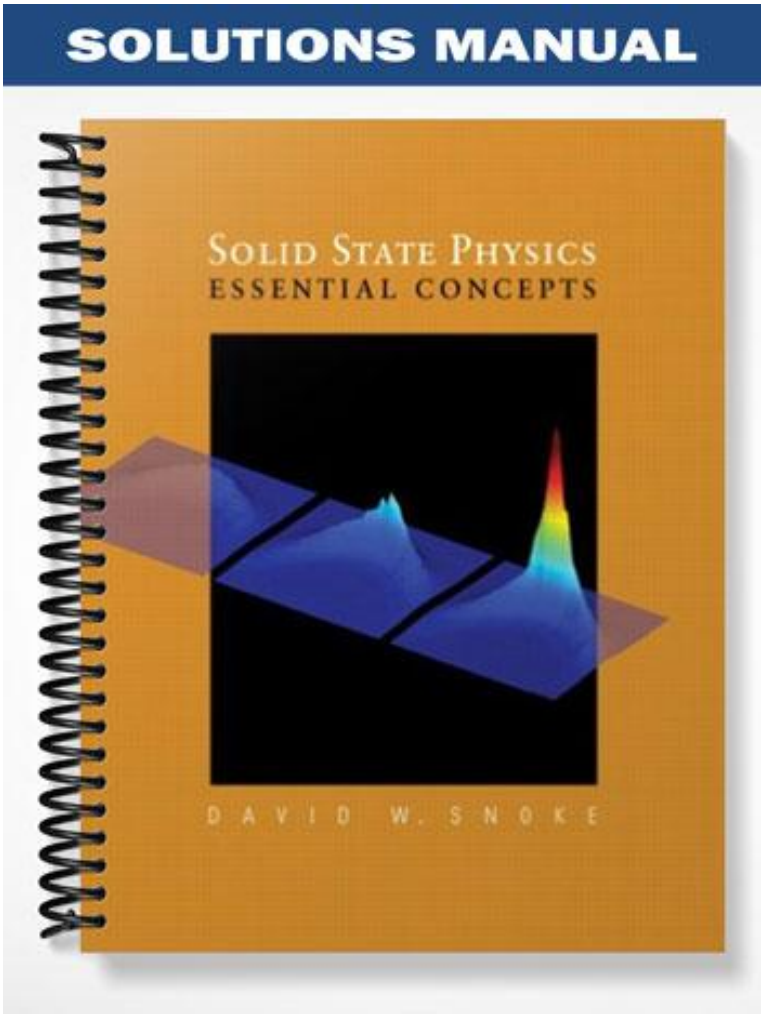
SOLUTIONS MANUAL



Contents

Problems marked with * are more difficult.

Problems marked with † are substantially affected by typos which are included in the Errata.

Chapter 1

Solutions to Chapter 1 Exercises

Exercise 1.1. According to the prescription of the text, we assume that the solutions in the two regions take the form

$$\Psi_1(x) = A_1 \sin(kx) + B_1 \cos(kx) \ , \tag{1}$$

and

$$\Psi_2(x) = A_2 e^{\kappa x} + B_2 e^{-\kappa x} \ . \tag{2}$$

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

$$\Psi_1\left(x = -a - \frac{b}{2}\right) = 0 \longrightarrow A_1 \sin\left(k\left(-a - \frac{b}{2}\right)\right) + B_1 \cos\left(k\left(-a - \frac{b}{2}\right)\right) = 0 \ . \tag{3}$$

$$\Psi_1\left(x = -\frac{b}{2}\right) = \Psi_2\left(x = -\frac{b}{2}\right) \longrightarrow A_1 \sin\left(k\left(-\frac{b}{2}\right)\right) + B_1 \cos\left(k\left(-\frac{b}{2}\right)\right) = A_2 e^{-\kappa\frac{b}{2}} + B_2 e^{\kappa\frac{b}{2}} \tag{4}$$

$$\left.\frac{\Psi_1}{dx}\right|_{x=-\frac{b}{2}} = \left.\frac{\Psi_2}{dx}\right|_{x=-\frac{b}{2}} \longrightarrow A_1 k \cos\left(k\left(-\frac{b}{2}\right)\right) - B_1 k \sin\left(k\left(-\frac{b}{2}\right)\right) = A_2 \kappa e^{\kappa\frac{b}{2}} - B_2 \kappa e^{-\kappa\frac{b}{2}} \ , \tag{5}$$

and finally,

$$\Psi_2(x = 0) = 0 \longrightarrow A_2 + B_2 = 0 \tag{6}$$

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

$$\left.\frac{\Psi_2}{dx}\right|_{x=0} = 0 \longrightarrow A_2\kappa - B_2\kappa = 0 \ , \tag{7}$$

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

$$\kappa \sin ak \cosh \frac{\kappa b}{2} + k \cos ak \sinh \frac{\kappa b}{2} = 0 \tag{8}$$

for the antisymmetric case, and

$$\kappa \sin ak \sinh \frac{\kappa b}{2} + k \cos ak \cosh \frac{\kappa b}{2} = 0 \tag{9}$$

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

$$\frac{\tan ak}{k} = -\frac{\tanh \frac{b\kappa}{2}}{\kappa} \tag{10}$$

$$\frac{\tan ak}{k} = -\frac{\coth \frac{b\kappa}{2}}{\kappa} \tag{11}$$

for the antisymmetric and symmetric case, respectively.

