

Part 6. The Electronic Structure of Materials

Part 6. The Electronic Structure of Materials

Atomic orbitals and molecular bonds

The particle in the box approximation completely ignores the internal structure of conductors. For example, it treats an insulator such as diamond the same as a conductor such as gold. Despite this it can be surprisingly useful, as we have seen in the discussion of ballistic transistors.

We are concerned now with more accurate calculations of electronic structure. Unfortunately, exact solutions are not usually possible. Determining the energies and wavefunctions of multiple electrons in a solid is a classic '*many body problem*'. For example, to solve for the electrons, we must know the exact position of each atom in the solid, and also calculate all interactions between multiple electrons.

Nevertheless, there is much to be learnt from a first principles analysis of electronic structure. We'll begin at the bottom, with the hydrogen atom.

The hydrogen atom

Hydrogen is the simplest element. There are just two components: an electron and a positively charged nucleus comprised of a single proton.

The electron experiences the attractive potential of the nucleus. The nuclear potential is spherically symmetric and given by the Coulomb potential

$$V(r) = -\frac{Zq^2}{4\pi\epsilon_0 r} \quad (6.1)$$

where r is the radial separation of the electron and the nucleus ϵ_0 is the dielectric constant and Z is the number of positive charges at the nucleus. For hydrogen there is one proton, and $Z = 1$.

Recall that a general expression for the kinetic energy operator in three dimensions is:

$$\hat{T} = -\frac{\hbar^2}{2m_e} \nabla^2 \quad (6.2)$$

where ∇^2 is the Laplacian operator.

In rectilinear coordinates (x, y, z)

$$\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \quad (6.3)$$

In spherical coordinates (r, θ, ϕ)

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$$\nabla^2 = \frac{1}{r} \frac{d^2}{dr^2} r + \frac{1}{r^2} \frac{1}{\sin^2 \theta} \frac{d^2}{d\phi^2} + \frac{1}{r^2} \frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} \quad (6.4)$$

Thus, the Hamiltonian for the hydrogen atom is

$$\begin{aligned} \hat{H} &= -\frac{\hbar^2}{2m} \nabla^2 - \frac{Zq^2}{4\pi\epsilon_0 r} \\ &= -\frac{\hbar^2}{2m} \left(\frac{1}{r} \frac{d^2}{dr^2} r + \frac{1}{r^2} \frac{1}{\sin^2 \theta} \frac{d^2}{d\phi^2} + \frac{1}{r^2} \frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} \right) - \frac{Zq^2}{4\pi\epsilon_0 r} \end{aligned} \quad (6.5)$$

This takes a bit of algebra to solve for the atomic orbitals and associated energies. An approximate solution (assuming a box potential rather than the correct Coulomb potential) is contained in Appendix 2.

The lowest energy solutions are plotted in Fig. 6.1, below.

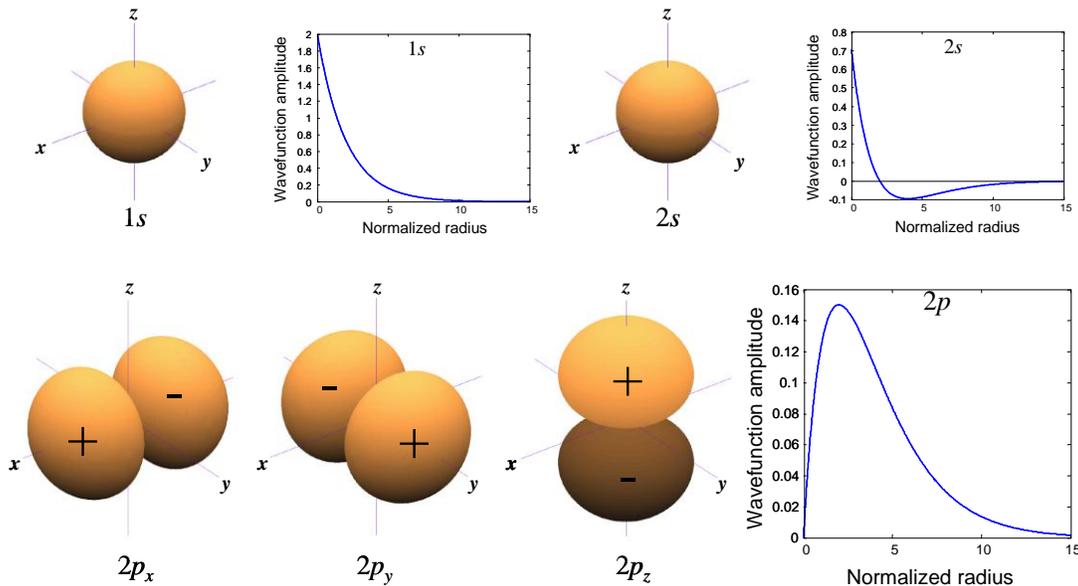


Fig. 6.1. The first five orbitals of the hydrogen atom together with their radial profiles.

Each of the solutions shown in Fig. 6.1 is labeled either *s* or *p*. These letters describe the angular symmetry of solution. They are the index for the **orbital angular momentum** of the electron. ‘*s*’ orbitals exhibit even symmetry about the origin in every dimension. Orbitals that exhibit odd symmetry about the origin in one dimension are labeled ‘*p*’. We show in Appendix 1 that the eigenfunctions of an electron restricted to the surface of a sphere are characterized by quantized angular momentum. We are only showing the *s* and *p* solutions but there are an infinite set of solutions, e.g. *s*, *p*, *d*, *f*... corresponding to orbital angular momenta of 0, 1, 2, 3...

The energy of each atomic orbital is also labeled by an integer known as the **principal quantum number**. Thus, the 1s orbital is the lowest energy *s* orbital, 2p and 2s orbitals are degenerate first excited states.

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Knowledge of the exact atomic orbitals is not necessary for our purposes. Rather, we will use the orbitals as symbolic building blocks in the construction of molecular orbitals: electron wavefunctions in molecules.

Atoms to Molecules

We now seek to determine the electronic states of whole molecules – molecular orbitals. Although we will begin with relatively small molecules, the calculation techniques that we will introduce can be extended to larger materials that we don't usually think of as molecules: like Si crystals, for example.

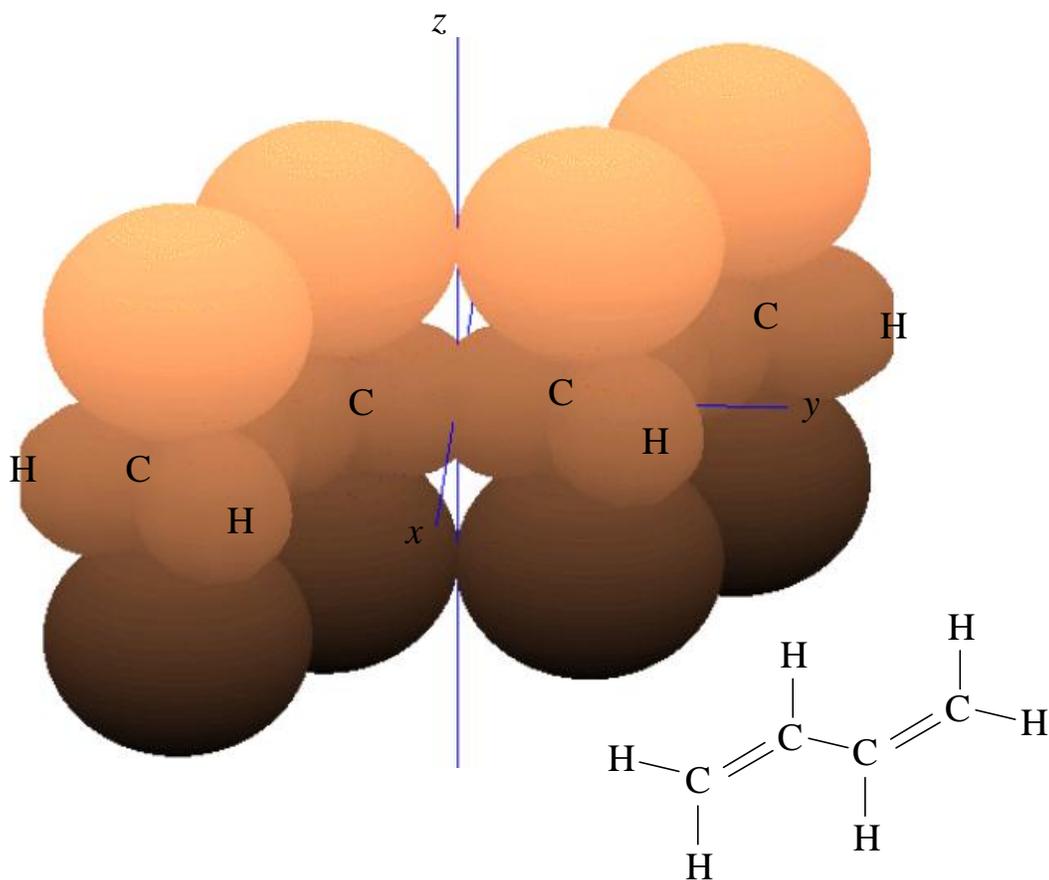


Fig. 6.2. The molecule 1,3-butadiene. Clouds of electron probability density are shown around each atom. They combine to form *molecular orbitals*.

In the previous discussion of atomic orbitals, we implicitly assumed that the nucleus is stationary. This is an example of the *Born-Oppenheimer approximation*, which notes that the mass of the electron, m_e , is much less than the mass of the nucleus, m_N . Consequently, electrons respond almost instantly to changes in nuclear coordinates.

In calculations of the electronic structure of molecules, we have to consider multiple electrons and multiple nuclei. We can simplify the calculation considerably by assuming

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that the nuclear positions are fixed. The Schrödinger equation is then solved for the electrons in a static potential; see Appendix 3. Different arrangements of the nuclei are chosen and the solution is optimized.

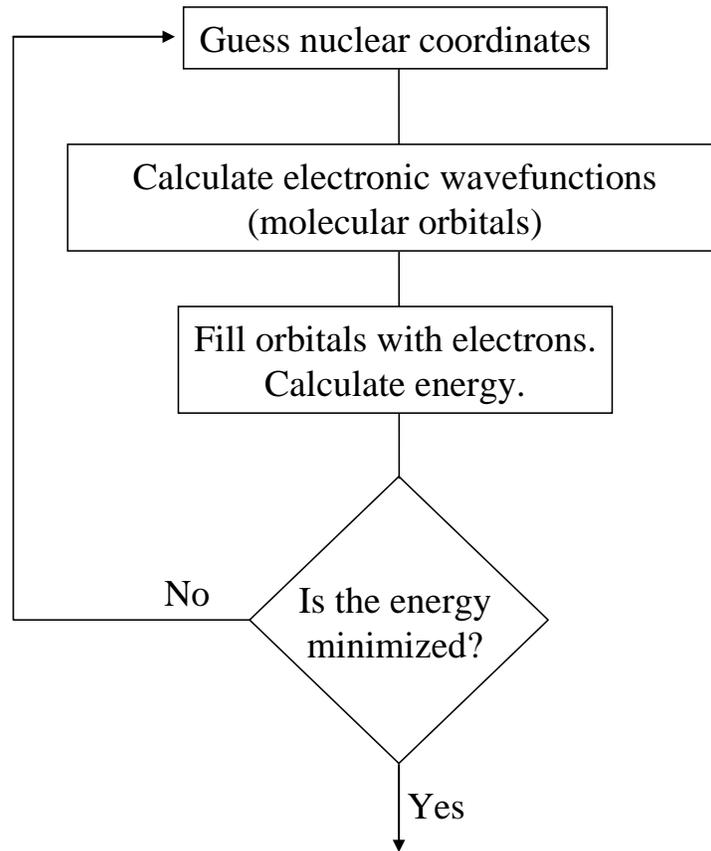


Fig. 6.3. Technique for calculating the electronic structure of materials.

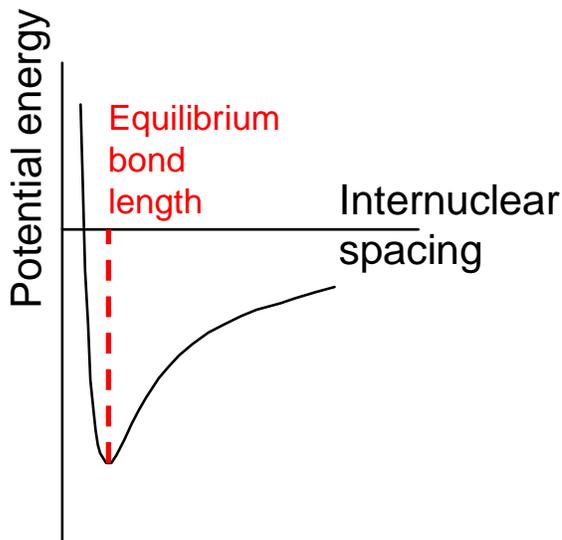


Fig. 6.4. The equilibrium internuclear spacing (bond length) in a molecule results from competition between a close-range repulsive force typically with exponential dependence on intermolecular spacing, and a longer-range attractive Coulomb force. Typically the molecular orbitals must be calculated for each internuclear spacing. The energy minima is the equilibrium bond length. Calculating the electronic states for fixed nuclear coordinates is an example of the Born-Oppenheimer approximation.

