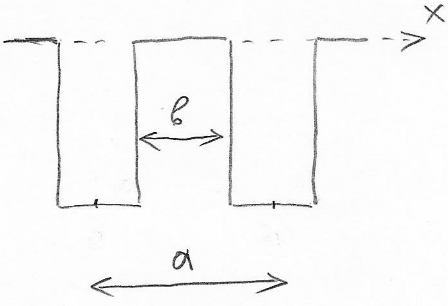
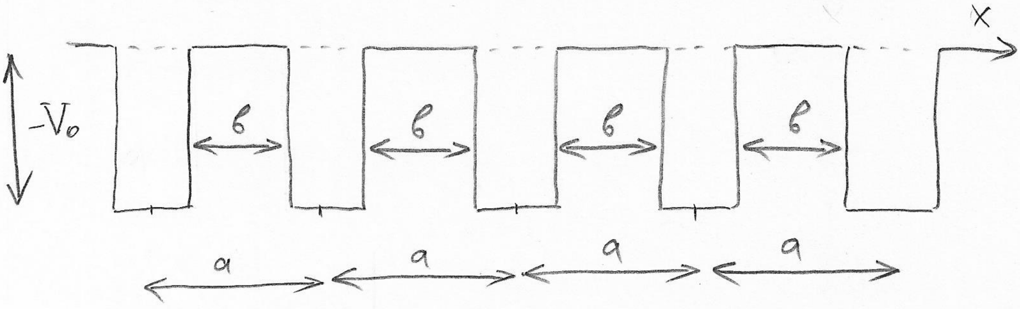
Particle in a chain of 1D wells. Development of energy bands

Our goal here is to capture the qualitative behavior of energy levels is systems that feature multiple (in the limiting case – infinite) wells. For simplicity we will work in 1D. Examples of such chains of potential wells are shown below:

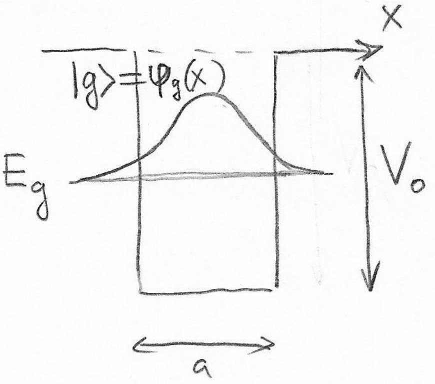


two wells



five wells

In order to make things as simple as possible we further assume that each individual well has just one possible bound state. In other words, we will assume that parameters a and V_0 are such that when we consider only a single well we obtain only a single bound state (the ground state):



Let us begin with the case of two wells. Our task is to solve the stationary Schrödinger equation

$$H|\psi\rangle = E|\psi\rangle$$

where the Hamiltonian H includes the usual kinetic energy of the single particle (electron) and the potential energy (two wells separated by b) depicted above. The two wells represent a crude model of two atoms (ions) in 1D. Thus here we have a kind of a "diatomic molecule". As we are only interested in qualitative picture we will use an approximate approach to solve the Schrödinger equation known as LCAO – Linear Combination of Atomic Orbitals. Because we have only one electron in our problem we do not concern ourselves with any indistinguishability of identical particles. We simply assume that if we have more than one electron they do not interact with each other (independent electron approximation) and occupy allowed energy states according to the Pauli principle.

Let us denote the wave function corresponding to each (single) well as φ_g. Since both wells have the same shape the wave functions for both wells are essentially the same except that one is displaced by a with respect to the other. So we will denote

$$|1\rangle \equiv \varphi_g(x-a) \qquad |2\rangle \equiv \varphi_g(x-2a)$$

The LCAO method approximates the "molecular" state (i.e. the state for which we have both wells present) in the form of the linear combination of the known "atomic" states:

$$|\psi\rangle = C_1|1\rangle + C_2|2\rangle$$

Then we can write our Hamiltonian in the basis $\{|1\rangle, |2\rangle\}$ as

$$H = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

where $\alpha = H_{11} = H_{22} = \langle 1|H|1\rangle = \langle 2|H|2\rangle$

$$\beta = H_{12} = H_{21} = \langle 1|H|2\rangle = \langle 2|H|1\rangle$$

It turns out that the important qualitative features of the band structure will not depend on the exact values of α and β. So we will proceed without knowing what exactly those are.

