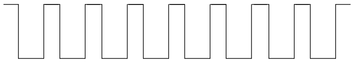
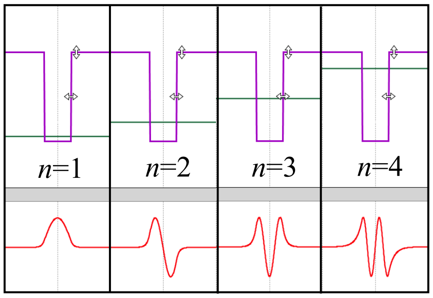
Many-particle Systems, 7

Electronic energy bands in crystalline solids: The finite well model

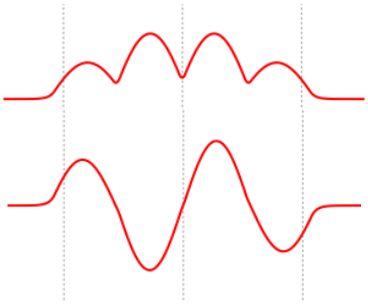
Previously, we have considered the "conduction electrons" in a metal as if they were an ideal gas in a 3D infinite well. What allows us to do that? A crystalline solid consists of a periodic array of atoms, packed so close to one another that "flow" (long range relative motion of groups of atoms) is essentially impossible. It is useful to think of a solid as a giant (rigid) molecule. The periodic structure of the atoms has profound consequences for the behavior of the solid's electrons. While, in detail, the electronic properties depend fussily on what kind of atoms are involved, what the exact periodic array geometry is, and so forth, important insight into electronic states in solids can be achieved by considering the atomic nuclei to be finite square wells arrayed in a line. The figure to the right is the potential energy for an electron interacting with such a periodic line of "nuclei." The goal is to approximate what the single electron wave functions might look like and to estimate the allowed single particle energy eigenvalues.



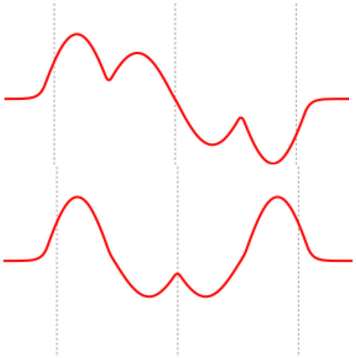
Ignoring spin, the single particle wavefunctions for a potential energy corresponding to **one 1D finite well** are labeled by **one** quantum number n = 1, 2, 3, … . The figure to the right shows energy levels (top row) and spatial wavefunctions, $\psi_n(x)$ (bottom row), for the four bound states allowed by the well shown. (Images generated using the program *band-structure_en.jar*, downloadable from http://phet.colorado.edu/en/get-phet/full-install.)



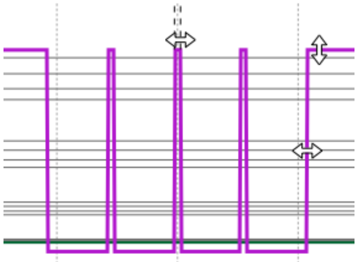
The N-well single particle wavefunctions are constructed by superposing N 1-well wavefunctions all with the same n value. If the wells are far apart, the wavefunctions go to zero between the wells. In that case, the probability of finding a particle somewhere is greater than zero only in the wells, which is equivalent to N 1-well problems. The single particle energy level for that case is just E_n for 1-well. When the wells are close together, however, the "tails" of the wavefunctions that "leak" into the classically forbidden (kinetic energy < 0) regions can be connected to construct wavefunctions of various shapes. For concreteness, suppose there are four wells and the single particle quantum number is 1. When the wells are far apart the single particle wavefunctions look like the leftmost one in the figure above. Of course, that function could be multiplied by –1 without changing the probability density, $|\psi(x)|^2$, or the energy level. Thus, the wavefunctions consisting of "up-up-up-up" and "up-down-up-down" (or those with "up" and "down" flipped) are degenerate (both have energy level E_1). When the wells are close these wavefunctions look like those shown to the right. The top wavefunction starts on the left at zero, is positive with some wiggles in between, then returns to zero on the right. It has no intermediate nodes. The bottom wavefunction, on the other hand, starts at zero, goes positive, then negative, then positive, then negative, before returning to zero. It has three intermediate nodes. Mathematically, the magnitude of the second derivative, $\left|d^2\psi/dx^2\right|$, of the second wavefunction is greater than that of the first. Because **kinetic energy density** is $-(\hbar^2/2m)(\psi^* d^2\psi/dx^2)$– while the potential energy is the same for both wavefunctions–the second wavefunction must

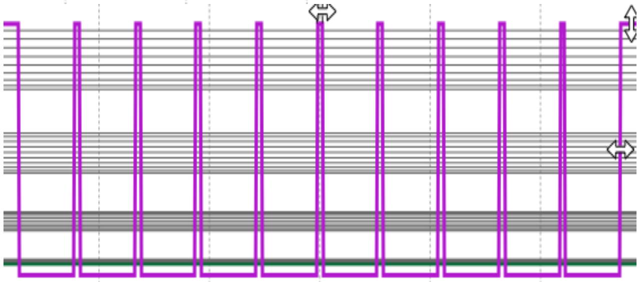


have a higher energy level than the first. That is, bringing the wells close together removes the degeneracy that exists when the wells are far apart. In fact, there are two other wavefunctions for the 4-well example, with intermediate energies, that can be constructed from various “up” and “down” combinations. They are shown to the right. (Can you tell which of these has the higher energy? Why are their energy levels intermediate between those of the wavefunctions above? Hint: count the number of times each function passes through zero. The more nodes, the higher the energy.)