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Molecular orbitals

Unfortunately, even when we apply the Born-Oppenheimer approximation and hold the nuclear coordinates fixed, the solution to the Schrödinger equation (Eq. (6.5)) is extremely complex in all but the simplest molecules. Usually numerical methods are preferred. But some conceptual insight may be gained by assuming that the molecular orbitals are linear combinations of atomic orbitals, *i.e.*, we write:

$$\varphi = \sum_r c_r \phi_r \quad (6.6)$$

where φ is the molecular orbital and ϕ is an atomic orbital. A filled molecular orbital with lower energy than the constituent atomic orbitals stabilizes the molecule and is known as a chemical bond.

We can define two types of molecular orbitals built from s and p atomic orbitals:

σ molecular orbitals: These are localized between atoms and are invariant with respect to rotations about the internuclear axis. If we can take the x -axis as the internuclear axis, then both s and p_x atomic orbitals can participate in σ molecular orbitals. p_y and p_z atomic orbitals cannot contribute to σ molecular orbitals because they each have zero probability density on the x -axis.

π molecular orbitals: Electrons in π molecular orbitals are more easily shared between atoms. The probability density is not as localized as in a σ molecular orbital. A π molecular orbital is also not invariant with respect to rotations about the internuclear axis. linear combinations of p_y and p_z atomic orbitals form π molecular orbitals.

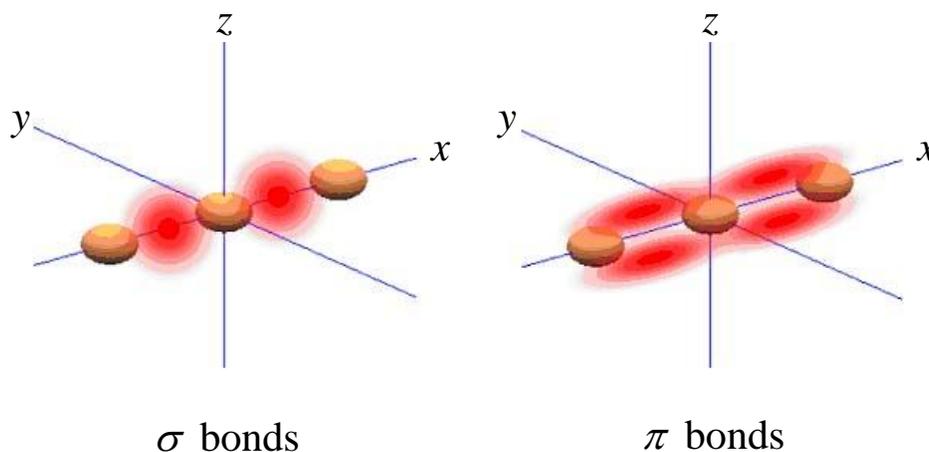


Fig. 6.5. Examples of σ and π bonds. σ bonds are localized between atoms whereas π bonds are delocalized above the internuclear axis.

Linear combination of atomic orbitals (LCAO)

The expansion of a molecular orbital in terms of atomic orbitals is an extremely important approximation, known as the Linear combination of atomic orbitals (LCAO). The atomic orbitals used in this expansion constitute the *basis set* for the calculation. Ideally, the number of atomic orbitals used should be infinite such that we could re-express any given wavefunction exactly in terms of a linear combination of atomic orbitals. In this case, we say that the basis set is also infinite. But computational limitations usually force the basis set to be finite in practice. Choice of the basis set is an especially important consideration in numerical simulations; for example we might consider *s*, *p* and *d* orbitals, but not *f* or higher orbitals.

In some cases, we can take good guesses at the weighting coefficients, c_r , based on the likely nuclear arrangement. However, depending on the nuclear arrangement, it often helps to define new atomic orbitals that are linear combinations of the familiar *s* and *p* atomic orbitals. These are known as symmetry adapted linear combinations (SALCs) because they are chosen based on the nuclear symmetry. They are also known as hybrid atomic orbitals. We discuss SALCs in Appendix 4.

The tight binding approximation

Each atom in a conductor typically possesses many electrons. We can simplify molecular orbital calculations significantly by neglecting all but a few of the electrons. The basis for discriminating between the electrons is energy. The electrons occupy different atomic orbitals: some electrons require a lot of energy to be pulled out the atom, and others are more weakly bound.

Our first assumption is that electrons in the deep atomic orbitals do not participate in charge transport. Recall that charge conduction only occurs through states close to the Fermi level. Thus, we are concerned with only the most weakly bound electrons occupying so-called *frontier* atomic orbitals.

In this class, we will exclusively consider carbon-based materials. Furthermore, we will only consider carbon in the triangular geometry that yields sp^2 hybridized atomic orbitals; see Appendix 4 for a full discussion. In these materials, each carbon atom has *one* electron in an unhybridized p_z orbital. The unhybridized p_z atomic orbital is the frontier orbital. It is the most weakly bound and also contributes to π molecular orbitals that provide a convenient conduction path for electrons along the molecule. We will assume that the molecular orbitals of the conductor relevant to charge transport are linear combinations of frontier atomic orbitals.

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For example, let's consider the central carbon atom in Fig. 6.6. Assume that the atom is part of a triangular network and that consequently it contains one electron in a frontier p_z atomic orbital. Let's consider the effect of the neighboring carbon atom to the right of the central atom.

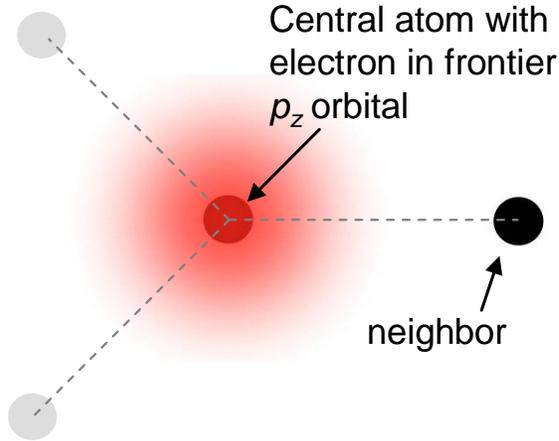


Fig. 6.6. One carbon atom with a single frontier electron and its neighboring nucleus. The Hamiltonian of the system contains potential terms for each of the two nuclei.

Assuming the positions of the atoms are fixed, the Hamiltonian of the system consists of a kinetic energy operator, and two Coulombic potential terms: one for the central atom and one for its neighbor:

$$H = T + V_1 + V_2 \quad (6.7)$$

Now, consider an integral of the form:

$$\langle \phi_r | H | \psi \rangle = \langle \phi_r | E | \psi \rangle \quad (6.8)$$

Following Eq. (6.6), the wavefunction in this two atom system can be written as

$$\psi = c_1 \phi_1 + c_2 \phi_2 \quad (6.9)$$

We can expand the LHS of Eq. (6.8) as follows:

$$\langle \phi_r | H | \psi \rangle = c_1 \langle \phi_r | T + V_1 | \phi_1 \rangle + c_1 \langle \phi_r | V_2 | \phi_1 \rangle + c_2 \langle \phi_r | T + V_2 | \phi_2 \rangle + c_2 \langle \phi_r | V_1 | \phi_2 \rangle \quad (6.10)$$

The RHS expands as

$$\langle \phi_r | E | \psi \rangle = c_1 E \langle \phi_r | \phi_1 \rangle + c_2 E \langle \phi_r | \phi_2 \rangle \quad (6.11)$$

The terms in these expansions are not equally important. We can considerably simplify the calculation by categorizing the various interactions and ignoring the least important.

(a) Overlap integrals

First of all, let's define the *overlap integral* between frontier orbitals on atomic sites s and r :

$$S_{sr} = \langle \phi_s | \phi_r \rangle. \quad (6.12)$$

These integrals yield the overlap between atomic orbitals at different sites in the solid. Spatial separation usually ensures that $S_{sr} \ll 1$ for $s \neq r$. Of course, for normalized atomic orbitals $S_{sr} = 1$ for $s = r$.

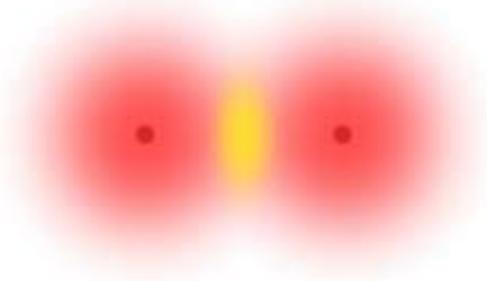


Fig. 6.7. The overlap between two adjacent atomic orbitals is shaded in yellow. In the tight binding approximation we will assume that the overlap between frontier atomic orbitals on different sites is zero.

(b) The self-energy

Next, let's define the *self-energy*. At a particular atomic site, we have

$$T + V_r |\phi_r\rangle = \alpha_r |\phi_r\rangle \quad (6.13)$$

where α_r is the self energy, *i.e.*:

$$\alpha_r = \langle \phi_r | T + V_r | \phi_r \rangle. \quad (6.14)$$

The self energy, α , is defined to be negative for an electron in a positively charge nuclear potential. Note that if the interaction between the atoms is weak then the self energy is similar to the energy, E , of the combined system.

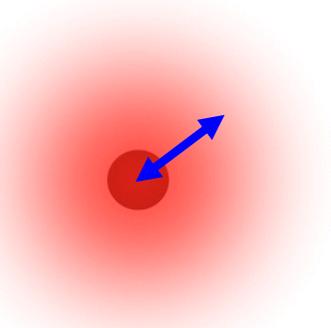


Fig. 6.8. The interaction between a nucleus and its frontier atomic orbital is known as the self energy.

(c) Hopping interactions

Let's define the *hopping interaction* between different sites s and r :

$$\beta_{sr} = \langle \phi_s | V_s | \phi_r \rangle \quad (6.15)$$

The hopping interaction, β , is defined to be negative for an electron in a positively charge nuclear potential.

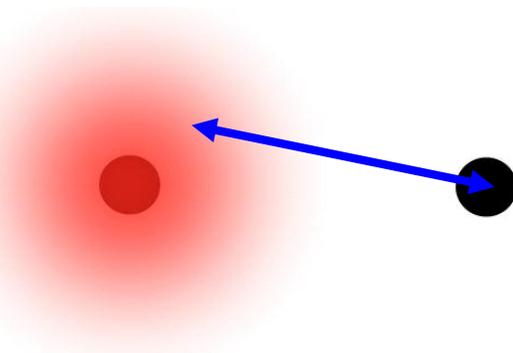


Fig. 6.9. The interaction between a nucleus and the neighboring frontier atomic orbital is known as the hopping interaction.

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(d) The remaining interactions

The remaining interaction considers the interaction of a frontier orbital on one site with the potential on another site. It has the form

$$\langle \phi_r | V_s | \phi_r \rangle \quad (6.16)$$

where $s \neq r$. It may not be immediately evident that this interaction is usually much weaker than the hopping interaction of Eq. (6.15). But if the individual frontier orbitals decay exponentially with distance as $\exp[-ka]$ where a is the spacing between the atoms, then this term behaves as $\exp[-2ka]$ whereas the hopping term and overlap integral S_{sr} for $s \neq r$ both follow $\exp[-ka]$.

Consequently, we will neglect this interaction.

Thus, Eq. (6.8) can be re-written for $r = 1$ and $r = 2$ as

$$\begin{aligned} c_1\alpha_1 + c_2\beta_{12} + c_2\alpha_2 S_{12} &= c_1E + c_2ES_{12} \\ c_1\beta_{21} + c_1\alpha_1 S_{21} + c_2\alpha_2 &= c_1ES_{21} + c_2E \end{aligned} \quad (6.17)$$

Terms containing only the self energy or energy, E , of the combined system are large. The small terms are highlighted below in red:

$$\begin{aligned} c_1\alpha_1 + c_2\beta_{12} + c_2(\alpha_2 - E)S_{12} &= c_1E \\ c_1\beta_{21} + c_1(\alpha_1 - E)S_{21} + c_2\alpha_2 &= c_2E \end{aligned} \quad (6.18)$$

Next, we note that the difference between the self energies, α_1 and α_2 , and the energy, E , of the combined system may be small. Under this limit, we can reduce the equations further to

$$\begin{aligned} c_1\alpha_1 + c_2\beta_{12} &= c_1E \\ c_1\beta_{21} + c_2\alpha_2 &= c_2E \end{aligned} \quad (6.19)$$

Written as a matrix, we get

$$\begin{pmatrix} \alpha_1 & \beta_{12} \\ \beta_{21} & \alpha_2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad (6.20)$$

Thus, we can ignore the overlap integrals of separated atoms.

In summary, tight binding theory makes the following approximations:

1. Consider only frontier atomic orbitals
2. Consider only interactions between the frontier atomic orbitals of nearest neighbors. This is the tight binding approximation.
3. Ignore the overlap integrals of separated atoms, *i.e.* $S_{sr} = \delta_{sr}$. This is valid only when $\alpha_1 \approx \alpha_2 \approx E$. We will assume $S_{sr} = \delta_{sr}$ generally to simplify the mathematics.

The self energy, α , and the hopping interaction, β , could be calculated numerically given the potential and the frontier atomic orbital. But, in this class, we will not actually determine α and β . Rather we are interested in the form of the molecular wavefunctions and the dispersion relations for their energies. With this information we can determine whether the conductor is a metal or an insulator, and its density of states.

