PHY4905: Intro to Solid State Physics

Tight-binding Model

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REMINDER: TUNNELING

Quantum particles can penetrate into regions where classical motion is forbidden. For example, consider a rectangular potential barrier. To the left of the barrier, the motion is free. To the right of the barrier, the Shroedinger equation reads

$$-\hbar^2\frac{d^2\psi}{dx^2}+V_0\psi=E\psi. \tag{1}$$

Classically, the motion is forbidden for energies smaller than the barrier height. The quantum-mechanical wave-function is not equal to zero, however. Re-arranging the terms in the equation above, we get

$$-\frac{d^2\psi}{dx^2}=\frac{2m}{\hbar^2}(E-V_0)\psi. \tag{2}$$

This looks like a simple harmonic oscillator equation in Classical Mechanics (upon replacement $x\to t$ and $\frac{2m}{\hbar^2}(E-V_0)\to\omega^2$); however, the sign of the coefficient in front of ψ on the right-hand side depends on the relation between V_0 and E. For $E>V_0$, the sign is positive. Then this is really a simple harmonic oscillator equation which solutions being $\psi=C\exp(ikx)$, where $k=\sqrt{2m(E-V_0)}/\hbar$ is the wavenumber. Since the wavenumber is real, the real and imaginary parts of the wave-function oscillate in space. For $E<V_0$, the sign is negative. The solution formally remains the same but now k, being the root of a negative number, is imaginary:

$$k=\sqrt{2m(E-V_0)}/\hbar=\sqrt{-2m(V_0-E)}/\hbar=i\sqrt{2m(V_0-E)}/\hbar\equiv i\kappa. \tag{3}$$

Consequently, the wave-function $\psi=C\exp(ikx)=C\exp(i(i\kappa)x)=C\exp(-\kappa x)$ falls off exponentially with distance inside the barrier. (Notice that we have chosen the the square root with positive imaginary part. Another mathematically possible choice $k=-i\kappa$ would result in the wave-function $\psi=C\exp(\kappa x)$ which *grows* exponentially with x. Such a solution is not permissible and therefore discarded.)

As a specific example, you can think of of a square well [1].: $U_0(x)=0$ for $0<x<d$ and $U(x)=U_0$ for $x<0$ and for $x>d$ (green line in Fig. 5) If the potential energy outside the well were infinite, the wave-function $\psi_0(x)=\sqrt{2/d}\sin(\pi x/d)$ (blue line), corresponding to the lowest energy eigenstate $E_0=\pi^2/2md^2$, would vanish at both boundaries of the well. If the potential energy is finite but large ($U_0\gg E_0$), the wave-function inside the well acquires a small phase shift $\delta\approx\sqrt{E_0/V_0}$, and the wavenumber inside the well changes to $k=\pi/d-2\delta$: $\psi_0(x)=\sqrt{2/d}\sin\left[(\pi-2\delta)x/d+\delta\right]$. The wave-function does not vanish anymore at $x=0,d$ but is small there in proportion to δ: $\psi(0)=\psi(d)=\sqrt{2/d}\sin(\delta)\approx\sqrt{2/d}\delta$. Outside the well, the wave-function falls off exponentially fast: $\psi_0(x)|_{x\geq d}=\sqrt{2/d}\delta\exp(-\kappa(x-d))$ and $\psi(x)|_{x\leq 0}=\sqrt{2/d}\delta\exp(\kappa x)$, where $\kappa=\sqrt{2m(U_0-E_0)}/\hbar\approx\sqrt{2mU_0}/\hbar$. The actual profile of the wave-function is shown by the red line.

DOUBLE-WELL SYSTEM

As a first step towards building a crystal, we consider a double-well system. When the wells are separated, they have discrete energy levels $E_0,E_1\ldots$ and corresponding wave functions $\psi_0(x),\psi_1(x)\ldots$. Now we place two wells at a distance a (see Fig.2), which is larger than the localization radius of the wave-function, and focus only on the lowest energy state. The wave-functions of the states localized in the individual wells overlap only slightly. However weak the overlap is, it does nevertheless give rise to a new effect: splitting of the energy levels.

