa x} e^{-\kappa(2a+b)} \\ &= 2ABe^{-\kappa(2a+b)} \left[\frac{(\kappa \sin ka - k \cos ka)e^{\kappa a}}{\kappa^2 + k^2} + \frac{k}{\kappa^2 + k^2} \right] + B^2 be^{-\kappa(2a+b)} \\ &= 2ABe^{-\kappa(2a+b)} \left[\frac{\hbar^2((\kappa \sin ka - k \cos ka)e^{\kappa a} + k)}{2mU_0} \right] + B^2 be^{-\kappa(2a+b)} \end{aligned} \tag{1.1.43}$$

where we used the result of Eq.(1.1.36).

We will also need the integral for U_{12}, i.e.,

$$-U_{12} = \int_0^{2a+b} dx \ \phi_2(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \phi_1^*(x). \tag{1.1.44}$$

Since the wave functions are real, $U_{12} = U_{21}$ is real. Now, since $U(x) = U_0$ for $a < x < a + b$

and 0 otherwise,

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+U(x)\right]\phi_1(x)=\begin{cases}\dfrac{\hbar^2k^2}{2m}\phi_1(x)\ , & 0<x<a\\ \left(\dfrac{-\hbar^2\kappa^2}{2m}+U_0\right)\phi_1(x)=\dfrac{\hbar^2k^2}{2m}\phi_1(x), & a<x<a+b\\ -\dfrac{\hbar^2\kappa^2}{2m}\phi_1(x)\ , & a+b<x<2a+b\end{cases} \tag{1.1.45}$$

where we have used Eq. (1.1.36). Therefore, since $E=\hbar^2k^2/2m$,

$$\begin{aligned}-U_{12}-EI_{12}&=AB\int_{a+b}^{2a+b}dx\sin[k(2a+b-x)]e^{-\kappa a}\frac{\hbar^2}{2m}(-\kappa^2-k^2)\\&=-ABU_0\int_{a+b}^{2a+b}dx\sin[k(2a+b-x)]e^{-\kappa a}\\&=-ABU_0e^{-\kappa(2a+b)}\frac{k+e^{\kappa a}(\kappa\sin ka-k\cos ka)}{\kappa^2+k^2}\\&=-\frac{\hbar^2}{2m}ABe^{-\kappa(2a+b)}[k+e^{\kappa a}(\kappa\sin ka-k\cos ka)],\end{aligned} \tag{1.1.46}$$

which is always negative for $E<U$ and $k<\pi/a$, as assumed.

In the Mathematica code given below, we compare the results of Exercise 1.1.1, using K from (1.1.10)-(1.1.11) and κ from (1.1.14) of that exercise, and Eq. (1.1.27) of the present exercise, using (1.1.43) for I_{12} and (1.1.46) for U_{12}, with (1.1.39) and (1.1.40) for A and B and (1.1.35) and (1.1.36) for k and κ. Fig. 1.4 shows the main results. These are plotted as a function of the separation b of the two "atoms", for the case $a=1$, and $2mU_0/\hbar^2=100$. We choose the units in such a way that $2m/\hbar^2=1$. The approximation is quite good down to about $b=0.1$.

If we do not account for the overlap integral, then using (1.1.45), we have

$$-U_{12}=\frac{\hbar^2}{2m}(k^2-\kappa^2)ABe^{-\kappa(2a+b)}\left[\frac{((\kappa\sin ka-k\cos ka)e^{\kappa a}+k)}{k^2+\kappa^2}\right]+\frac{\hbar^2k^2}{2m}B^2be^{-\kappa(2a+b)} \tag{1.1.47}$$

Equation (1.1.27) is used with $I_{12}=0$. As seen in Figure 1.4, this approximation is good down to about $b=0.2$.

Mathematica code:

```
(* ======== Full solution from Exercise 1.1 ============= *)

Clear[b]
U = 100;
a = 1;
kappa := Sqrt[U - K^2]
k2p := K /. FindRoot[Tan[K*a]/K + Tanh[b*kappa/2]/kappa, {K, 1.5, 4}]
k2n := K /. FindRoot[Tan[K*a]/K + Coth[b*kappa/2]/kappa, {K, 2, 4}]

(* ======== Now LCAO solution using same parameters ============= *)

Ep := E1 + Abs[V12]
```