Solving for the energy

Considering the tight binding matrix of Eq. (6.20), non trivial solutions for the weighting factors, c_1 and c_2 are obtained from

$$\det \begin{vmatrix} \alpha_1 - E & \beta_{12} \\ \beta_{21} & \alpha_2 - E \end{vmatrix} = 0 \quad (6.21)$$

Let's assume that the hopping interactions are equal $\beta_{12} = \beta_{21} = \beta$. We'll consider two cases for equal and different self energies.

(a) Equal self energies $\alpha_1 = \alpha_2 = \alpha$

When $\alpha_1 = \alpha_2 = \alpha$, the energy is

$$E = \alpha \pm \beta \quad (6.22)$$

Substituting the energy back into Eq. (6.20) to obtain the coefficients c_1 and c_2 yields two normalized solutions:

$$\varphi = \frac{\phi_1 \pm \phi_2}{\sqrt{2}}. \quad (6.23)$$

These two orbitals can be defined by their **parity**: their symmetry if their position vectors are rotated. For example, we could exchange their coordinates. In this example the molecular orbital:

$$\varphi = \frac{\phi_1 + \phi_2}{\sqrt{2}} \quad (6.24)$$

does not change sign under exchange of electrons. It is classified as having *gerade* symmetry, denoted by *g*, where *gerade* is German for even. In contrast, the other orbital:

$$\varphi = \frac{\phi_1 - \phi_2}{\sqrt{2}} \quad (6.25)$$

does change sign under exchange of electrons. It is classified with *ungerade* symmetry, denoted by *u*, where *ungerade* is German for odd.

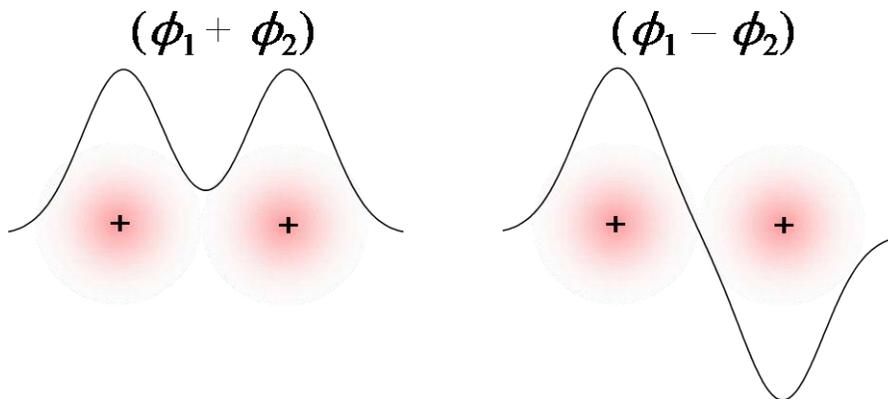


Fig. 6.10. The probability density plotted for the two linear combinations of two frontier orbitals. Due to the increased electron density between the nuclei, the $\phi_1 + \phi_2$ has lower energy.

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Since the molecular orbital:

$$\varphi = \frac{\phi_1 + \phi_2}{\sqrt{2}} \quad (6.26)$$

has energy, $E = \alpha + \beta$, below that of the self energy, α , of each atomic orbital, the molecule is stabilized in this configuration. This is known as a bonding orbital because it describes a stable chemical bond. Recall that α and β are defined to be negative for an electron in a positively charge nuclear potential.

The other molecular orbital

$$\varphi = \frac{\phi_1 - \phi_2}{\sqrt{2}} \quad (6.27)$$

has energy, $E = \alpha - \beta$, greater than that of the self energy, α , of each atomic orbital. Thus, this configuration is not stable. It is known as an antibonding orbital.

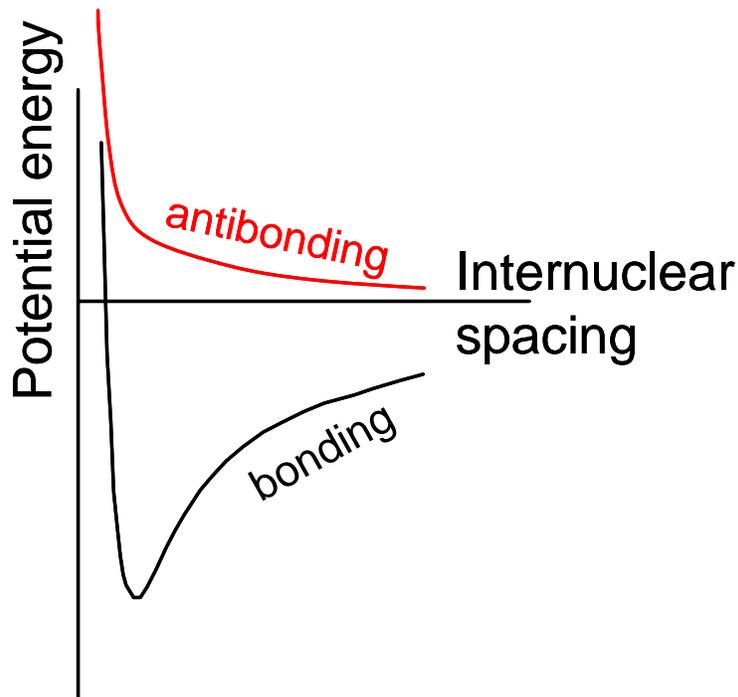


Fig. 6.11. Antibonding and bonding molecular potential energy curves. Note that the antibonding energy is typically substantially larger than shown.

(b) Different self energies

If $|\alpha_1 - \alpha_2| \gg \beta$ and $\alpha_1 > \alpha_2$ then the solutions are:

$$E = \alpha_1 + \frac{\beta^2}{\alpha_1 - \alpha_2}, \quad E = \alpha_2 - \frac{\beta^2}{\alpha_1 - \alpha_2} \quad (6.28)$$

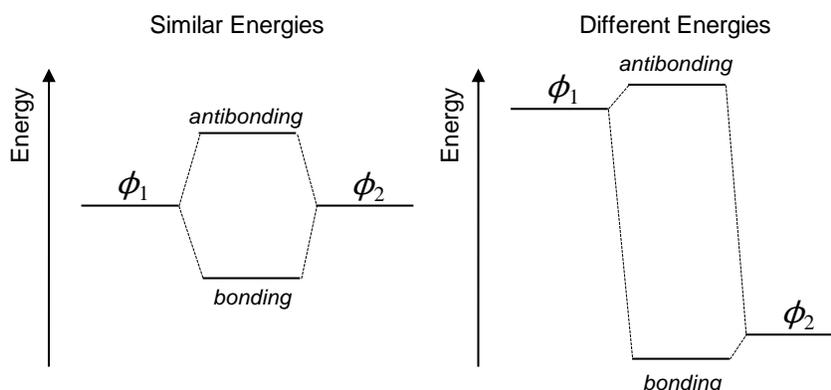


Fig. 6.12. The strongest bonds are formed from atomic orbitals with similar energies. In these diagrams the constituent atomic orbitals are shown at left and right. The molecular orbitals are in the center.

Thus, the splitting increases with the similarity in energy of the participating atomic orbitals, *i.e.* the bonding orbital becomes more stable. This is a general attribute of the interaction between two quantum states. The more similar their initial energies, the stronger the interaction.

Examples of tight binding calculations

Let's consider a conductor consisting of four atoms, each of which provides a frontier atomic orbital containing a single electron. A molecular equivalent to this model conductor is 1,3-butadiene; see Fig. 6.13. Here each carbon atom contributes one electron in a frontier atomic orbital.

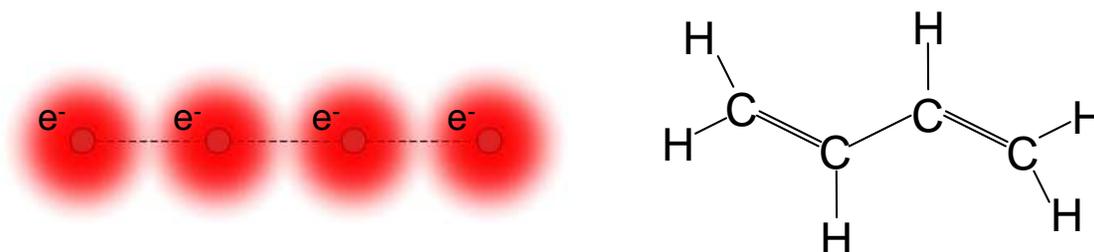


Fig. 6.13. (left) A model four atom conductor, where each atom contributes a single electron in a frontier atomic orbital. **(right)** An approximate chemical equivalent is 1,3-butadiene, where the carbon atoms provide the frontier orbitals.

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We'll ignore the hydrogen atoms, since the frontier electrons are donated by the carbon atoms. Let's label the four carbon frontier atomic orbitals ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4 .

Following Eq. (6.6), we let the molecular orbitals be

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 \quad (6.29)$$

where the c coefficients are yet to be determined.

Let's next consider integrals of the form:

$$\langle \phi_m | H | \psi \rangle = \langle \phi_m | E | \psi \rangle = E \langle \phi_m | \psi \rangle \quad (6.30)$$

Considering $m = 1, 2, 3$ and 4 in turn, we get four equations:

$$\begin{aligned} \langle \phi_1 | H | \psi \rangle &= c_1\alpha_1 + c_2\beta_{12} = c_1E \\ \langle \phi_2 | H | \psi \rangle &= c_2\alpha_2 + c_1\beta_{21} + c_3\beta_{23} = c_2E \\ \langle \phi_3 | H | \psi \rangle &= c_3\alpha_3 + c_2\beta_{32} + c_4\beta_{34} = c_3E \\ \langle \phi_4 | H | \psi \rangle &= c_4\alpha_4 + c_3\beta_{43} = c_4E \end{aligned} \quad (6.31)$$

You can think of each equation as describing the interactions between a particular carbon atom, and itself and its neighbors. Solving these equations gives the coefficients c_1 , c_2 , c_3 , and c_4 . To simplify, we will assume that the self energy at each carbon atom is the same, *i.e.*

$$\alpha = \alpha_1 = \alpha_2 = \alpha_3 = \alpha_4.$$

In addition, we will assume that the hopping interactions between neighboring carbon atoms are the same, *i.e.*

$$\beta = \beta_{12} = \beta_{21} = \beta_{23} = \beta_{32} = \beta_{34} = \beta_{43}.$$

Perhaps the best way to solve the equations systematically is via a matrix. The equations can be re-written:

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \quad (6.32)$$

This equation is of the familiar form

$$H|\psi\rangle = E|\psi\rangle \quad (6.33)$$

where the Hamiltonian is in the form of a matrix, and the wavefunction is a column vector containing the coefficients that weight the atomic orbitals:

$$H = \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix}, \quad \psi = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \quad (6.34)$$

Expressing the Hamiltonian and wavefunction in this form is an example of *matrix mechanics*, a version of quantum mechanics formulated by Werner Heisenberg that is

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convenient for many problems. Apart from this example, we won't pursue matrix mechanics in this class.

But it's worth taking a moment to examine the structure of the Hamiltonian matrix. Each row now describes the interactions between frontier orbitals on a carbon atom, and itself and its neighbors. The diagonal of the matrix contains the self-energies, and the off-diagonal elements are the hopping interactions. This particular example is *tridiagonal*, *i.e.* the matrix elements are zero, except for the diagonal, and its immediately adjacent matrix elements. Linear molecules with alternating single and double bonds always possess tridiagonal matrices.

After a bit of practice with tight binding calculations you should be able to skip directly to writing down the Hamiltonian matrix. For example, consider cyclobutadiene; shown below.

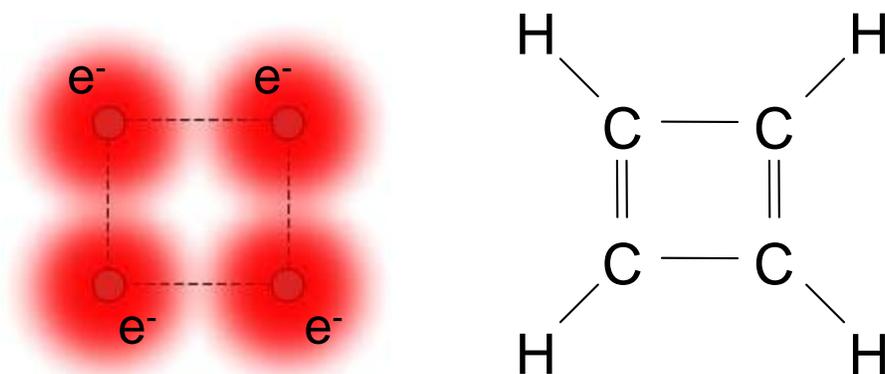


Fig. 6.14. A cyclic four atom molecule and its chemical equivalent, cyclo-butadiene.

Because of its ring structure, cyclobutadiene has additional hopping interactions between the carbons #1 and #4 that were on the ends of the chain in 1,3-butadiene. These interactions at the 1,4 and 4,1 positions are labeled in red in Eq. (6.35) below.

$$H = \begin{pmatrix} \alpha & \beta & 0 & \beta \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ \beta & 0 & \beta & \alpha \end{pmatrix} \quad (6.35)$$

As you can probably imagine, for all but the simplest molecules, these matrices can get extremely large and unwieldy. And solving them can be extremely computationally intensive. In fact, tight binding calculations are almost never done by hand. But some insight can be gained by analytically solving simple linear molecules.