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

$$\frac{\hbar^2 k^2}{2m} = E \tag{12}$$

$$\frac{\hbar^2 \kappa^2}{2m} = V_0 - E \ , \tag{13}$$

i.e.,

$$\kappa = \sqrt{\frac{2mV_0}{\hbar^2} - k^2} \ . \tag{14}$$

Then the two equations above, Eqs. (10-11), lead to two equations for k, where a, b and $2mV_0/\hbar^2$ play the role of parameters. Let us note that in Eq. (14), κ becomes imaginary, when $\hbar^2 k^2/2m > V_0$. 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, where $a = 1$, $2mV_0/\hbar^2 = 100$, 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. (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. (10) tends to 0, i.e., all solutions of that equation will be at integar 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.

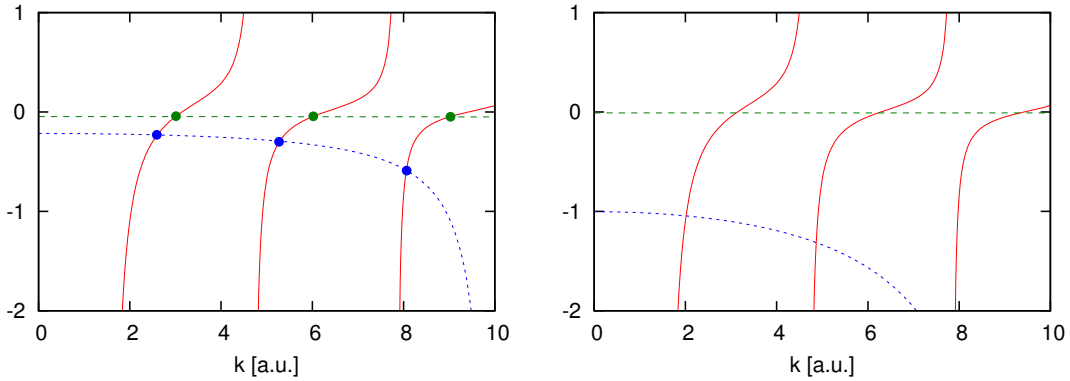


Figure 1.1: The functions in Eqs. (10)-(11) of Exercise 1.1 for $a = 1$, $b = 0.1$, and $2mV_0/\hbar = 100$ on the left hand side, and for $a = 1$, $b = 0.02$, and $2mV_0/\hbar^2 = 100$ on the right hand side. The common left hand side of the equations is shown in solid red, long-dashed green is the right hand side of Eq. (10), the asymmetric solution, while the short-dashed blue line is the right hand side of Eq. (11), the symmetric solution. Also shown are the corresponding solutions for $b = 0.1$ on the left hand side.

Next, we calculate the first roots of Eqs.(10)-(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 $a = 1$, $2mV_0/\hbar = 100$, and $b = 0.1$, or $b = 0.3$.

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* **Exercise 1.2.** a) The eigenvectors belonging to the matrix of the Hamiltonian,

$$H = \begin{pmatrix} E_1 & -V_{12} \\ -V_{12}^* & E_2 \end{pmatrix} \tag{1}$$

are

$$v_1 = \left(1, \frac{\sqrt{4|V_{12}|^2 + (E_1 - E_2)^2} + E_1 - E_2}{2V_{12}}\right) \tag{2}$$

$$v_2 = \left(1, -\frac{\sqrt{4|V_{12}|^2 + (E_1 - E_2)^2} + E_2 - E_1}{2V_{12}}\right) \tag{3}$$