In what follows, the actual form of the potential does not matter; instead of two square wells, we can think of a smooth Mexican-hat–like potential in Fig. 3, represented by a sum of two single-well potentials

$$U(x)=U_0(x)+U_0(-x). \tag{4}$$

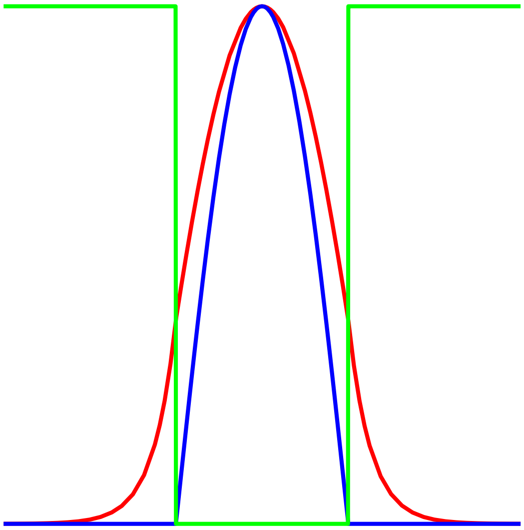

FIG. 1: Green: square-well potential. Blue: the wave-function for the case of infinite potential barrier outside the well. Red: the wave-function for large but finite potential barrier.

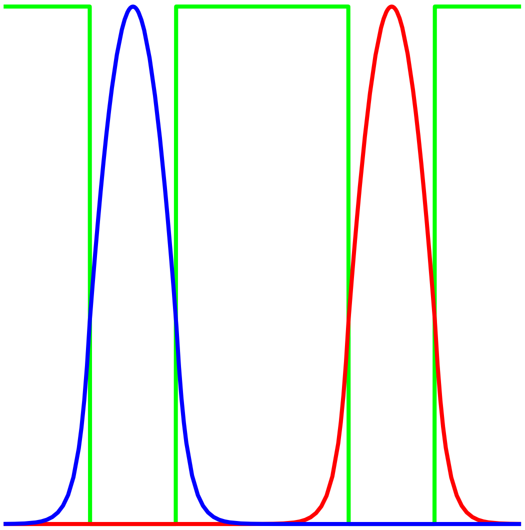

FIG. 2: Green: potential of two square wells. Blue and red: wave-functions localized in the individual wells.

The wave-function of a double-well system can be represented by either symmetric or asymmetric combination of the single-well wave-functions

$$\psi_{s,a} = \frac{1}{\sqrt{2}} \left[\psi_0(x) \pm \psi_0(-x) \right]. \tag{5}$$

The single-well wave function satisfies the Schroedinger equation

$$-\frac{\hbar^2}{2m} {\psi_0}'' + U_0(x)\psi_0(x) = E_0 \psi_0(x). \tag{6}$$

However, neither ψ_0 nor E_0 would change significantly if we add the potential of other well to this equation, because its effect on the wave function in the first well is very small. Thus we replace $U_0(x) \to U_0(x) + U_0(-x) = U(x)$ in Eq. (6) so it becomes

$$-\frac{\hbar^2}{2m} {\psi_0}'' + U(x)\psi_0(x) = E_0 \psi_0(x). \tag{7}$$

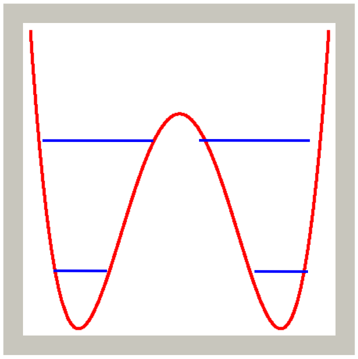

FIG. 3: A smooth double-well potential with the first two energy levels in the absence of splitting.