Returning to 1,3-butadiene, rearranging Eq. (6.32), we get:

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$$\begin{pmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0 \quad (6.36)$$

To find the non-trivial solution (i.e. solutions other than $c_1 = c_2 = c_3 = c_4 = 0$) we take the determinant:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad (6.37)$$

The solutions are:

$$E = \alpha \pm \beta \sqrt{\frac{3}{2} \pm \frac{\sqrt{5}}{2}} \quad (6.38)$$

And the eigenfunctions are:

$$c_j = \sin\left(jn\frac{\pi}{5}\right), \quad j, n = 1, 2, 3, 4. \quad (6.39)$$

These solutions are summarized in Fig. 6.15. The molecular orbitals are similar to the standing waves expected for a particle in a box.

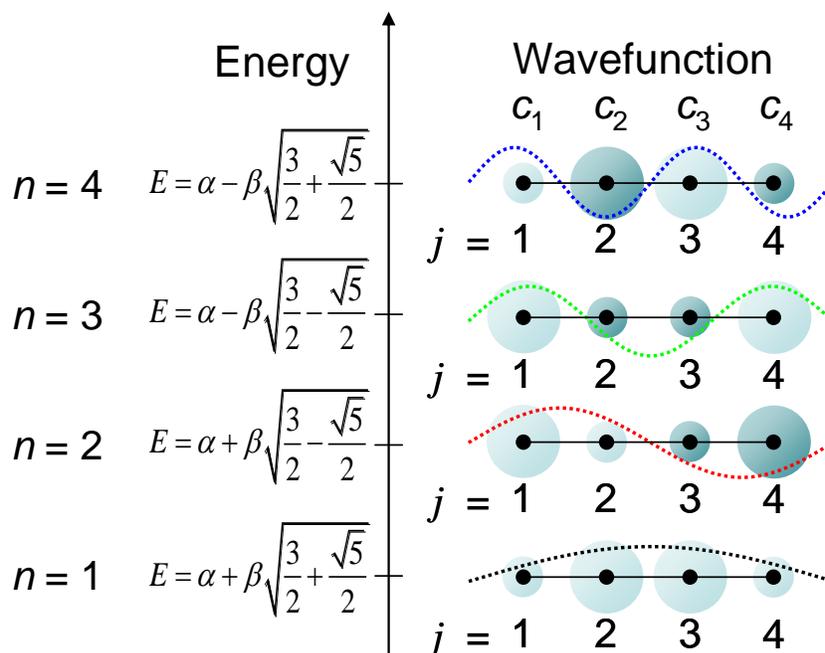


Fig. 6.15. The molecular orbitals and their energies for 1,3-butadiene. After 'Molecular Quantum Mechanics', by Atkins and Friedman, 3rd edition, Cambridge University Press, 1997.

Polyacetylene

Next, let's consider a longer chain of carbon atoms. Very long molecules are known as polymers, and a polymer equivalent of the idealized conductor in Fig. 6.16 is known as polyacetylene.

Specifically, let's solve for a carbon chain of N atoms. Equation (6.37) is an example of a tridiagonal determinant. In general, an $N \times N$ tridiagonal determinant has eigenvalues:[†]

$$E_n = \alpha + 2\beta \cos\left(\frac{n\pi}{N+1}\right), \quad n = 1, 2, \dots, N. \quad (6.40)$$

and eigenvectors:

$$c_j = \sin\left(jn \frac{\pi}{N+1}\right), \quad j, n = 1, 2, \dots, N. \quad (6.41)$$

Note that Eqns. (6.40)-(6.41) reduce to Eqns. (6.38)-(6.39) by using the identity:

$$\cos\left(\frac{2\pi}{5}\right) = \frac{1}{4}(-1 + \sqrt{5})$$

Thus, we have solved for the molecular orbitals in a molecule modeled by an arbitrarily long chain of frontier atomic orbitals, each containing a single electron.

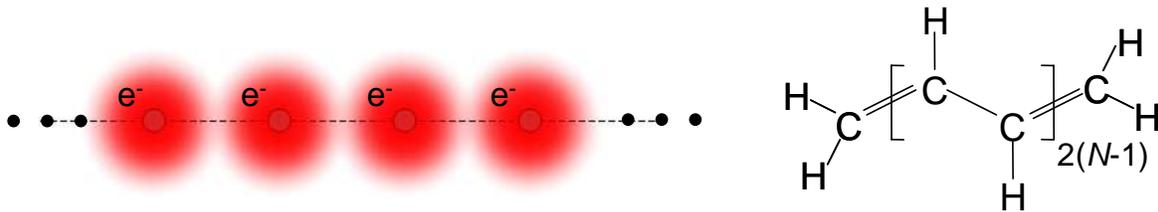


Fig. 6.16. (left) An infinite chain of atoms each contributing a single electron in a frontier orbital. **(right)** The equivalent polymer polyacetylene.

Next, let's re-express our solutions for polyacetylene in terms of a wavevector, k . Note that because the atoms are discretely positioned in a chain, k is also discrete. There are only N allowed values of k .

Given $x = ja_0$, where a_0 is the spacing between carbon atoms, we get:

$$c(x) = \sin(kx) \quad (6.42)$$

and

$$E_n = \alpha + 2\beta \cos(ka_0) \quad (6.43)$$

where

$$k = \frac{\pi}{a_0} \frac{n}{N+1}, \quad n = 1, 2, \dots, N \quad (6.44)$$

[†] If you are interested and have a few spare hours you can try to prove this. After evaluating the first few determinants of simple tridiagonal matrices, $N=1$, $N=2$, $N=3$, etc.. find and solve a difference equation for the determinants as a function of the matrix dimension, N .

Part 6. The Electronic Structure of Materials

The dispersion relation of polyacetylene is plotted in Fig. 6.17. The energy states are restricted to energies $E = \alpha \pm 2\beta$, forming a *band*, of width 4β , centered at α . The bandwidth (4β) is directly related to the hopping interaction between neighboring carbon atoms. This is a general property: the stronger the interaction between an electron and the neighboring atoms, the larger the bandwidth. And as we shall, the broader the electronic bandwidth, the better the electron conduction within the material.

There are N states in the band, each separated by

$$\Delta k = \frac{\pi}{a_0(N+1)}. \quad (6.45)$$

Note that the length of the chain is $L = (N-1)a_0$. Thus for long chains the separation between states in the band is approximately

$$\Delta k \approx \frac{\pi}{L} \quad (6.46)$$

Now each carbon atom contributes a single electron in the frontier atomic orbitals that comprise the molecular orbitals. Thus for a N -repeat polymer, there are N electrons. But each state holds two electrons, one of each spin. Filling the lowest energy states first, only the first $N/2$ k states are filled; see Fig. 6.17. Thus, the band is only half full, and so, if the polymer was connected to contacts we might expect polyacetylene to be a metal.

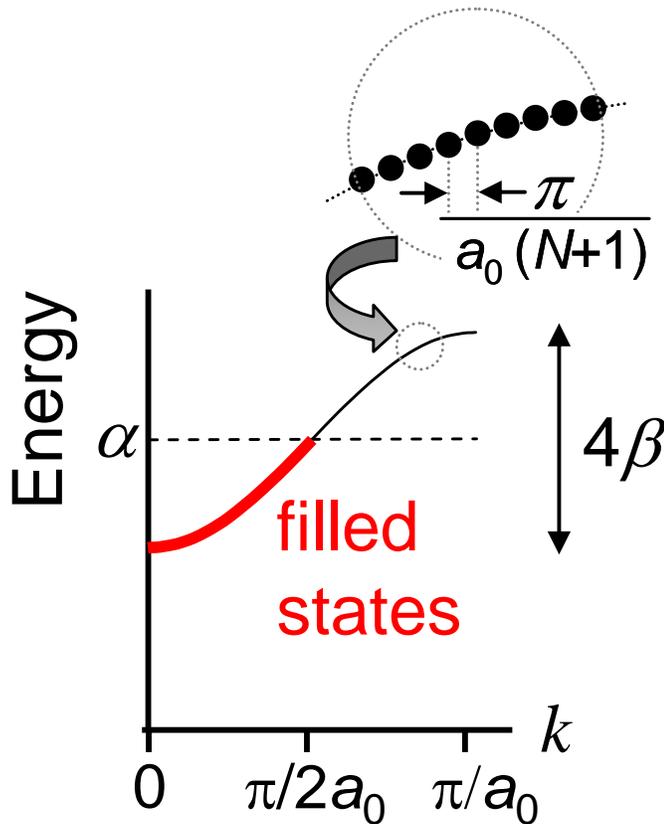


Fig. 6.17. The dispersion relation of polyacetylene as determined by a tight binding analysis. For N atoms, each donating a single electron in a frontier atomic orbital, there are N molecular orbitals with energies arranged in a band. Since the band of states is only half full this material might be expected to be a metal.

Crystals and periodic molecules

The particle in a box approximation is too crude for most problems. Tight binding, on the other hand, is often quite computationally intensive. But fortunately, we can make simplifications when the material is periodic. In this lecture, we are interested in first describing 1d, 2d and 3d periodic materials, and then calculating their wavefunctions. We'll begin with some definitions.

The Primitive Unit Cell

A primitive unit cell of a periodic material is the smallest possible arrangement of atoms that can be copied to construct the entire material.

Primitive Lattice Vectors

Given a primitive unit cell, we can construct the periodic material by translating the unit cell by multiples of the primitive lattice vectors.

Some examples may help

Polyacetylene (average bond model)

The carbon backbone of polyacetylene consists of alternating single and double bonds. Thus, there are two possible configurations: single-double-single-double or double-single-double-single.

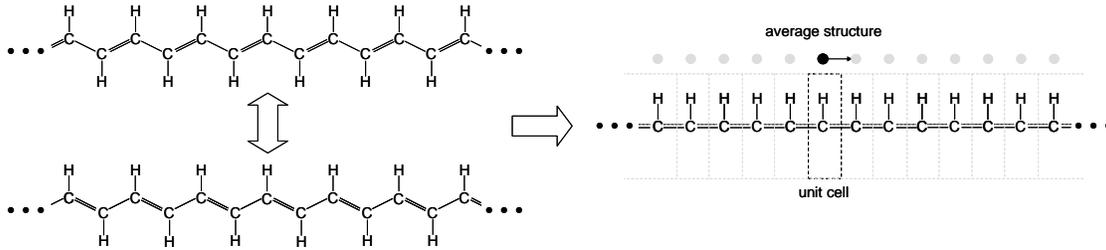


Fig. 6.18. The simplest model for polyacetylene is an average of the two possible alternating single-double bond configurations.

The simplest model assumes that every carbon atom in polyacetylene is identical. The carbon-carbon bonds are then an average of single and double, and the unit cell is a single carbon atom and its associated hydrogen atom. Under this model, to construct a polyacetylene chain, we should translate the primitive unit cell a distance a_0 . Thus the primitive lattice vector is $\tilde{\mathbf{a}}_1 = a_0 \tilde{\mathbf{x}}$, where we arbitrarily positioned the chain parallel to the x -axis.

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Polyacetylene (alternating bond model)

A more accurate model of polyacetylene includes the effects of alternating single and double carbon-carbon bonds on the polymer backbone. Since double bonds contain a slightly higher electron density than single bonds, they are slightly shorter. Thus, the single-double bond alternation establishes a static deformation with twice the period, a_0 , of the average bond model for polyacetylene. The periodic charge density established by the deformation is known as a *charge density wave*. The primitive lattice vector is $\tilde{\mathbf{a}}_1 = 2a_0\tilde{\mathbf{x}}$.

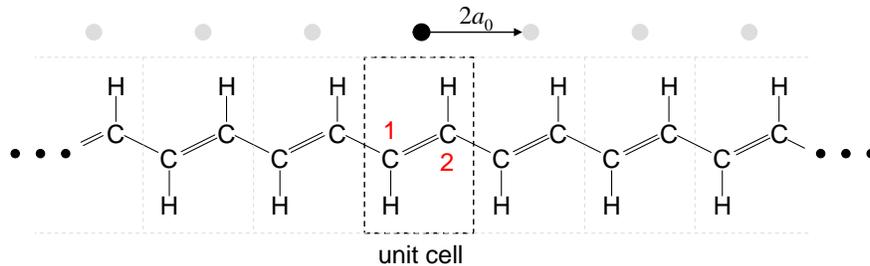


Fig. 6.19. A more accurate model for polyacetylene, including the alternating single and double bonds.