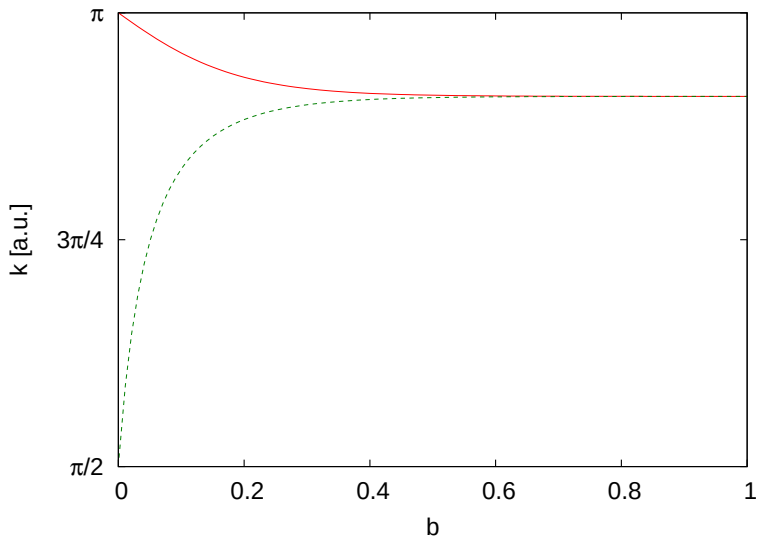

Figure 1.2: The first roots of Eqs.(10)-(11) of Exercise 1.1 as a function of b, for $a = 1$, and $2mV_0/\hbar^2 = 100$. The solid red line belongs to the antisymmetric solution, while the dashed green line to the symmetric case.

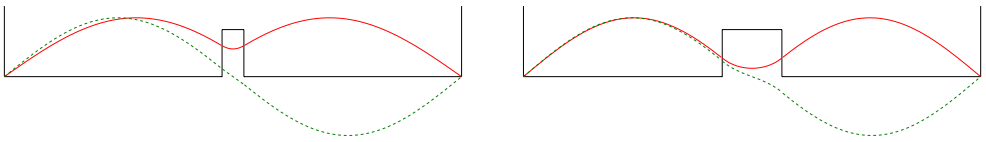

Figure 1.3: The symmetric (solid red line) and antisymmetric (dashed green line) wave functions for Exercise 1.1 for $a = 1$, $b = 0.1$, and $2mV_0/\hbar = 100$ on the left hand side, while $a = 1$, $b = 0.3$, and $2mV_0/\hbar = 100$ on the right hand side.

with the eigenvalues

$$\tilde{E}_1 = \frac{E_1+E_2}{2} - \sqrt{\left(\frac{E_1-E_2}{2}\right)^2 + |V_{12}|^2} \quad (4)$$

$$\tilde{E}_2 = \frac{E_1+E_2}{2} + \sqrt{\left(\frac{E_1-E_2}{2}\right)^2 + |V_{12}|^2} \; . \quad (5)$$

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

$$v_1 = \left(1, \frac{|V_{12}|}{V_{12}}\right) \quad (6)$$

$$v_2 = \left(1, -\frac{|V_{12}|}{V_{12}}\right) \; , \quad (7)$$

while the eigenvalues become

$$\tilde{E}_1 = E_1 - |V_{12}| \quad (8)$$

$$\tilde{E}_2 = E_1 + |V_{12}| \; . \quad (9)$$

Therefore, the magnitudes of the coefficients of the second basis vector, $|\Psi_2\rangle$, are the same, but the signs are opposite, while the coefficients of the first basis vector are equal. Since the new wavefunction should still be normalized, i.e.,

$$1 = \langle\Psi|\Psi\rangle = \left(c_1^*\langle\phi_1| \pm c_1^*\langle\phi_2|\right)\left(c_1|\phi_1\rangle \pm c_1|\phi_2\rangle\right) = |c_1|^2 \underbrace{\langle\phi_1|\phi_1\rangle}_{=1} + |c_1|^2 \underbrace{\langle\phi_2|\phi_2\rangle}_{=1} = 2|c_1|^2 \; , \quad (10)$$

and the phases of the wavefunctions can be chosen at will, we conclude that $c_1 = 1/\sqrt{2}$ and $c_2 = \pm 1/\sqrt{2}$. Note that in the last step we made use of the fact that the overlap between different wavefunctions is small, i.e., $|\phi_1\rangle$ and $|\phi_2\rangle$ are 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 wavefunctions, we have to calculate the energy from

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \; . \quad (11)$$

For the case of identical atoms, the eigenstates are still of the form

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle \pm |\phi_2\rangle) \; , \quad (12)$$

i.e.,

$$\langle\Psi|\Psi\rangle = \frac{1}{\sqrt{2}}\left(\langle\phi_1| \pm \langle\phi_2|\right)\frac{1}{\sqrt{2}}\left(|\phi_1\rangle \pm |\phi_2\rangle\right) = \frac{1}{2}(2 + \langle\phi_1|\phi_2\rangle + \langle\phi_2|\phi_1\rangle) \quad (13)$$

$$= 1 + \mathsf{Re}\; I_{12} \quad (14)$$

where

$$I_{12} = \langle \phi_1 | \phi_2 \rangle \tag{15}$$

is the overlap integral of the two states. The expectation value of the Hamiltonian operator for the case of two identical atoms is given above. Therefore, the energy of the system is