The wave functions of the individual wells are normalized to unity in the entire space

$$\int_{-\infty}^{\infty} dx \psi_0^2(x) = 1 \tag{8}$$

(the wave-functions of the 1D problem can always be chosen real, so we do not make a distinction between ψ_0 and ψ_0^*). However, since the wave function is localized well in the right half-axis, the normalization condition can be applied only to the half-axis

$$\int_{0}^{\infty} dx \psi_0^2(x) \approx 1. \tag{9}$$

The symmetric/asymmetric wave-functions $\psi_{s,a}$ are the solutions of the exact Schroedinger equation for the double-well system, for example,

$$-\frac{\hbar^2}{2m}\psi_{s,a}{}'' + U(x)\psi_{s,a}(x) = E_{s,a}\psi_s(x), \tag{10}$$

where $E_{s,a}$ are the corresponding energy levels which differ from E_0. To find the new energy levels, we multiply the equation for ψ_0 (7) by, e.g., ψ_s, and the equation for ψ_s by ψ_0, the subtract the resulting equations from each other, and integrate the difference of the two equations over x from 0 to ∞. The potential energy term vanishes, while the rest of the equation reads

$$(E_s - E_0)\int_0^{\infty} dx \psi_0 \psi_s = -\frac{\hbar^2}{2m}\int_0^{\infty} dx \left(\psi_s^{''}\psi_0 - \psi_0^{''}\psi_s\right) \tag{11}$$

Substituting ψ_s into the integral in the right-hand side of the equation above, we obtain

$$\int_0^{\infty} dx \psi_0(x)\psi_s(x) = \frac{1}{\sqrt{2}}\int_0^{\infty} \psi_0(x)\left[\psi_0(x) + \psi_0(-x)\right] \approx \frac{1}{\sqrt{2}}\int_0^{\infty} \psi_0^2(x) \approx \frac{1}{\sqrt{2}}, \tag{12}$$

where we neglected the term $\psi_0(x)\psi_0(-x)$ as it corresponds to overlap of the wave-functions localized in different wells. Integrating by parts in the left-hand side (taking into account that $\psi_0(\infty) = \psi_s(\infty) = 0$), we obtain

$$\frac{1}{\sqrt{2}}(E_s - E_0) = -\frac{\hbar^2}{2m}\left[\psi_0'(0)\psi_s(0) - \psi_s'(0)\psi_0(0)\right]. \tag{13}$$

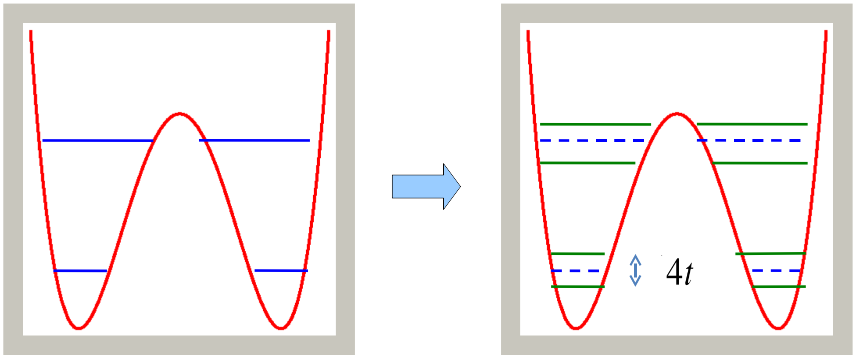

FIG. 4: Splitting of the energy levels in a double-well system.

According to Eq. (5), $\psi_s(0) = \sqrt{2}\psi_0(0)$ whereas

$$\psi_s'(x) = \frac{1}{\sqrt{2}}\left[\psi_0'(x) - \psi_0'(-x)\right] \tag{14}$$

and, therefore, $\psi_s'(0) = 0$. Then

$$E_s = E_0 - \frac{\hbar^2}{m}\psi_0'(0)\psi_0(0) \equiv E_0 - 2t. \tag{15}$$

Notice that $\psi_0'(0) > 0$, so that $E_s > E_0$. Likewise,

$$E_a = E_0 + \frac{\hbar^2}{m}\psi_0'(0)\psi_0(0) \equiv E_0 + 2t, \tag{16}$$

and $E_a < E_0$.

As a result, a single-well energy level splits into two levels separated by $E_s - E_t = 4t$. The energy t is exponentially small because both $\psi_0(0)$ and $\psi_0'(0)$ are exponentially small. Likewise, the higher energy states ($E_1 \ldots$) also get split.