Graphene

Polyacetylene is a 1d chain of carbon atoms, each contributing one electron in a frontier atomic orbital. It is also possible to form 2d sheets of carbon atoms with a single electron in their frontier atomic orbitals. See for example graphene in Fig. 6.20.[†]

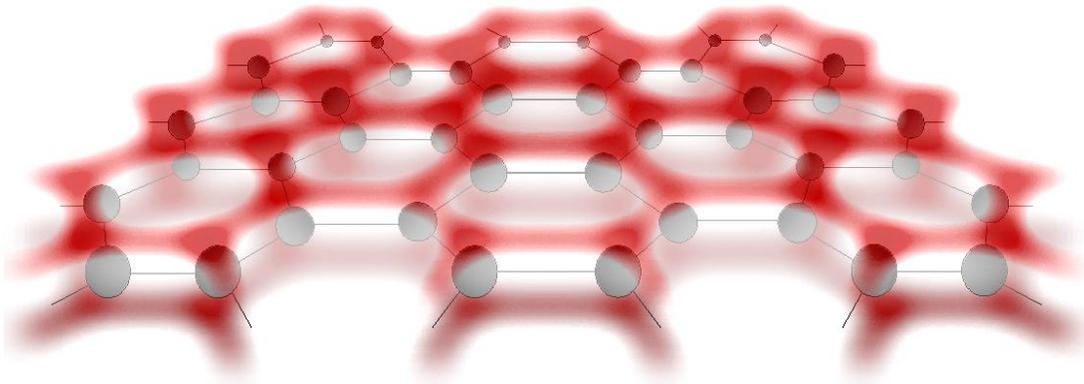


Fig. 6.20. Graphene is a 2d sheet of hexagonal carbon atoms. Electrons in frontier atomic orbitals are found above and below the plane.

[†] In graphene extended π orbitals are formed above and below the plane of a sheet of hexagonal carbon atoms, increasing the rigidity of the structure and enhancing charge transport.

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Graphene may also be rolled up into cylinders to form *carbon nanotubes* – unique structures that we will consider in detail later on in the class.

The unit cell of graphene contains two carbon atoms labeled 1 and 2 in Fig. 6.21. The lattice is generated by shifting the unit cell with the primitive lattice vectors $\tilde{\mathbf{a}}_1 = a_0(-\sqrt{3}/2, 3/2)$ and $\tilde{\mathbf{a}}_2 = a_0(\sqrt{3}/2, 3/2)$, where a_0 is the carbon-carbon bond length.

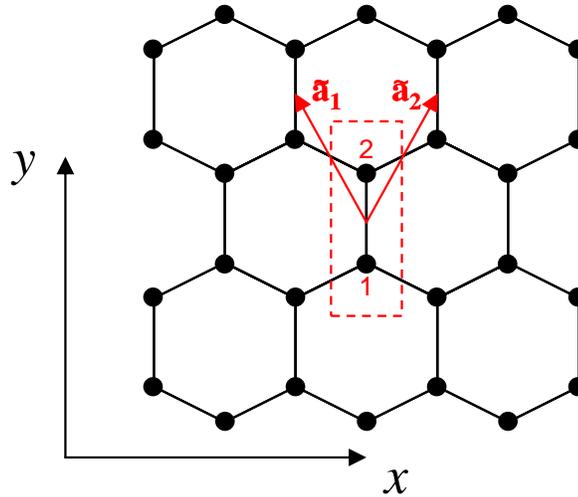


Fig. 6.21. A graphene lattice showing the unit cell and primitive lattice vectors.

Simple cubic, face centered cubic and diamond lattices

Fig. 6.22 shows the simplest 3-d crystal structure – the simple cubic lattice. The primitive lattice vectors are $\mathbf{a}_1 = a_0\hat{\mathbf{x}}$, $\mathbf{a}_2 = a_0\hat{\mathbf{y}}$, $\mathbf{a}_3 = a_0\hat{\mathbf{z}}$, where a_0 is the spacing between neighboring atoms. Very few materials, however, exhibit the simple cubic structure. The major semiconductors, including silicon and gallium arsenide, possess the same structure as diamond.

As also shown in Fig. 6.22, to describe the diamond structure, we first define the face centered cubic (FCC) lattice. Here the simple cubic structure is augmented by an atom in each of the faces of the cube. The primitive lattice vectors are:

$$\mathbf{a}_1 = \frac{a_0}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}}), \quad \mathbf{a}_2 = \frac{a_0}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_3 = \frac{a_0}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}),$$

where a_0 is now the cube edge length.

In the diamond lattice, each atom is sp_3 -hybridized. Thus, every atom is at the center of a tetrahedron. We can construct the diamond lattice from a face centered cubic lattice with a two atom unit cell. For example, in Fig. 6.22, our unit cell has one atom at $(0,0,0)$, and another at $a_0/4.(1,1,1)$.

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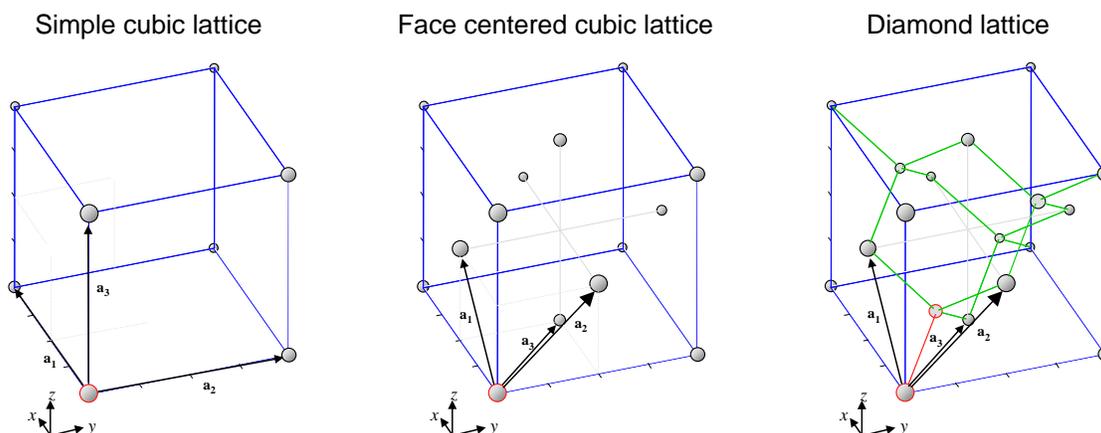


Fig. 6.22. A diamond lattice is simply a face-centered cubic lattice with a two atom unit cell (outlined in red).

Bloch functions: wavefunctions in periodic molecules

Wavefunctions in periodic materials are described by *Bloch functions*. To better understand their properties, it is instructive for us to derive Bloch functions.[†]

First, let's consider a periodic molecule, comprised of unit cells translated by multiples of the primitive lattice vectors. Let the wavefunction of the unit cell be ϕ_0 . Under the tight

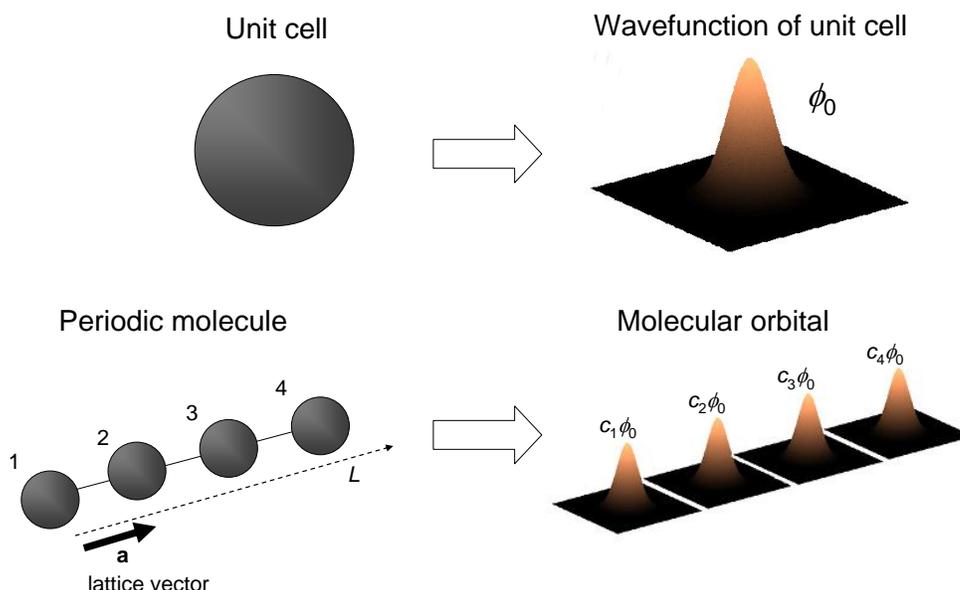


Fig. 6.23. The molecular orbitals of periodic molecules are linear combinations of the wavefunctions of the unit cells.

[†] Our method follows the derivation of Kittel in 'Introduction to Solid State Physics', Wiley, 7th Edition, 1996.

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binding approximation, the wavefunction of the unit cell is itself constructed from a linear combination of frontier atomic orbitals.

Now, the molecular orbitals will be composed of linear combinations of the wavefunction of the unit cell, i.e.

$$\psi = \sum_r c_r \phi_0 \quad (6.47)$$

where once again c_r is a set of coefficients. Note that, unlike approximations of molecular orbitals using linear combinations of frontier atomic orbitals, Eq. (6.47) is exact. We emphasize that ϕ_0 in Eq. (6.47) is the *exact* wavefunction of a unit cell of the complete molecule. In molecular orbital calculations ϕ_0 is typically calculated using tight binding, or another approximate technique. But for the moment we will assume that we know it exactly.

The aim of this derivation is to determine the coefficients c_r given that the material is periodic. Quite generally, we can relate the two coefficients c_1 and c_2 of the first two unit cells by

$$c_2 = \alpha c_1 \quad (6.48)$$

where α is some constant.

The symmetry of the material allows us to translate indistinguishably and consequently,

$$c_{r+1} = \alpha c_r \quad (6.49)$$

where $0 < r < N$, where N is the number of unit cells in the material.

Now if we *assume periodic boundary conditions*, we can compare the identical unit cells at r and $r + N$:

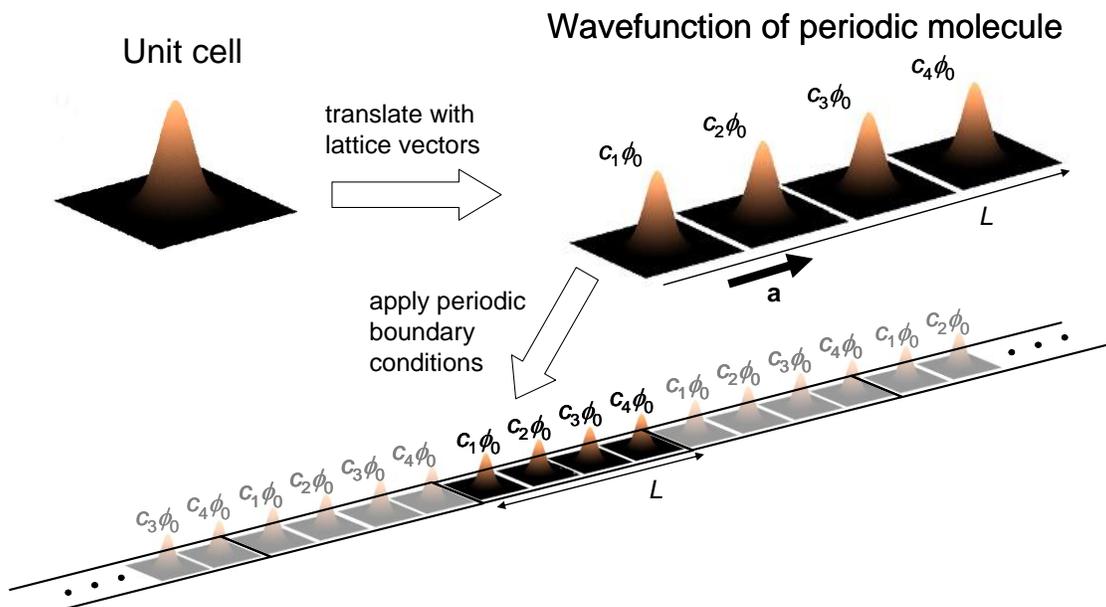


Fig. 6.24. The application of periodic boundary conditions to an already periodic molecule.

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$$c_{N+1} = \alpha^N c_1 \quad (6.50)$$

But since $c_{N+1} = c_1$, α must be one of N roots of unity, i.e. $\alpha = \exp[i2\pi n/N]$, where n is an integer. Thus, the coefficients are phase factors; the wavefunction corresponding to each unit cell is modulated by a phase factor in a periodic molecule. Consequently, if we set $c_N = 1$ (which we can do since absolute phase is arbitrary):

$$c_r = e^{i\frac{2\pi n}{N}r} \quad (6.51)$$

Alternately, approximating the coefficients by a continuous function, we can write:

$$c(x) = e^{ikx} \quad (6.52)$$

where

$$k = \frac{2\pi n}{L} \quad (6.53)$$

Once again, only certain k values are allowed by the application of periodic boundary conditions. After all, standing waves in the molecule can possess only certain wavelengths. Recall also that Fourier transforms of periodic signals are discrete; see Fig. 6.25. Thus, it follows from a Fourier analysis of the coefficients that k must be discrete. In addition, the Fourier transform of the coefficients is itself periodic since the coefficients are discrete (recall discrete time Fourier series - DTFS).

The first Brillouin zone

Since there are only N distinct values of the coefficients (corresponding to one period of the Fourier transform), we typically restrict k to the N values in the range $-N/2 < n \leq N/2$, i.e.

$$-\frac{\pi}{a_0} < k \leq \frac{\pi}{a_0} \quad (6.54)$$

This is known as the **first Brillouin zone**. Other values of k are either not permitted by periodic boundary conditions, or $c(x) = \exp[ikx]$ reduces to one of the N solutions. For example, consider $k = 2\pi(n+N)/L$:

$$c(x) = e^{i\frac{2\pi(n+N)}{L}x} = e^{i\frac{2\pi(n+N)}{Na_0}ra_0} = e^{i\frac{2\pi n}{N}r+i2\pi r} = e^{i\frac{2\pi n}{N}r} = e^{i\frac{2\pi n}{L}x} \quad (6.55)$$

where a_0 is the spacing between unit cells.