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{E_1 + E_2 \mp V_{12}}{1 + \mathsf{Re}\ I_{12}} \ . \tag{16}$$

c) In the 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 V_0 on the other side. That is, in the notation of the figure, for the lowest-lying state, we can search for the solution as

$$\Psi_I(x) = A \sin(kx) \tag{17}$$
$$\Psi_{II}(x) = Be^{-\kappa x} \ , \tag{18}$$

with the boundary conditions

$$\Psi_I(x=0) = 0 \tag{19}$$
$$\Psi_I(x=a) = \Psi_{II}(x=a) \tag{20}$$
$$\left.\frac{d\Psi_I}{dx}\right|_{x=a} = \left.\frac{d\Psi_{II}}{dx}\right|_{x=a} \ . \tag{21}$$

With the specific choice in Eq.(17), the boundary condition in Eq.(19) is automatically satisfied, while the second and third boundary condition leads to the two equations

$$A \sin(ka) = Be^{-\kappa a} \tag{22}$$
$$Ak \cos(ka) = -B\kappa e^{-\kappa a} \ , \tag{23}$$

or, in matrix form,

$$\begin{pmatrix} \sin(ka) & -e^{-\kappa a} \\ k\cos(ka) & -\kappa e^{-\kappa a} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = 0 \ . \tag{24}$$

This homogeneous equation has solutions for A and B if and only if the determinant of the matrix is zero, i.e., if

$$\kappa \sin(ka) + k \cos(ka) = 0 \ , \tag{25}$$

or

$$\frac{\tan ka}{k} = -\frac{1}{\kappa} \ . \tag{26}$$

(This latter result can also easily be obtained by dividing Eq.(22) by Eq.(23).) As in Exercise 1, we still have

$$\kappa = \sqrt{\frac{2mV_0}{\hbar^2} - k^2} \ . \tag{27}$$

From the same numerical approach as used in Exercise 1.1, we find for the case $a = 1$, $b = 0.1$ and $2mV_0/\hbar^2 = 100$, that the lowest k that satisfies Eq.(26) is $k = 2.85$. The reason for choosing this value of V_0 is that this is the one that we thoroughly studied in Exercise 1.1.

The value of A and B still has an ambiguity, because we can multiply them by any number, and still get a valid solution. The value of A and B are fixed by the condition that the wavefunction is normalized. We could simply pick $A = 1$, and leave the wavefunction un-normalized, since it will not affect the energyies. Alternatvely, we can impose the normalization condition

$$1 = A^2 \int_0^a dx\ \sin^2 kx + B^2 \int_a^\infty dx\ e^{-2\kappa x} = \frac{A^2(2ka - \sin 2ka)}{4k} + \frac{B^2 e^{-2a\kappa}}{2\kappa}\ . \tag{28}$$

Using the continuity condition in Eq. (22), we can rewrite the normalization as

$$1 = \frac{A^2(2ka - \sin 2ka)}{4k} + \frac{A^2 \sin^2 ka}{2\kappa}\ , \tag{29}$$

i.e.,

$$A = \left(\frac{(2ka - \sin 2ka)}{4k} + \frac{\sin^2 ka}{2\kappa} \right)^{-1/2}\ , \tag{30}$$

and

$$B = \left(\frac{(2ka - \sin 2ka)}{4k} + \frac{\sin^2 ka}{2\kappa} \right)^{-1/2} e^{\kappa a} \sin ka\ . \tag{31}$$

This gives us one of the basis functions, which we denote by $\phi_1(x)$. We get the other one by "centering" it on the second well, i.e., after reflecting it with respect to $x = 0$, and shifting it to the right by $2a + b$, we get $\phi_2(x) = \phi_1(-x + 2a + b)$. Having obtained the two basis functions, we can calculate the energy of the system using Eq. (16).

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,

$$\begin{aligned}
\int_{-\infty}^{\infty} dx\ \phi_1(x)\phi_2(x) &= \int_0^{2a+b} dx\ \phi_1(x)\phi_2(x) \\
&= 2AB \int_0^a dx\ \sin kx\ e^{\kappa x} e^{-\kappa(2a+b)} + B^2 \int_a^{a+b} dx\ e^{-\kappa x} e^{\kappa x} e^{-\kappa(2a+b)} \\
&= 2ABe^{-\kappa(2a+b)} \left[\frac{(\kappa \sin ak - k \cos ka)e^{\kappa a}}{\kappa^2 + k^2} + \frac{k}{\kappa^2 + k^2} - \right] + B^2 b e^{-\kappa(2a+b)} \\
&= 2ABe^{-\kappa(2a+b)} \left[\frac{\hbar^2((\kappa \sin ak - k \cos ka)e^{\kappa a} + k)}{2mV_0} \right] + B^2 b e^{-\kappa(2a+b)}\ ,
\end{aligned} \tag{32}$$

where we used the result of Eq.(27).