The two diagonal terms are equal and the two off-diagonal terms are equal. This happens because of the symmetry of the two-well chain. Indeed, if we for a moment place the origin of the coordinate system exactly between the wells, i.e.

$$y = x + \frac{3}{2}a$$

$$|1\rangle = \varphi\left(y+\frac{a}{2}\right) \qquad |2\rangle = \varphi\left(y-\frac{a}{2}\right)$$

we see that, e.g.

$$\langle 1|H|1\rangle = \left\langle \varphi\left(y+\tfrac{a}{2}\right)\right| -\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + V(y) \left|\varphi\left(y+\tfrac{a}{2}\right)\right\rangle =$$

$$= \left\langle \varphi\left(y+\tfrac{a}{2}\right)\right| -\frac{\hbar^2}{2m}\frac{d^2}{d(-y)^2} + V(-y) \left|\varphi\left(y+\tfrac{a}{2}\right)\right\rangle = \left| y \leftrightarrow -y \right|$$

$$= \left\langle \varphi\left(-y+\tfrac{a}{2}\right)\right| -\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + V(y) \left|\varphi\left(-y+\tfrac{a}{2}\right)\right\rangle = \left|\varphi(-z) = \varphi(z)\right|$$

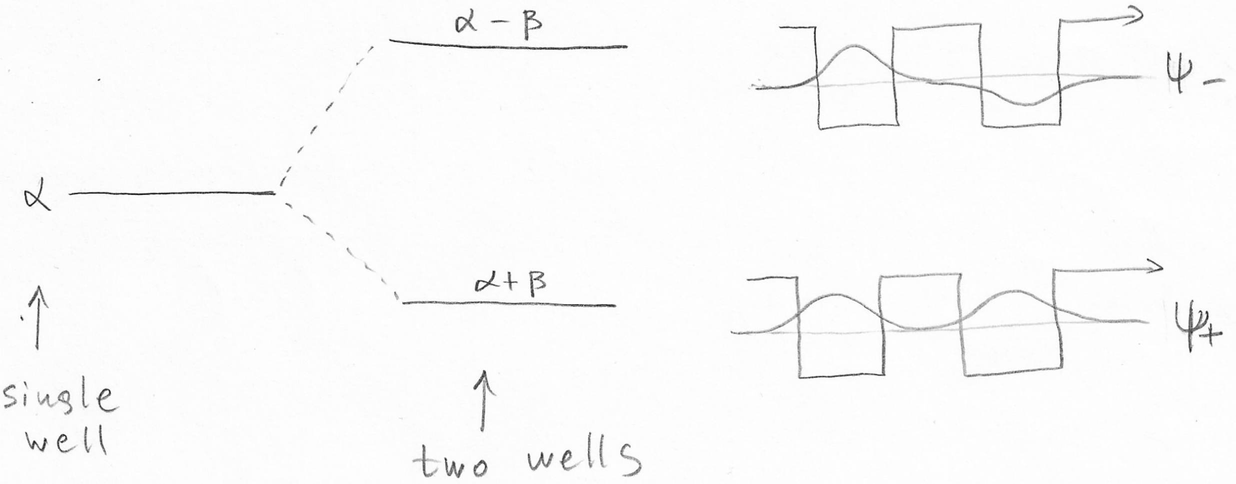
$$\left\langle \varphi\left(y-\tfrac{a}{2}\right)\right| -\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + V(y) \left|\varphi\left(y-\tfrac{a}{2}\right)\right\rangle =$$

$$= \langle 2|H|2\rangle$$

If the separation between the wells is sufficiently large than it is also easy to see that α is close to the energy of the "atomic" state and $|\beta|$ is small compared to $|\alpha|$. Also, one could find that $\beta<0$ because $H\varphi_g(y\pm\frac{a}{2}) \approx E_g \varphi_g(y\pm\frac{a}{2})$ where $E_g<0$.
Diagonalizing a 2×2 matrix yields the following energies and the corresponding eigenstates:

$$E_+ = \alpha+\beta \qquad\qquad E_- = \alpha-\beta$$

$$|\psi_+\rangle = \frac{1}{\sqrt{2}}|1\rangle + \frac{1}{\sqrt{2}}|2\rangle \qquad\qquad |\psi_-\rangle = \frac{1}{\sqrt{2}}|1\rangle - \frac{1}{\sqrt{2}}|2\rangle$$



We end up with two "moleculor" states or "molecular orbitals" that are formed by symmetric and anti-symmetric linear combination of atomic states (orbitals)

Now let us consider a chain of N wells. As N increases more and more, the "molecule" grows bigger and eventually it should become large enough to resemble a solid.