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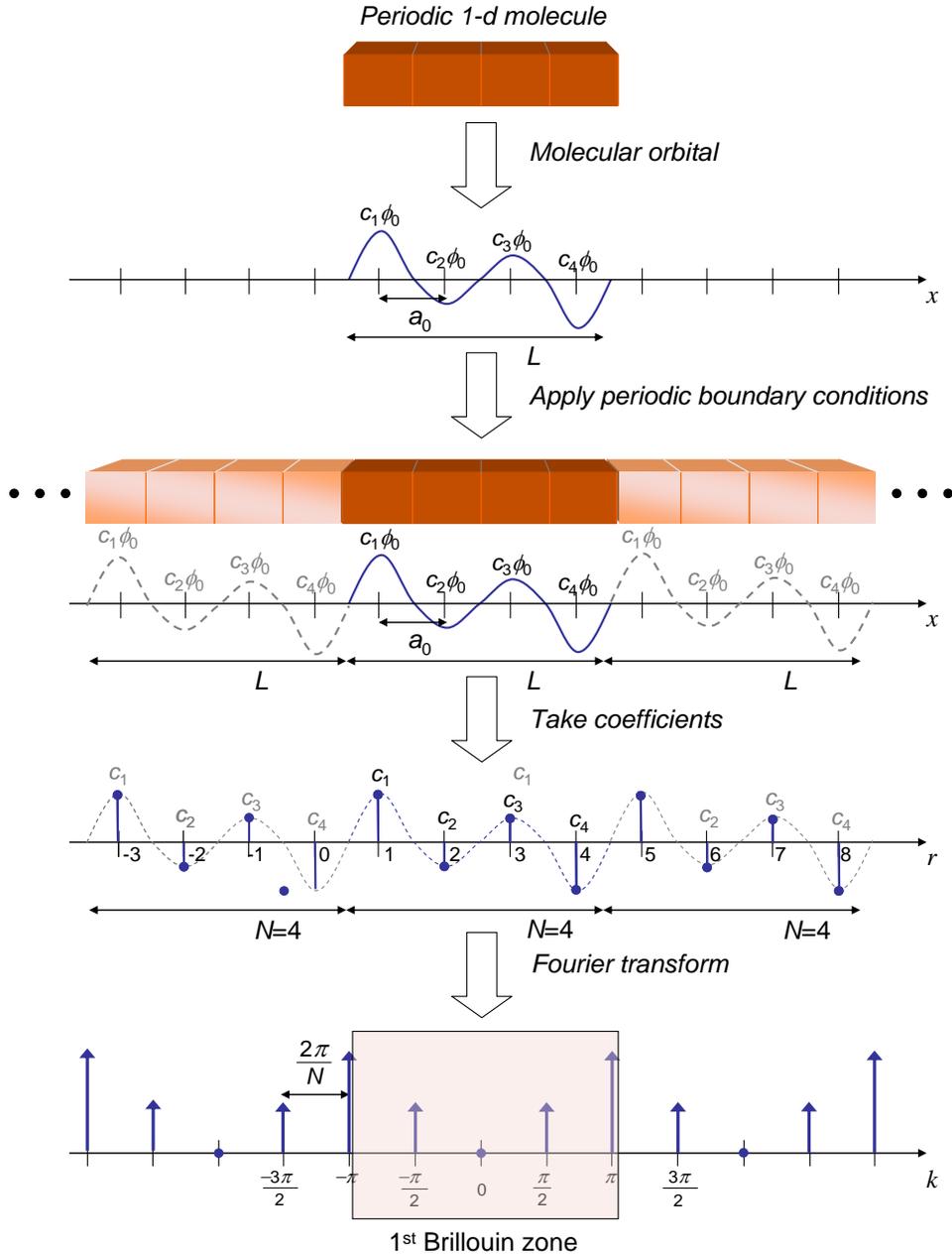


Fig. 6.25. A molecular orbital is described by linear combinations of the wavefunction of the unit cell. The coefficients, c_r , are phase factors. The phase coefficients are discrete – there are only N of them. Thus, the Fourier transform of the coefficients contains only N unique values (it is periodic). We can restrict the range of k values without losing information. Typically, we chose k values in the first Brillouin zone ($-\pi/a_0 < k \leq \pi/a_0$). Note also that the application of periodic boundary conditions fixes the spacing between k values at $2\pi/L$.

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2-d and 3-d periodic materials

Applying Bloch functions to periodic 2d and 3d molecules follows the same principles as in 1d; see Fig. 6.26.

The molecular orbitals in 2-d and 3-d periodic materials are still composed of linear combinations of the wavefunction of the unit cell, ϕ_0 , i.e.

$$\psi = \sum_r c_r \phi_0. \quad (6.56)$$

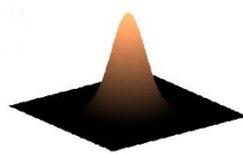
Once again, when we apply periodic boundary conditions the area occupied in k -space per k -state is: (for 2-d and 3-d, respectively)

$$\Delta k^2 = \Delta k_x \Delta k_y = \frac{2\pi}{L_x} \frac{2\pi}{L_y} = \frac{4\pi^2}{A}, \quad \Delta k^3 = \Delta k_x \Delta k_y \Delta k_z = \frac{2\pi}{L_x} \frac{2\pi}{L_y} \frac{2\pi}{L_z} = \frac{8\pi^3}{V} \quad (6.57)$$

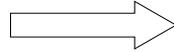
where A is the area of the molecule, and V is its volume.

3-d periodic materials are usually known as crystals. Si and the rest of the common semiconductor materials fall into the category of 3-d periodic materials.

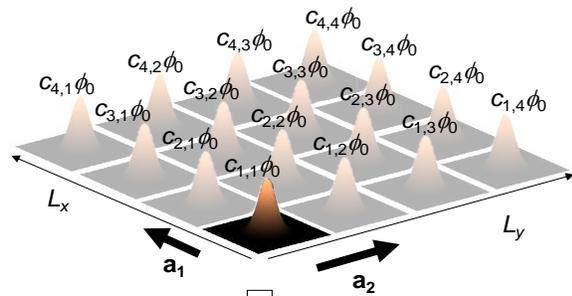
Wavefunction of a unit cell



translate with
lattice vectors



Bloch function



apply periodic
boundary
conditions

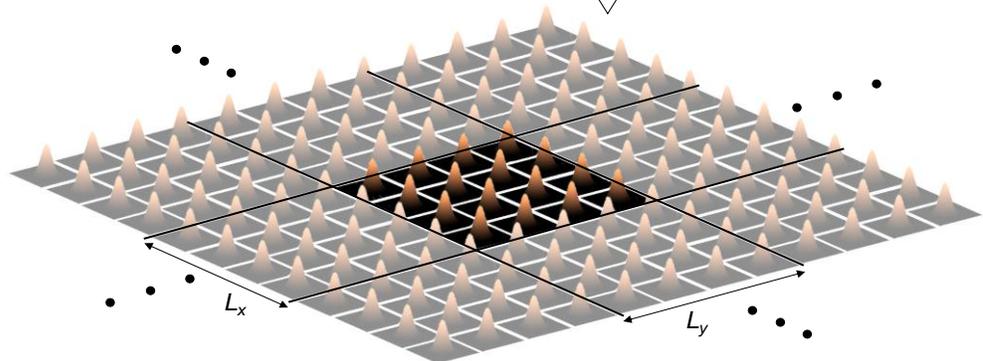
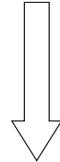


Fig. 6.26. An example of a 2-d periodic material.

Tight Binding Calculations in Periodic molecules and crystals

Polyacetylene (average bond model)

We now repeat the polyacetylene calculation, but this time we impose periodic boundary conditions and assume molecular wavefunctions of the Bloch form. The solutions are almost identical to the previous calculation in the absence of periodic boundary conditions, but there are some subtle yet important differences in the dispersion relation.

The unit cell of polyacetylene under the average bond model has only a single carbon atom. Let the wavefunction of the j th unit cell be $\phi(j)$, defined as the frontier atomic orbital of carbon. Since polyacetylene is periodic, we use a Bloch function to describe the molecular orbitals

$$\psi(x) = \sum_j e^{i\frac{2\pi n}{N}j} \phi(x - ja_0) \quad (6.58)$$

To derive the energy levels consider $\langle \phi_j | H | \psi(x) \rangle$. Now,

$$\langle \phi_j | H | \psi(x) \rangle = \varepsilon \langle \phi_j | \psi(x) \rangle \quad (6.59)$$

Under the tight binding approximation, this simplifies to

$$\beta \exp\left[i\frac{2\pi n}{N}(j-1)\right] + \alpha \exp\left[i\frac{2\pi n}{N}j\right] + \beta \exp\left[i\frac{2\pi n}{N}(j+1)\right] = \varepsilon \exp\left[i\frac{2\pi n}{N}j\right] \quad (6.60)$$

where $\beta = \langle \phi_j | H | \phi_{j+1} \rangle$ and $\alpha = \langle \phi_j | H | \phi_j \rangle$.

Simplifying gives (compare Eq. (6.43))

$$\varepsilon_n = \alpha + 2\beta \cos \frac{2\pi n}{N}. \quad (6.61)$$

Re-writing Eq. (6.61) gives

$$\varepsilon_k = \alpha + 2\beta \cos ka_0 \quad (6.62)$$

where

$$k = \frac{2\pi n}{Na_0} = \frac{2\pi n}{L} \quad (6.63)$$

Once again, we note that each carbon atom contributes a single electron to its frontier orbital, thus for a N -repeat polymer, there are N electrons.

We can determine whether polyacetylene is a metal or insulator by counting k states. The spacing between k states is $2\pi/L$. Thus in the first Brillouin zone, there must be $2\pi/a_0 / 2\pi/L = L/a_0 = N$ states. But each molecular orbital holds two electrons, one of each spin. Filling the lowest energy states first, only the first $N/2$ k states are filled; see Fig. 6.27. With only half its k states filled, polyacetylene might be expected to be a metal.

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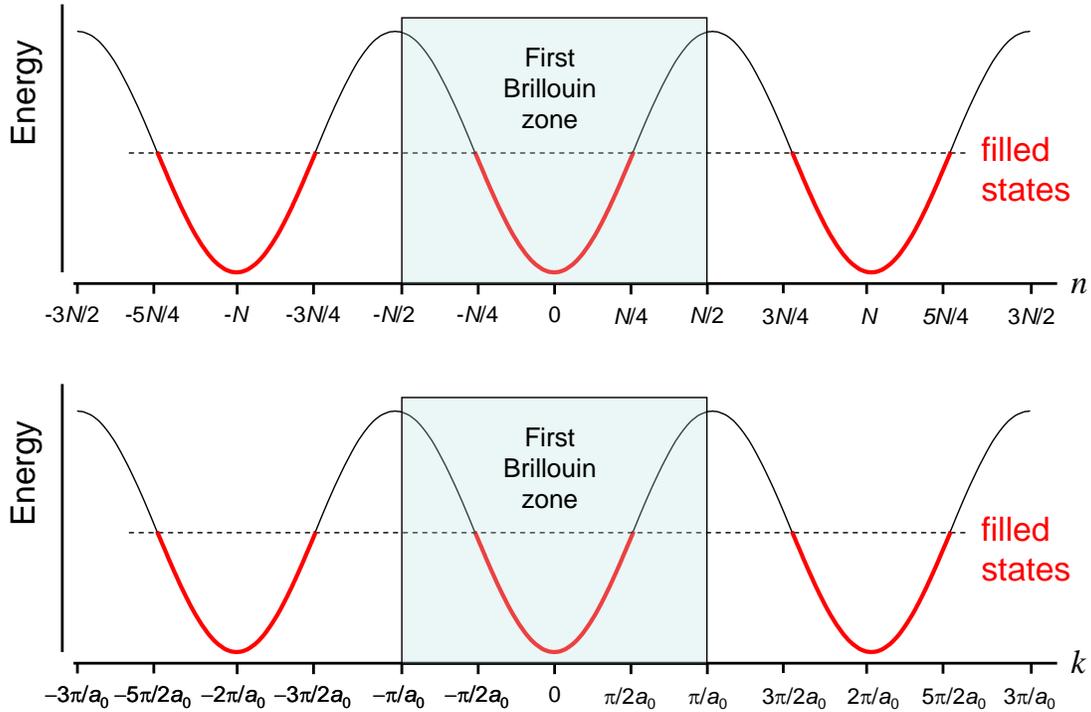


Fig. 6.27. Energy states in polyacetylene as determined by a tight binding analysis. Since the band of states is only half full this material might be expected to be a metal.

Question: Why does the spacing between k states under periodic boundary conditions differ from that calculated for an isolated strand of polyacetylene – see Eq.(6.46)?

Answer: In the previous section, we analyzed the allowed k states in a periodic linear molecule, polyacetylene. We did not employ periodic boundary conditions, thus we would expect that the solutions would only be comparable as the number, N , of unit cells increases, proportionately reducing the impact of the differing boundary conditions. But for $N \rightarrow \infty$ we still find $\Delta k(\text{isolated polyacetylene}) = \frac{1}{2} \Delta k(\text{polyacetylene in periodic boundary conditions})$.