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

$$V_{12} = \int_0^{2a+b} dx\ \phi_2(x) \left[\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - V(x) \right] \phi_1^*(x)\ . \tag{33}$$

Since the Hamiltonian is Hermitian, $V_{21} = V_{12}$. This also follows from the symmetry of the wavefunctions. Now, since $V(x) = V_0$ for $a < x < a + b$ and 0 otherwise,

$$\left[\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - V(x)\right]\phi_1(x) = \begin{cases} \dfrac{\hbar^2 k^2}{2m}\phi_1(x) \ , & \text{if} \quad 0 < x < a + b \\ \dfrac{\hbar^2 \kappa^2}{2m}\phi_1(x) \ , & \text{if} \quad a + b < x < 2a + b \end{cases} \tag{34}$$

Therefore,

$$\begin{aligned} V_{21} &= AB\frac{\hbar^2 k^2}{2m}\int_0^a dx\ e^{-\kappa(2a+b)}e^{\kappa x}\sin kx && (35)\\ &\quad + B^2\frac{\hbar^2 k^2}{2m}\int_a^{a+b} dx\ e^{-\kappa(2a+b)}e^{\kappa x}e^{-\kappa x} && (36)\\ &\quad + AB\frac{\hbar^2 \kappa^2}{2m}\int_{a+b}^{2a+b} dx\ e^{-\kappa x}\sin[(2a+b-x)k] && (37)\\ &= \frac{\hbar^2}{2m}\left[ABk^2\left(\frac{k-(\kappa\sin ka + k\cos ka)e^{-\kappa a}}{k^2+\kappa^2}\right) + B^2k^2be^{-\kappa(2a+b)}\right. && (38)\\ &\quad \left. + AB\kappa^2\left(\frac{ke^{-\kappa(2a+b)} + (\kappa\sin ka - k\cos ka)e^{-\kappa(a+b)}}{k^2+\kappa^2}\right)\right] && (39) \end{aligned}$$

In the Mathematica code presented at the end of this chapter, we implement the integrals involved in a numerical routine. Fig. 1.4 shows the main results. On the left-hand side of the figure, the overlap integral and the potential term is plotted as a function of the separation of the two "atoms", for the case $a = 1$, and $2mV_0/\hbar^2 = 100$, while b is the variable. On the right hand side, the energy of the symmetric and antisymmetric combinations is shown. For comparison, we also plot the results of the numerical solution for the full two-well system. We choose the units in such a way that $2m/\hbar^2 = 1$.

Looking at the left hand side of Fig. 1.4, we notice that both the overlap integral and the potential term quickly decrease as the atomic separation is increased, which is the expected result. From the right hand side of the figure, we infer that the LCAO approximation is a fairly good one, except for the antisymmetric combination at small separation. The deviation from the exact result very quickly tends to zero, and becomes negligible in the range where the overlap integral is zero.

Exercise 1.3. In the two regions, we seek for the solution in the form

$$\Phi_1(x) = A_1e^{iKx} + B_1e^{-iKx} \ , \tag{1}$$

and

$$\Phi_2(x) = A_2e^{\kappa x} + B_2e^{-\kappa x} \ . \tag{2}$$

Since the energy eigenvalues do not depend on a global phase factor e^{ikx}, the complete wave function can be assumed in the form

$$\Psi_1(x) = e^{ikx}\Phi_1(x) \quad \text{and} \quad \Psi_2(x) = e^{ikx}\Phi_2(x) \ . \tag{3}$$