The same argument leads to identical results for other n values. The figure to the left shows four close wells and the resulting four sublevels for each n. On this scale the four n= 1 levels are so close they look like the same level. Notice that the level splitting increases as n increases. The figure directly below shows energy levels for ten wells. In this case each n has 10 sublevels. The energies might be labeled E_{nj}, where j= 1, 2, …, N designates the sublevel of the n-band. If the particles in the system are electrons, each nj state can accommodate two, one with spin up, one with spin down. Note that the spacings between different j-levels for each n in the 10-well system are significantly smaller than in the 4-well system. Also, note that the spread in energies increases as n increases. In addition, as n increases, the single particle wavefunctions look more-and-more like harmonic standing waves with ever decreasing wavelengths, i.e., similar to quantum states in an infinite well.



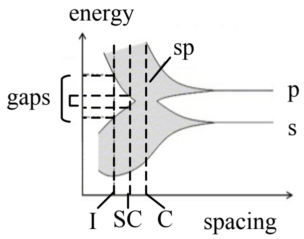


In real 3D solids, the “wells” are atoms and the single particle states are labeled by the atomic electron quantum numbers $nlm_l m_s$ and j. As above, j ranges from 1 to N for every nlm_l combination, but for real solids N might be $\sim 10^{23}$. In solids, the level spacings for successive j values are exceedingly small. Consequently, in solids each nl combination can accommodate $2(2l+1)N$ electrons with virtually continuous energies; each of these combinations is called an “nl energy band.”

As in atoms, it is useful to think of filling a solid’s electronic states from lowest to highest energy. Thus, for N atoms, the 1s band can accommodate $2N$ electrons ($l=0$), the 2s band $2N$ electrons ($l=0$), the 2p band $6N$ electrons ($l=1$), and so on. At $T=0$K, there are no excitations. The highest energy completely filled band is called the “valence band (VB).” The next higher band is called the “conduction band (CB)” and at $T=0$K that band might be empty or partially filled. The energy separation between the VB and the CB is called the “band gap.” If the CB is partially filled, that solid is a good electrical conductor (has a low electrical resistivity); such solids are also called “metals”—and the gap has no significance for the electrical properties of metals. On the other hand, the gap is very important for the electrical properties of solids with empty CB at $T=0$K. If the gap is large (a few eV or so) the solid is a poor electrical conductor at “room” temperatures and is called an “insulator.” If the gap is small (about 1 eV or less), the solid is called a “semiconductor” because at room temperatures it conducts electric current, though not nearly as well as a metal.

Example: Lithium (Z = 3) has three electrons. At $T = 0$K, in solid lithium with N atoms, there are $2N$ electrons in the 1s band and $1N$ electrons in the 2s band. Thus, the VB is 1s for Li and the CB is 2s. Because the CB is partially full Li is a good conductor.

Example: Solid beryllium (Z = 4) has two four electrons per atom, $2N$ in the 1s band and, seemingly, $2N$ in the 2s band. Thus, it might be expected that Be would be an insulator or semiconductor. Interestingly, Be's electrical resistivity is *lower* than Li's. It is a *better* conductor. **How can that be?**



The answer to the latter question is revealed in how the s and p bands spread with decreasing atomic spacing. The figure to the right shows that the s states are $2N$-fold degenerate at large atomic spacing (and equal to the s atomic energy level) and the p states are $6N$-fold degenerate (and equal to the p atomic energy level). As atomic spacing decreases the degeneracies are removed and the bands spread. At some critical atomic spacing the s and p bands overlap forming an **sp-hybrid band** capable of accommodating $8N$ electrons. As Be has only $2N$ electrons to fill this hybrid band it is an excellent electrical conductor (e.g., "C" in the figure). (Be is a better conductor than Li because it has $2N$ conduction electrons compared with Li's $1N$.)

A similar hybridization of s and p states occurs for the elements C, Si, Ge, Sn, and Pb, all with two p electrons. The atomic spacing ranges from least for C to most for Pb. Pb and Sn are both conductors; their spacings must place them in the conductor region of the figure. (Sn is better than Pb because Pb's larger spacing puts it close to where the sp band splits into s and p.) Ge's smaller spacing makes it a semiconductor ("SC" in the figure) as does Si's; because Si's spacing is smaller than Ge's its band gap is larger (1.1 eV to 0.7 eV)—Ge is a better conductor than Si at lower temperatures. C (in the diamond phase, at least) has the smallest spacing and a band gap of 6 eV; it is an electrical insulator ("I" in the figure).