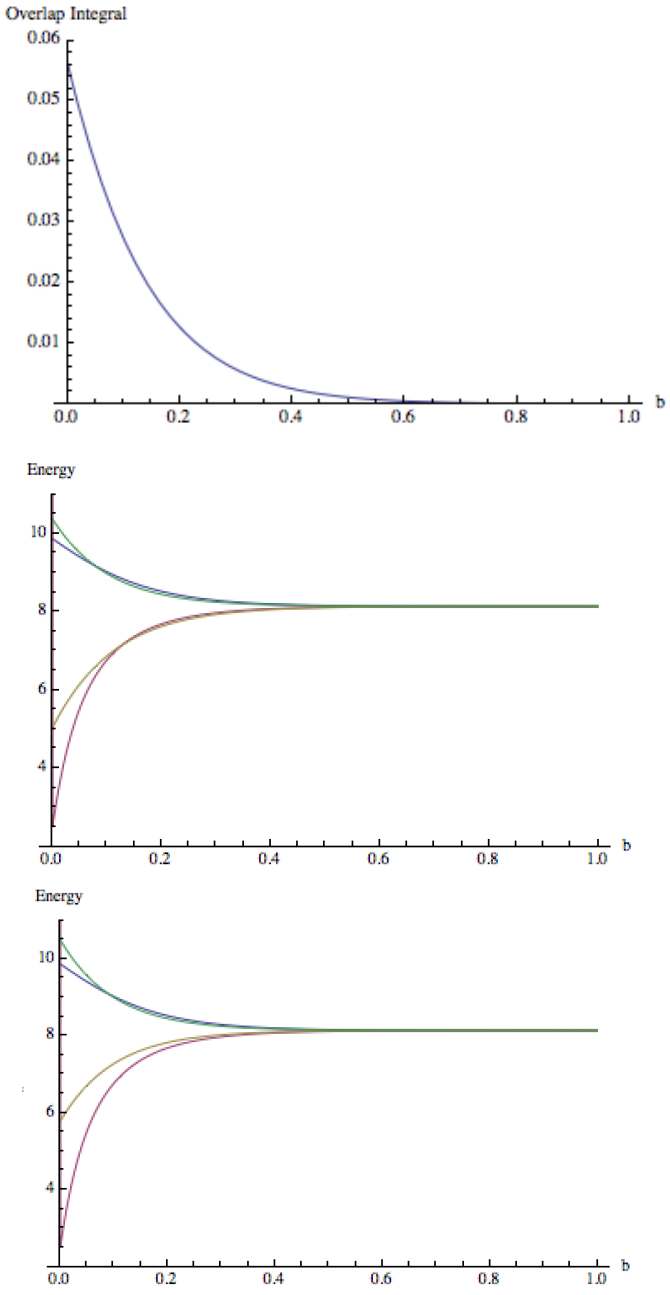

Fig. 1.4 LCAO approximation compared to the full solution for the case $2mU_0/\hbar^2 = 100$, $a = 1$, for Exercise 1.2. Top: the overlap integral I_{12} as a function of the atomic separation b. Middle: the energy of the LCAO approximation (blue and yellow lines) compared to the full solution (red and green lines). Bottom: the energy of the LCAO approximation with no correction for the overlap integral (blue and yellow lines) compared to the full solution (red and green lines).

```
En := E1 - Abs[V12]
k1 = K /. FindRoot[Tan[K*a]/K + 1/Sqrt[U - K^2], {K, 1.5, 4}];
kappa1 = Sqrt[U - k1^2];
A = 1/Sqrt[(2*k1*a - Sin[2*k1*a])/(4*k1) + Sin[k1*a]^2/(2*kappa1)];
B = A*Exp[kappa1*a]*Sin[k1*a];
V12 := A*B*
  Exp[-kappa1*(2*a + b)]*(k1 +
    Exp[kappa1*a]*(kappa1*Sin[k1*a] - k1*Cos[k1*a]))
E1 := k1^2
I12 := 2*A*B*
   Exp[-kappa1*(2*a + b)]*((kappa1*Sin[k1*a] - k1*Cos[k1*a])*
       Exp[kappa1*a] + k1)/U + B^2*b*Exp[-kappa1*(2*a + b)]

(* ======== Now LCAO solution with no overlap correction ============= *)

V12no := (k1^2 - kappa1^2) A*B*
   Exp[-kappa1*(2*a + b)]*(k1 +
      Exp[kappa1*a]*(kappa1*Sin[k1*a] - k1*Cos[k1*a]))/(k1^2 +
      kappa1^2) + k1^2*B^2*b*Exp[-kappa1*(2*a + b)]
Epno := E1 + Abs[V12no]
Enno := E1 - Abs[V12no]


(* We plot the results here. Only variable is b *)

Plot[I12, {b, 0, 1}, PlotRange -> {0, .06}]
Plot[{k2p^2, k2n^2, En/(1 + I12), Ep/(1 + I12)}, {b, 0, 1},
 PlotRange -> {2, 11}]
Plot[{k2p^2, k2n^2, Enno, Epno}, {b, 0, 1}, PlotRange -> {2, 11}]
```

1.2

Exercise 1.2.1 In the two regions, we seek for the solution in the form

$$\Psi_1(x) = A_1 e^{iKx} + B_1 e^{-iKx} \ , \tag{1.2.1}$$

and

$$\Psi_2(x) = A_2 e^{\kappa x} + B_2 e^{-\kappa x} \ . \tag{1.2.2}$$

The boundary conditions at $x = 0$ are

$$\Psi_1(x=0) = \Psi_2(x=0) \longrightarrow A_1 + B_1 = A_2 + B_2 \ . \tag{1.2.3}$$

$$\left.\frac{d\Psi_1}{dx}\right|_{x=0} = \left.\frac{d\Psi_2}{dx}\right|_{x=0} \tag{1.2.4}$$

$$\longrightarrow A_1 iK - B_1 iK = \kappa A_2 - \kappa B_2 \ . \tag{1.2.5}$$

Similarly, at $x = a$, using the fact that

$$\Psi_3(x=a) = \Psi_2(x=-b) e^{ik(a+b)} \ , \tag{1.2.6}$$