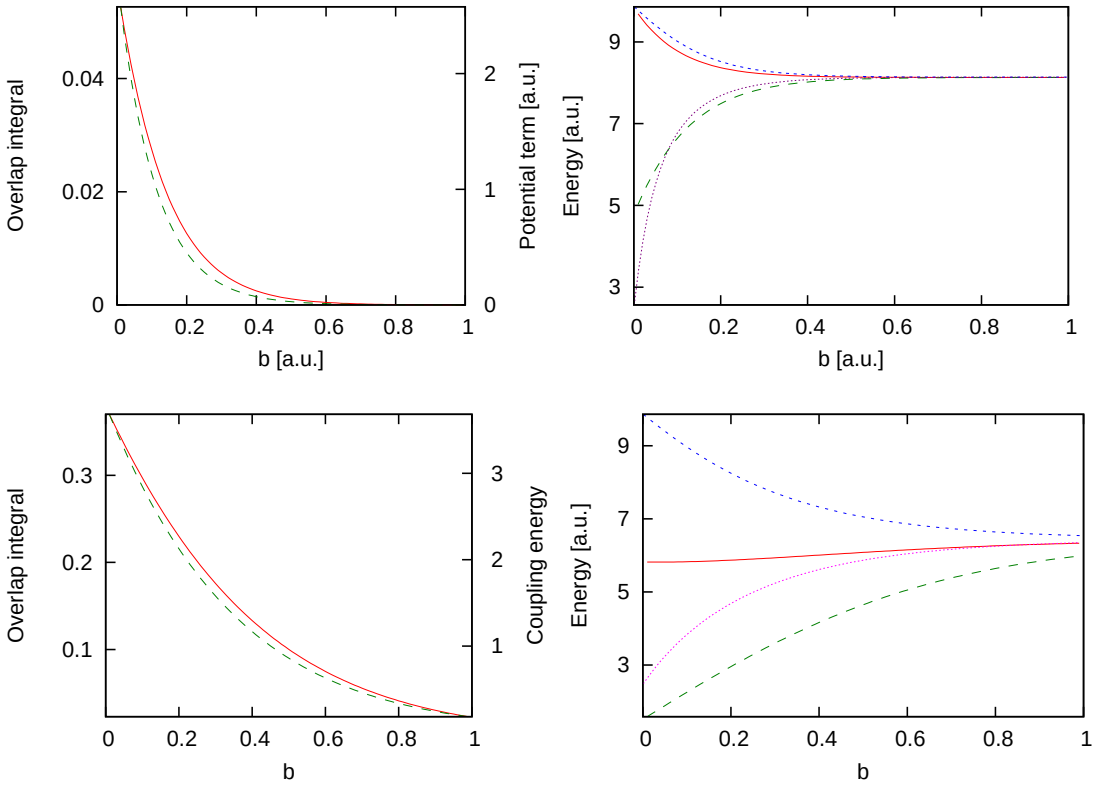

Figure 1.4: LCAO approximation compared to the full numerical solution for the two cases $2mV_0/\hbar = 100$ (top two plots) and $2mV_0/\hbar = 20$ (bottom two plots), for Exercise 1.2 ($a = 1$ in both cases). Left hand side: the overlap integral I_{12} (solid red, left axis), and the coupling energy V_{12} (dashed green, right axis) as a function of the atomic separation, b. Right hand side: the energy of the symmetric (solid red), and the antisymmetric combination (long dashed green) for the LCAO approximation using these parameters. The full numerical result is the short dashed blue line (symmetric) and the fine dashed purple line (antisymmetric).

Hence, the boundary conditions at $x = 0$ are

$$\Psi_1(x=0) = \Psi_2(x=0) \longrightarrow \Phi_1(x=0) = \Phi_2(x=0) \longrightarrow A_1 + B_1 = A_2 + B_2 \ . \tag{4}$$

$$\left.\frac{d\Psi_1}{dx}\right|_{x=0} = \left.\frac{d\Psi_2}{dx}\right|_{x=0} \longrightarrow \left.\frac{d\Phi_1}{dx}\right|_{x=0} + ik\Phi_1(x=0) = \left.\frac{d\Phi_2}{dx}\right|_{x=0} + ik\Phi_2(x=0) \tag{5}$$

$$\longrightarrow \left.\frac{d\Phi_1}{dx}\right|_{x=0} = \left.\frac{d\Phi_2}{dx}\right|_{x=0} \longrightarrow A_1 iK - B_1 iK = \kappa A_2 - \kappa B_2 \ . \tag{6}$$

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

$$\Psi_3(x) = \Psi_2(x) e^{ik(a+b)} \ , \tag{7}$$

we get

$$\Psi_1(x=a) = \Psi_3(x=a) \longrightarrow \Psi_1(x=a) = \Psi_2(x=-b) e^{ik(a+b)} \tag{8}$$

$$\longrightarrow A_1 e^{iK} + B_1 e^{-iK} = A_2 e^{-\kappa b} e^{ik(a_b)} + B_2 e^{\kappa b} e^{ik(a+b)} \ , \tag{9}$$

and finally,

$$\left.\tfrac{d\Psi_1}{dx}\right|_{x=a} = \left.\tfrac{d\Psi_3}{dx}\right|_{x=a} \longrightarrow \left.\tfrac{d\Phi_1}{dx}\right|_{x=a} + ik\Phi_1(x=a) = e^{ik(a+b)} \left[\left.\tfrac{d\Phi_2}{dx}\right|_{x=-b} + ik\Phi_2(x=-b) \right] \tag{10}$$

$$\longrightarrow A_1(iK+ik)e^{iKa} - B_1(iK-ik)e^{-iKa} = e^{ik(a+b)} \left[A_2(\kappa+ik)e^{-\kappa b} - B_2(\kappa-ik)e^{\kappa b} \right] \ . \tag{11}$$

Regarding the amplitudes A_1, B_1, A_2, B_2 as the unknowns, and rendering Eqs. (4)-(11) into matrix form, we have a set of four linear equations with zero right hand side, which means that the determinant of the matrix must vanish. The attached Mathematica code contains the calculations. In the last step, we take the real part of the expression, since if it is equal to 0, then both the real and imaginary parts must be equal to zero. If, instead of the real, we had taken the imaginary part, we would have arrived at the same result, namely, Eq. (1.10) in the text.