TIGHT-BINDING MODEL

The tight-binding model for a 1D chain of atoms is a straightforward generalization of the double-well model, except for we need to take into account the Bloch theorem, which states that wave-function of an electron in a periodic potential must satisfy the following property

$$\Psi_k(x + a) = exp(ika)\Psi(x). \tag{17}$$

We construct the wave-function for the chain a linear superposition of atomic wave-functions localized at atomes located at $x = na$

$$\Psi_k(x) = \sum_{n=-\infty}^{n=\infty} \psi_0(x - na)\exp(ikna). \tag{18}$$

It is easy to see that the wave-function in Eq. (18) does satisfy the Bloch theorem. Indeed,

$$\Psi(x+a)=\sum_{n=-\infty}^{n=\infty}\psi_0(x+a-na)\exp(ikna)=\exp(ika)\sum_{n'=-\infty}^{n'=\infty}\psi_0(x-n'a)\exp(ikn'a)=\exp(ika)\Psi(x), \tag{19}$$

where we relabeled $n'=n-1$. Notice that the Bloch wave-function is, in general, complex. The Bloch wave-function satisfies the Schroedinger equation

$$-\frac{\hbar^2}{2m}\Psi_k''+\sum_{n=-\infty}^{n=\infty}U_0(x-na)\Psi(x)=E_k\Psi_k(x), \tag{20}$$

where $U_0(x)$ is the single-atom potential. The atomic wave-function satisfies Eq. (6) where, as in the double-well problem, we can replace U_0 by the potential produced by all atoms without any significant changes. Therefore,

$$-\frac{\hbar^2}{2m}\psi_0{}''+\sum_{n=-\infty}^{n=\infty}U_0(x-na)\psi_0(x)=E_0\psi_0(x). \tag{21}$$

Now we perform the same operations as for the double-well problem: 1) multiply Eq. (20) by ψ_0; 2) multiply Eq. (21) by Ψ_k^*; subtract the resulting equations; and 4) integrate the rest over one lattice period $-a/2\le x\le a/2$. This yields

$$(E_k-E_0)\int_{-a/2}^{a/2}dx\Psi_k\psi_0=-\frac{\hbar^2}{2m}\int_{-a/2}^{a/2}dx\left[\Psi_k''\psi_0-\psi_0''\Psi_k^*\right] \tag{22}$$

Integrating by parts,

$$(E_k-E_0)\int_{-a/2}^{a/2}dx\Psi_k\psi_0=-\frac{\hbar^2}{2m}\left[\Psi_k'(a/2)\psi_0(a/2)-\Psi_k'(-a/2)\psi_0(-a/2)-\psi_0'(a/2)\Psi_k^*(a/2)+\psi_0'(-a/2)\Psi_k^*(-a/2)\right] \tag{23}$$

The integral in the left-hand side reads

$$\int_{-a/2}^{a/2}dx\Psi_k\psi_0=\int_{-a/2}^{a/2}dx\sum_n\exp(ikna)\psi_0(x-na)\psi_0(x). \tag{24}$$

The largest term in the sum is $n=0$, which corresponds to overlap of the wave-functions on the same atom. Also, since a is much larger than the radius of the wave-function localization, the limits of the integration can extended to $\pm\infty$. As a result, the left-hand side simply reduces to E_k-E_0.

As far as the right-hand side is concerned, the algebra is simplified if we consider the cases of even and odd functions ψ_0 separately. If ψ_0 is even, $\psi_0(-a/2)=\psi_0(a/2)$, while $\psi_0'(-a/2)=-\psi_0'(a/2)$. The Bloch function also has certain properties, namely

$$\Psi_k(-x)=\sum_n\psi_0(-x-na)\exp(ikna)=\sum_n\psi_0(x+na)\exp(ikna)=\sum_n\psi_0(x-na)\exp(-ikna)=\Psi_k^*(x) \tag{25}$$

and

$$\Psi_k(-x)=\sum_n\psi_0'(-x-na)\exp(ikna)=-\sum_n\psi_0'(x+na)\exp(ikna)=-\sum_n\psi_0'(x-na)\exp(-ikna)=-\Psi_k^*(x) \tag{26}$$

Using these properties, we reduce the combination of the wave-functions to

$$\psi_0(a/2)\left[\Psi_k'(a/2)+(\Psi_k'(a/2))^*\right]-\psi_0'(a/2)\left[\Psi_k(a/2)+(\Psi_k(a/2))^*\right] \tag{27}$$