Again, let us approximate the "molecular" state as a LCAO:

$$|\psi\rangle = \sum_{j=1}^{N} c_j |j\rangle$$

The matrix representing the Hamiltonian of the system is now an N×N matrix. Let us make another reasonable simplification. We will assume that the off-diagonal matrix elements β are zero unless the two wells are adjacent. This is so called nearest-neighbor approximation. It makes sense because the wave function φ_g is exponentially decayin beyond the well where it is centered at. Thus if for two adjucent wells β is already small compared to α, for two wells that are further away matrix element $\langle j|H|i\rangle$ will be even smaller. With this assumption our Hamiltonian matrix will look as follows:

$$H = \begin{pmatrix} \alpha & \beta & 0 & 0 & \cdots \\ \beta & \alpha & \beta & 0 & \cdots \\ 0 & \beta & \alpha & \beta & \cdots \\ 0 & 0 & \beta & \alpha & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

$$\alpha = H_{jj} = \langle j|H|j\rangle$$

$$\beta = H_{j,j\pm1} = \langle j|H|j\pm1\rangle$$

It is a tridiagonal matrix. The eigenvalue problem

$$\begin{pmatrix} \alpha & \beta & 0 & 0 & \cdots \\ \beta & \alpha & \beta & 0 & \\ 0 & \beta & \alpha & \beta & \\ 0 & 0 & \beta & \alpha & \\ \vdots & & & & \ddots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \end{pmatrix}$$

results in the following set of equations:

$$\alpha c_1 + \beta c_2 = E c_1$$

$$\beta c_1 + \alpha c_2 + \beta c_2 = E c_2$$

$$\beta c_2 + \alpha c_3 + \beta c_4 = E c_3$$

$$\vdots$$

$$\beta c_{N-1} + \alpha c_N = E c_N$$

Except the first and last equations they all have an identical form:

$$\beta c_{q-1} + \alpha c_q + \beta c_{q+1} = E c_q \qquad (*)$$

and are identical to the equation of motion of a collection of classical coupled oscillators. The normal mode solutions to solve them for c_q and E are obtained by substituting

$$c_q = A e^{iqka}$$

where values of k and A are yet to be determined. With that, equations $(*)$ become

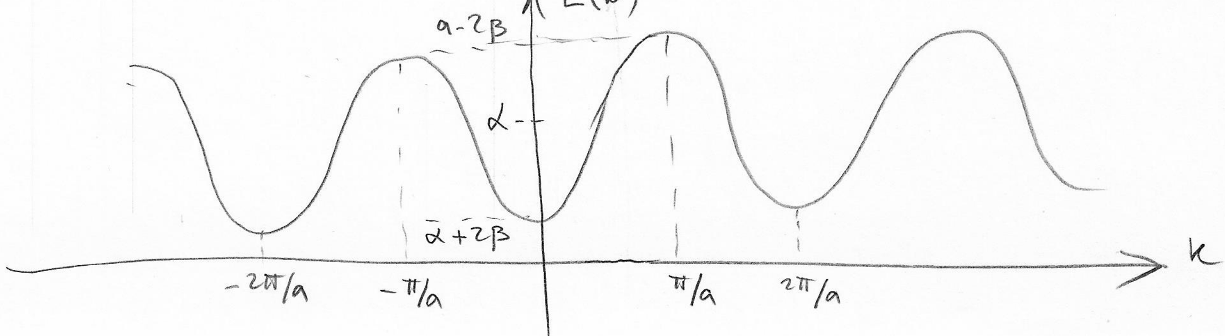
$$\beta A e^{i(q-1)ka} + (\alpha - E) A e^{iqka} + \beta A e^{i(q+1)ka} = 0$$

or

$$\beta e^{-ika} + (\alpha - E) + \beta e^{+ika} = 0$$

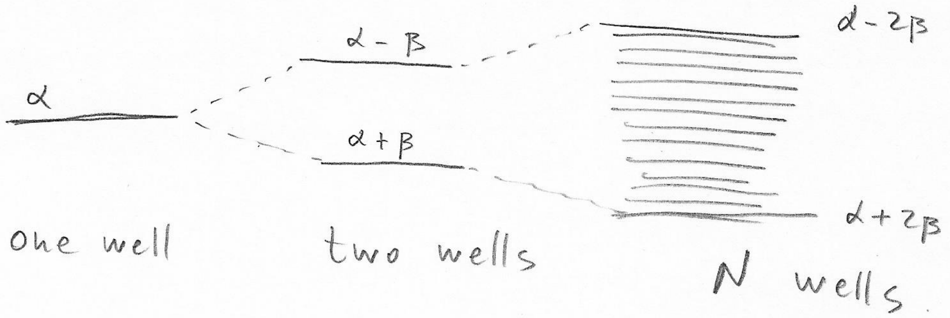
which gives:

$$E = \alpha + 2\beta \cos(ka) \qquad \leftarrow \text{dispersion relation}$$



Notice that E is determined by k value. Also, E is periodic in k with period $2\pi/a$, so we can limit ourselves with the consideration of e.g. $\left[-\frac{\pi}{a}, +\frac{\pi}{a}\right]$

The values of E lie between $\alpha - 2\beta$ and $\alpha + 2\beta$. Hence we have a band of allowed energies :



This banding of energies when $N \to \infty$ is probably the most important characteristic of the particle's energy spectrum in a solid.