According to Eq. (1.10),

$$\frac{\kappa^2 - K^2}{2\kappa K} \sinh(\kappa b) \sin(Ka) + \cosh(\kappa b) \cos(Ka) = \cos(k(a+b)) \ . \tag{12}$$

Now, as $\kappa b \to 0$ and $b \to 0$, $a + b \to a$, $\sinh(\kappa b) \to \kappa b$ and $\cosh(\kappa b) \to 1$. Inserting these into Eq. (12), we arrive at

$$\frac{\kappa^2 - K^2}{2\kappa K} (\kappa b) \sin(Ka) + \cos(Ka) = \cos(k(a)) \ , \tag{13}$$

i.e.,

$$\left(\frac{\kappa^2 b}{2K} - \frac{Kb}{2} \right) \sin(Ka) + \cos(Ka) = \cos(ka) \ , \tag{14}$$

hence

$$\frac{\kappa^2 b}{2K}\sin(Ka) + \cos(Ka) = \cos(ka) \ , \tag{15}$$

as is the result of Eq. (1.11) in the text.

Exercise 1.4. At $k = 0$, Eq. (1.11) reduces to

$$\frac{\kappa^2 b}{2K}\sin Ka + \cos Ka = 1 \ , \tag{1}$$

and with the approximation $\sin Ka \approx Ka$ and $\cos Ka = 1 - \frac{1}{2}(Ka)^2$, this can further be simplified to yield

$$\frac{\kappa^2 b}{2a} = \frac{1}{2}K^2 \ . \tag{2}$$

However, upon the definition of κ^2, after multiplying by $\hbar^2/m$, $\hbar^2\kappa^2/2m$ on the left hand side can be replaced by $V_0 - E$, while the right hand side simply becomes E_0, the zero-point energy. Thus we get

$$\frac{(V_0 - E)b}{a} = E_0 \ , \tag{3}$$

which, as $V_0 \to \infty$, is

$$\frac{V_0 b}{a} = E_0 \ . \tag{4}$$

Exercise 1.5. If we set $ka = \pi$, then Eq. (1.10) reduces to

$$\frac{\kappa^2 b}{2K}\sin Ka + \cos Ka = -1 \ , \tag{1}$$

which, with the expansion $Ka \approx \pi + \Delta Ka$, i.e., $\sin(Ka) \approx -\Delta Ka$ and $\cos Ka \approx -1 + \dfrac{(\Delta Ka)^2}{2}$, then becomes

$$\frac{\kappa^2 b}{2K}(-\Delta Ka) + \frac{(\Delta Ka)^2}{2} = 0 \ , \tag{2}$$

or,

$$\frac{\kappa^2 b}{\dfrac{2\pi}{a}\left(1 + \dfrac{\Delta Ka}{\pi}\right)}(-\Delta Ka) + \frac{(\Delta Ka)^2}{2} = 0 \ , \tag{3}$$

hence,

$$\frac{\kappa^2 ba}{2\pi}(-\Delta Ka) + \frac{(\Delta Ka)^2}{2}\left(1 + \frac{\Delta Ka}{\pi}\right) = 0 \ . \tag{4}$$

This equation has the obvious solution $\Delta K = 0$, and

$$\Delta K = \frac{-\pi \pm \sqrt{\pi^2 + 4ab\kappa^2}}{2a} \ . \tag{5}$$

One of the roots, namely, the one that corresponds to the negative sign, is approximately $-2\pi/a$, which is in contradiction with our original assumption that $\Delta K a \ll 1$, therefore, we retain only the root with the positive sign. That root, assuming that $4ab\kappa^2 \ll \pi$, can be expanded to yield

$$\Delta K = \frac{-\pi + \sqrt{\pi^2 + 4ab\kappa^2}}{2a} = \frac{-\pi + \pi\sqrt{1 + 4ab\kappa^2/\pi^2}}{2a} \approx \frac{-\pi + \pi(1 + 2ab\kappa^2/\pi^2)}{2a} = \frac{b\kappa^2}{\pi^2} \ . \tag{6}$$

The energy is simply $E = \dfrac{\hbar^2}{2m}K^2$, hence the energy difference between the two states is

$$\Delta E = \frac{\hbar^2}{2m}\left(\frac{\pi}{a} + \Delta K\right)^2 - \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 \approx \frac{\hbar^2}{2m}\frac{2\pi\Delta K}{a} = \frac{\hbar^2}{2m}\frac{2b\kappa^2}{a\pi} \ . \tag{7}$$

Since $\kappa^2 \sim (V_0 - E)$, when $V_0 \gg E$ and $V_0 b \to 0$, then $\kappa^2 b \to 0$. This also means that $\Delta E \to 0$.

Exercise 1.6. From Eq. (1.11), and using the definition of κ^2, furthermore, the simplifications $a = 1$, $\hbar^2/2m = 1$ and $E = K^2$, we have

$$\frac{(V_0 - K^2)b}{2K}\sin K + \cos K = \cos k \ , \tag{1}$$

or, after expressing everything as a function of the energy,

$$k(E) = \arccos\left(\cos\sqrt{E} + \frac{(V_0 - E)b}{2\sqrt{E}}\sin\sqrt{E}\right) \ . \tag{2}$$

In the attached Mathematica file, we define $k(E, V_0, b)$, i.e., the wavevector as a function of the energy and the coupling parameters V_0, b. Fig. 1.5 shows a typical plot of the magnitude of the wave vector as a function of the energy for $V_0 = 0.5$ and $b = 0.1$. We can clearly see the gaps that open at the points where k is equal to some integer multiple of π.