Consider the first term

$$\psi_0(a/2)\Psi_k'(a/2)=\psi_0(a/2)\sum_n\psi_0'(a/2-na)\exp(ikna). \tag{28}$$

The wave-function and its derivative are localized at $x=0$. The derivatives of the wave-functions in the sum have the largest value when their arguments are closest to zero, i.e., for $n=0$ and $n=1$. Therefore,

$$\psi_0(a/2)\Psi_k'(a/2)\approx\psi_0(a/2)\left[\psi_0'(a/2)+\psi_0'(-a/2)\exp(ika)\right]=\psi_0(a/2)\psi_0'(a/2)[1-\exp(ika)]. \tag{29}$$

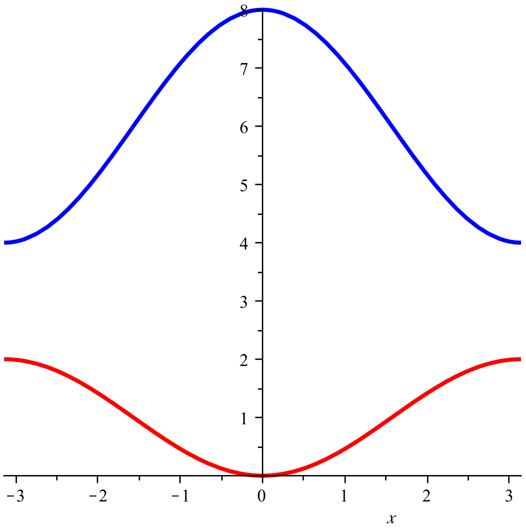

FIG. 5: The first two bands of the tight-binding model.

The second term is just a complex-conjugate to the first one, thus

$$\psi_0(a/2)\left[\Psi'_k(a/2)+(\Psi'_k(a/2))^*\right]=2\psi_0(a/2)\psi'_0(a/2)[1-\cos(ka)]. \tag{30}$$

Likewise,

$$\psi'_0(a/2)\Psi_k(a/2)\approx\psi'_0(a/2)\left[\psi_0(a/2)+\psi_0(-a/2)\exp(ika)\right]=\psi'_0(a/2)\psi_0(a/2)\left[1+\exp(ika)\right] \tag{31}$$

Collecting everything together, we obtain the spectrum of the tight-binding model

$$E_k=E_0+2\frac{\hbar^2}{m}\psi'_0(a/2)\psi_0(a/2)\cos(ka). \tag{32}$$

Notice that $\psi'_0(a/2)<0$, therefore the spectrum can be written that

$$E_k=E_0-2t\cos(ka)=E_0-2t+2t\left[1-\cos(ka)\right]. \tag{33}$$

where $t\equiv-\frac{\hbar^2}{m}\psi'_0(a/2)\psi_0(a/2)>0$ is the "hopping energy". Now, if the atomic wave-function is odd, the sign in the spectrum is changed

$$E_k=E_0+2t\cos(ka)=E_0+2t-2t\left[1-\cos(ka)\right] \tag{34}$$

The first term in Eqs. (**??**) is an energy shift which can be omitted. With that, the spectrum acquires a particularly simple form

$$E_k=\pm2t\left[1-\cos(ka)\right], \tag{35}$$

where ± corresponds to even/odd atomic wave-functions. Notice that E_k is periodic in the k space, in accord with the Bloch theorem. Instead of the entire k space, we need to consider only the first Brillouin zone $-\pi/a\leq k\leq\pi/a$. The bandwidth is $4t$.

Suppose that ψ_0 is the ground state and is, therefore, even.The next band occurs because of the overlap of higher-energy states. In 1D model, the wave-functions alternate between even and odd, in such a way the ground state wave-function is always even. Therefore, the band resulting from the overlap of the first excited state has an opposite sign in the dispersion (Fig. **??**). For the first two bands (restoring the constant energy shift in the second band)

$$\begin{aligned} E_k^0 &= 2t_0\left[1-\cos(ka)\right] \\ E_k^1 &= E_1-E_0+2t_1-2t_0+2t_1\left[1-\cos(ka)\right] \end{aligned} \tag{36}$$

where $t_{0,1}$ are the hopping energies.

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[1] See Griffiths, *Introduction to Quantum Mechanics*, p. 60