The answer to this conundrum is that isolated polyacetylene (i.e. actual polyacetylene – not polyacetylene with infinite copies to the left and right) can only support *standing* waves; there are no contacts that can inject charge, hence no solely left or right-propagating waves. Thus, considering both positive and negative values of k in isolated polyacetylene makes no sense. Rather, k ranges from 0 to π/a_0 . There must be N states in this range, and we obtain $\Delta k = \pi/L$.

Given periodic boundary conditions, the polymer has infinite length. A wave could propagate to the left or right indefinitely. So we must consider both positive and negative values of k , i.e. k ranges from $-\pi/a_0$ to π/a_0 . There must be N states in this range, and we obtain $\Delta k = 2\pi/L$.

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Interestingly, we are almost never interested in a completely isolated electronic material. For example, practical systems must have contacts to inject charge! Thus, periodic boundary conditions that allow for propagating waves often come closer to modeling practical systems.

Polacetylene (alternating bond model)

Next, let's see what happens to the dispersion relation under the alternating bond model. Now each unit cell has two carbon atoms; see Fig. 6.19. We'll model the unit cell with a *linear combination* of two frontier atomic orbitals because the contributions of each atomic orbital to the unit cell could vary.

Let the wavefunction of the j th unit cell be

$$\phi(j) = c_1\phi_1(j) + c_2\phi_2(j) \quad (6.64)$$

where $\phi_1(j)$ and $\phi_2(j)$ are the frontier atomic orbitals of the first and second carbon atom in the j th unit cell, respectively.

We must define two hopping integrals. For single bonds we have

$$\beta_S = \langle \phi_1(j-1) | H | \phi_2(j) \rangle \quad (6.65)$$

and for double bonds

$$\beta_D = \langle \phi_1(j) | H | \phi_2(j) \rangle. \quad (6.66)$$

As before, $\alpha = \langle \phi_1(j) | H | \phi_1(j) \rangle = \langle \phi_2(j) | H | \phi_2(j) \rangle$.

Assuming a wavefunction of the Bloch form (Eq. (6.58)) we take

$$\psi(x) = \sum_j e^{i\frac{2\pi n}{N}j} \phi(x - j2a_0), \quad (6.67)$$

where we note that the spacing between unit cells is now $2a_0$.

Let's now consider two overlap equations

$$\begin{aligned} \langle \phi_1(j) | H | \psi \rangle &= \varepsilon \langle \phi_1(j) | \psi \rangle \\ \langle \phi_2(j) | H | \psi \rangle &= \varepsilon \langle \phi_2(j) | \psi \rangle \end{aligned} \quad (6.68)$$

Under the tight binding approximations, the LHS of Eq. (6.68) expands to

$$\begin{aligned} \langle \phi_1(j) | H | \psi \rangle &= \left(c_2\beta_S \exp\left[-i\frac{2\pi n}{N}\right] + c_1\alpha + c_2\beta_D \right) \exp\left[i\frac{2\pi n}{N}j\right] \\ \langle \phi_2(j) | H | \psi \rangle &= \left(c_2\alpha + c_1\beta_D + c_1\beta_S \exp\left[i\frac{2\pi n}{N}\right] \right) \exp\left[i\frac{2\pi n}{N}j\right] \end{aligned} \quad (6.69)$$

The RHS of Eq. (6.68) expands to

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$$\begin{aligned}\varepsilon \langle \phi_1(j) | \psi \rangle &= \varepsilon c_1 \exp \left[i \frac{2\pi n}{N} j \right] \\ \varepsilon \langle \phi_2(j) | \psi \rangle &= \varepsilon c_2 \exp \left[i \frac{2\pi n}{N} j \right]\end{aligned}\tag{6.70}$$

The solution for non-trivial c_1, c_2 is given by

$$\begin{vmatrix} \alpha - \varepsilon & \beta_s \exp \left[-i \frac{2\pi n}{N} \right] + \beta_D \\ \beta_s \exp \left[i \frac{2\pi n}{N} \right] + \beta_D & \alpha - \varepsilon \end{vmatrix} = 0\tag{6.71}$$

i.e.

$$\varepsilon = \alpha \pm \sqrt{\beta_s^2 + \beta_D^2 + 2\beta_s\beta_D \cos 2ka_0}\tag{6.72}$$

In the alternating bond model, the period of polyacetylene is $2a_0$. Thus the number of distinct k values is $2\pi/2a_0 / 2\pi/L = N/2$, where N is the number of carbon atoms in the polymer backbone.

But there are two solutions for the energy at each k value (i.e. there are two energy bands), so the total number of states is N . Since each state holds two electrons, we find that the bottom band is completely full and the top band is completely empty. Thus, the periodic potential formed by alternating single and double bonds opens a *band gap* at $k = \pi/2a_0$, completing transforming the material from a metal to an insulator/semiconductor! Obviously, the accuracy of the DOS calculation is critical.

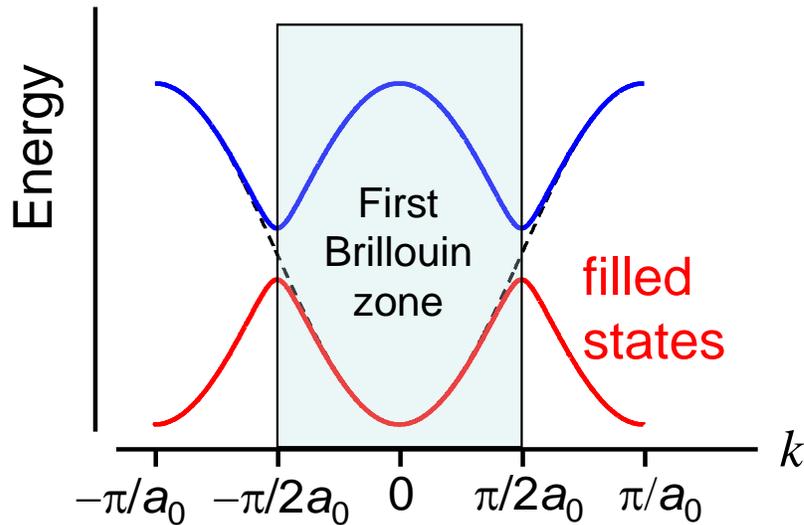


Fig. 6.28. A periodic perturbation with twice the interatomic spacing introduces a gap at the Fermi energy, transforming a metal into an insulator (wide bandgap semiconductor).

Graphene

Like polyacetylene in the alternating bond model, in graphene we have a unit cell with two carbon atoms. Let the wavefunction of the unit cell be

$$\phi = c_1\phi_1 + c_2\phi_2 \quad (6.73)$$

where ϕ_1 and ϕ_2 are the frontier atomic orbitals of the first and second carbon atom in the unit cell, respectively.

We assume a wavefunction of the Bloch form (Eq. (6.58)) but we re-write it in terms of a sum over all lattice vectors \mathbf{R} :

$$\psi(\mathbf{x}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi(\mathbf{x} - \mathbf{R}). \quad (6.74)$$

Next we define the hopping integral

$$\beta = \langle \phi_1 | H | \phi_2 \rangle \quad (6.75)$$

As before, $\alpha = \langle \phi_j | H | \phi_j \rangle$.

Let's now consider two overlap equations

$$\begin{aligned} \langle \phi_1(\mathbf{R}) | H | \psi(\mathbf{x}) \rangle &= \varepsilon \langle \phi_1(\mathbf{R}) | \psi(\mathbf{x}) \rangle \\ \langle \phi_2(\mathbf{R}) | H | \psi(\mathbf{x}) \rangle &= \varepsilon \langle \phi_2(\mathbf{R}) | \psi(\mathbf{x}) \rangle \end{aligned} \quad (6.76)$$

Under the Hückel/tight binding approximations, the LHS of Eq. (6.76) expands to

$$\begin{aligned} \langle \phi_1(\mathbf{R}) | H | \psi(\mathbf{x}) \rangle &= (c_1\alpha + c_2\beta(1 + e^{-i\mathbf{k}\cdot\tilde{\mathbf{a}}_1} + e^{-i\mathbf{k}\cdot\tilde{\mathbf{a}}_2})) e^{i\mathbf{k}\cdot\mathbf{R}} \\ \langle \phi_2(\mathbf{R}) | H | \psi(\mathbf{x}) \rangle &= (c_2\alpha + c_1\beta(1 + e^{i\mathbf{k}\cdot\tilde{\mathbf{a}}_1} + e^{i\mathbf{k}\cdot\tilde{\mathbf{a}}_2})) e^{i\mathbf{k}\cdot\mathbf{R}} \end{aligned} \quad (6.77)$$

The RHS of Eq. (6.76) expands to

$$\begin{aligned} \varepsilon \langle \phi_1(\mathbf{R}) | \psi(\mathbf{x}) \rangle &= \varepsilon c_1 e^{i\mathbf{k}\cdot\mathbf{R}} \\ \varepsilon \langle \phi_2(\mathbf{R}) | \psi(\mathbf{x}) \rangle &= \varepsilon c_2 e^{i\mathbf{k}\cdot\mathbf{R}} \end{aligned} \quad (6.78)$$

The solution for non-trivial c_1, c_2 is given by

$$\begin{vmatrix} \alpha - \varepsilon & \beta(1 + e^{-i\mathbf{k}\cdot\tilde{\mathbf{a}}_1} + e^{-i\mathbf{k}\cdot\tilde{\mathbf{a}}_2}) \\ \beta(1 + e^{i\mathbf{k}\cdot\tilde{\mathbf{a}}_1} + e^{i\mathbf{k}\cdot\tilde{\mathbf{a}}_2}) & \alpha - \varepsilon \end{vmatrix} = 0 \quad (6.79)$$

i.e.

$$\varepsilon = \alpha \pm \beta \sqrt{3 + 2\cos(\mathbf{k}\cdot\tilde{\mathbf{a}}_1) + 2\cos(\mathbf{k}\cdot\tilde{\mathbf{a}}_2) + 2\cos(\mathbf{k}\cdot(\tilde{\mathbf{a}}_1 - \tilde{\mathbf{a}}_2))} \quad (6.80)$$

This is plotted in Fig. 6.29, where we have arbitrarily set $\alpha = 0$.

Part 6. The Electronic Structure of Materials

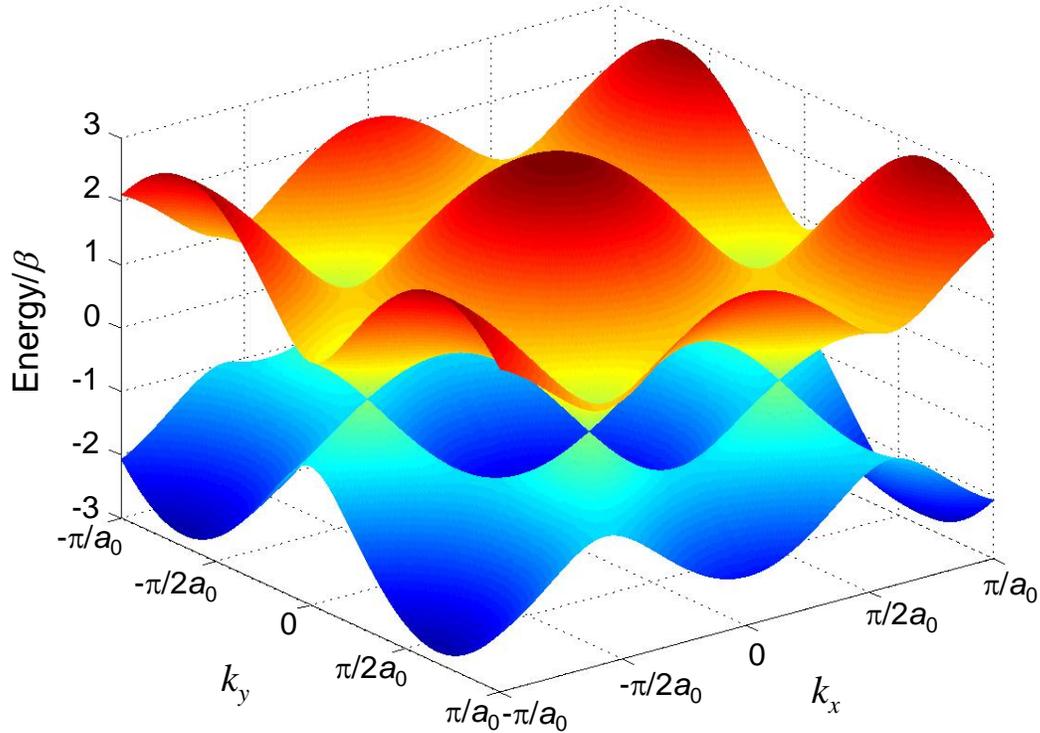


Fig. 6.29. The bandstructure of graphene.

Each unit cell contributes an orbital to a band; given N unit cells, each band has N states, or including spin, $2N$ states. Graphene, with two electrons per unit cell has two bands and $2N$ electrons. Thus, the lower band of graphene is completely filled.