Exercise 1.7. When $V_0 \to \infty$, apart from an irrelevant phase factor, the eigenfunctions will be $\sin Kx/2$, since the wavefuntion must nearly vanish at the two ends, but we have to use the dispersion relation that we derived in Eq. (1.10). By substituting $k = \pi/(2a)$, $a = 1$, $V_0 b = 100$ and $b \to 0$ into Eq. (1.10), we get an equation for K in the form

$$\frac{V_0 b}{2K}\sin K + \cos K = 0 \ , \tag{1}$$

i.e.,

$$50 = -K\operatorname{cotan} K \ , \tag{2}$$

from which we find the lowest root as $K \approx 3.08$. Thus the wavefunction is $\Phi(x) = A\sin 1.54x$. For the completely separated case, i.e., when $V_0 b \to \infty$, this would simply become $\Phi(x) = A\sin x\pi/2$.

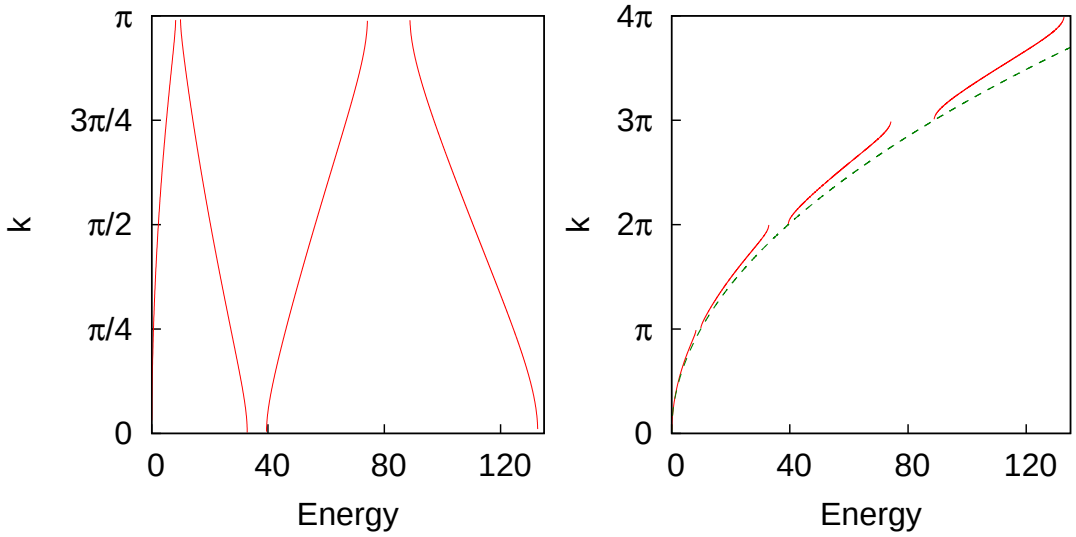

Figure 1.5: The dispersion relation in Eq. (2) for $V_0 = 0.5$ and $b = 0.1$ in the reduced Brillouin zone (left hand side) and in the extended zone (right hand side).

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*† **Exercise 1.8.** The lattices in the figures were generated by the Mathematica code in the Appendix. There are many lines of code but each command is essentially a cut-and-paste of the same lines but with different coordinates.

In the wurtzite lattice with $c = \sqrt{8/3}a$, each atom has four equidistant nearest neighbors.

There are three different types of atoms in the perovskite structure, which resembles an structure which is both face-centered and body centered. The body central atom has six nearest neighbors, the face-centered atoms have two nearest neighbors, and the corners have 12 nearest neighbors, namely the atoms at the centers of the faces.

The first basis atom of the fluorite structure produces an fcc structure. Each of the four fluorine atoms has four nearest neighbors consisting of Ca atoms in the fcc structure. This lattice is thus like a diamond lattice but with extra links so that each Ca atom has four nearest F neighbors.

Note that the cuprite lattice structure has an error as given in the book in Table 1.1; the basis vectors should be $(0, \frac{a}{2}(\hat{x}+\hat{y}+\hat{z}), \frac{a}{4}(\hat{x}+\hat{y}+\hat{z}), \frac{a}{4}(3\hat{x}+3\hat{y}+\hat{z}), \frac{a}{4}(3\hat{x}+\hat{y}+3\hat{z}), \frac{a}{4}(\hat{x}+3\hat{y}+3\hat{z})$. The first two atoms in the basis have four nearest neighbors, while the last four atoms each have two nearest neighbors.