We might therefore expect that graphene is an insulator, but the lower band touches the upper band at values of k known as the K points

$$\mathbf{K} = \left(\pm \frac{4\pi}{3\sqrt{3}a_0}, 0 \right), \left(\pm \frac{2\pi}{3\sqrt{3}a_0}, \pm \frac{2\pi}{3a_0} \right)$$

Thus, in these particular directions graphene conducts like a metal.

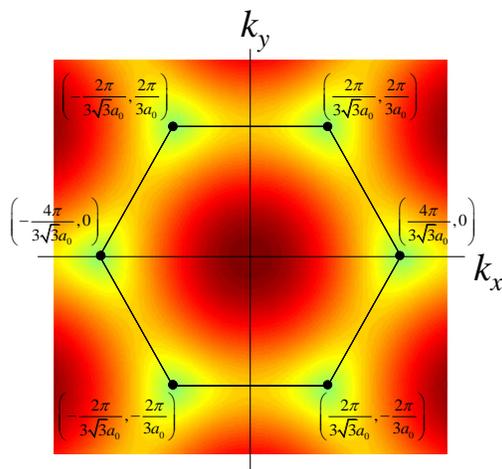


Fig. 6.30. The K points in graphene.

Carbon Nanotubes

Carbon nanotubes are remarkable materials. They are perhaps the most rigid materials known, and they have excellent charge transport properties.

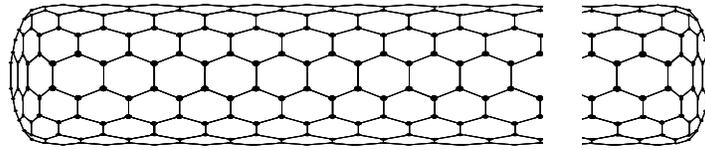


Fig. 6.31. An example of a carbon nanotube – composed of a rolled up graphene sheet. This particular tube is known as an armchair – you may be able to identify armchairs in the hexagonal lattice.

We will treat carbon nanotubes as rolled-up graphene sheets. The construction of a nanotube from a sheet of graphene can be imagined as in Fig. 6.32. We first draw the wrapping vector from one unit cell to another. When the tube is formed both ends of the wrapping vector will be connected. The wrapping vector is written

$$\mathbf{w} = n\tilde{\mathbf{a}}_1 + m\tilde{\mathbf{a}}_2 = (n, m) \quad (6.81)$$

The length of the wrapping vector determines the circumference of the tube, and as we shall see the vector (n, m) characterizes its electronic properties.

Next two parallel cuts are made perpendicular to the wrapping vector and the remaining piece is rolled up; see Fig. 6.33.[†]

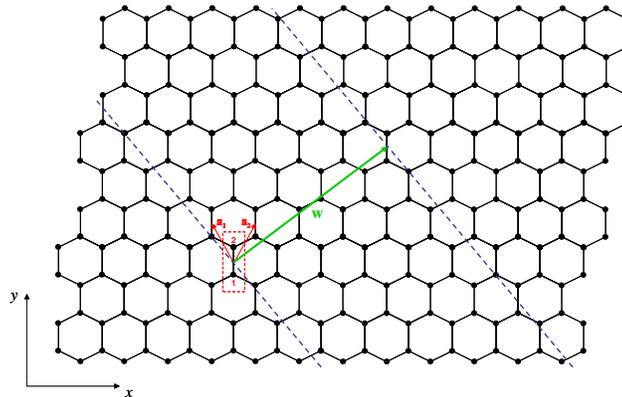


Fig. 6.32. Carbon nanotubes can be imagined to be constructed from rolled up pieces of graphene. In the example above, a wrapping vector, \mathbf{w} , is drawn between two unit cells that will be connected when the tube is rolled up. The graphene sheet is cut perpendicular to \mathbf{w} .

[†] Of course, carbon nanotubes are not actually made from graphene like this. There are many techniques including chemical vapor deposition using a catalyst particle that defines the width of the tube.

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After the tube is rolled up, periodic boundary conditions are established on the circumference of the tube. Thus, only certain values of the wavevector, k , are allowed perpendicular to the tube axis, i.e.

$$\mathbf{k} \cdot \mathbf{w} = 2\pi l, \quad l \in \mathbb{Z} \quad (6.82)$$

If the allowed k -states include the K points of graphene then the carbon nanotube will be a metal, otherwise it is a semiconductor. For example, consider a (4,4) armchair nanotube as shown below. We also plot the K points for graphene in k space.

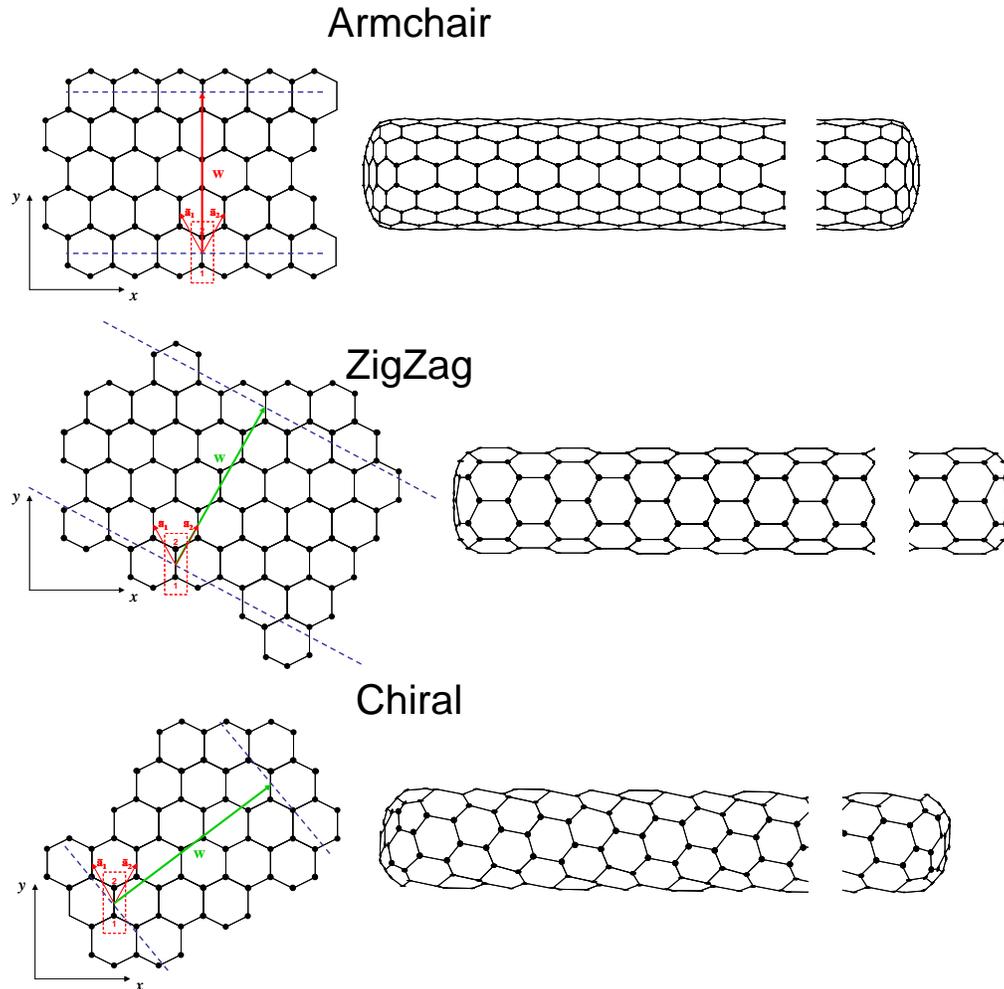


Fig. 6.33. Three types of nanotubes. The first two, armchair and zigzag are special cases with wrapping vectors (N,N) and $(N,0)$ or $(0,N)$, respectively. The third is the general case or chiral form with wrapping vector (n,m) .

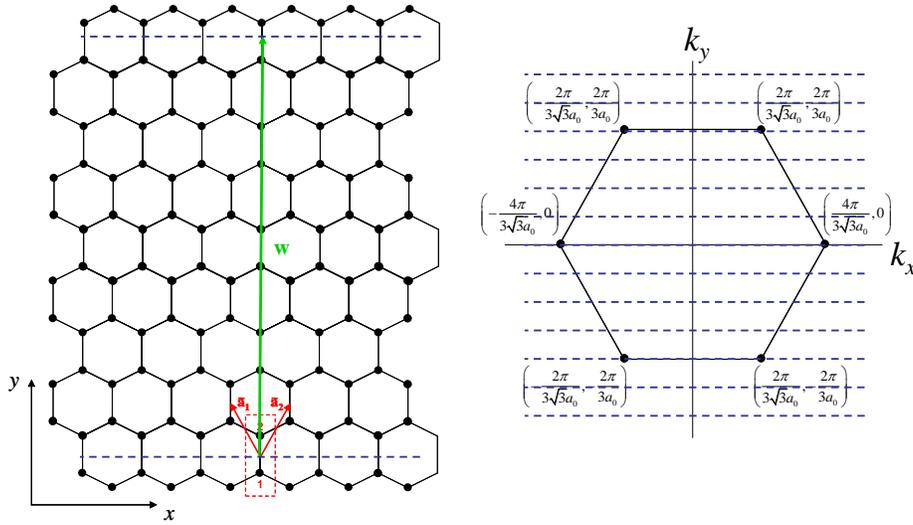


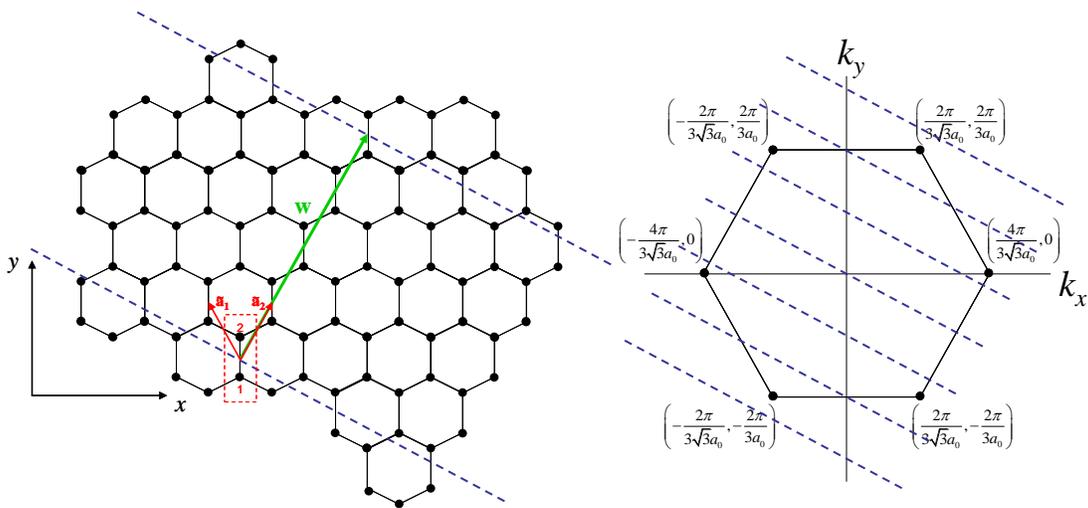
Fig. 6.34. At left, a (4,4) armchair nanotube. At right, the K points of graphene.

Let's begin by decomposing \mathbf{k} into a component perpendicular to the tube axis, \mathbf{k}_\perp , and a component parallel to the tube axis, \mathbf{k}_\parallel . For a (4,4) tube $\mathbf{w} = 12a_0\hat{\mathbf{y}}$. Thus, the allowed values of \mathbf{k} are given by

$$k_y = \frac{\pi l}{6a_0}. \tag{6.83}$$

As shown in Fig. 6.34, this set of allowed \mathbf{k}_\perp values includes the K points. Thus (4,4) tubes are metallic.

Next, let's examine a (0,4) zigzag tube.



For a (0,4) tube $\mathbf{w} = 2\sqrt{3}a_0\hat{\mathbf{x}} + 6a_0\hat{\mathbf{y}}$. Thus, the allowed values of \mathbf{k}_\perp are given by

Fig. 6.35. At left, a (0,4) zigzag nanotube. At right, the K points of graphene.

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$$2\sqrt{3}k_x + 6k_y = \frac{2\pi l}{a_0}. \quad (6.84)$$

As shown in Fig. 6.35, this set of allowed \mathbf{k} values does not include the K points. Thus (0,4) tubes are insulating/semiconducting.

Analytic approximations for the bandstructure of graphene and carbon nanotubes

Since the conduction properties of graphene are dominated by electrons occupying states at or near the K points, it is convenient to linearize the energy at $\boldsymbol{\kappa} = \mathbf{k} - \mathbf{K}$.

The exact tight binding solution from Eq. (6.80) is:

$$\varepsilon = \alpha \pm \beta \sqrt{3 + 2\cos(\mathbf{k} \cdot \tilde{\mathbf{a}}_1) + 2\cos(\mathbf{k} \cdot \tilde{\mathbf{a}}_2) + 2\cos(\mathbf{k} \cdot (\tilde{\mathbf{a}}_1 - \tilde{\mathbf{a}}_2))} \quad (6.85)$$

We substitute $\mathbf{k} = \mathbf{K} + \boldsymbol{\kappa}$ and expand the $\cos(\mathbf{K} + \boldsymbol{\kappa})$ terms as a Taylor series to second order in $\boldsymbol{\kappa}$. This yields:

$$\varepsilon = \alpha \pm \beta \sqrt{\begin{aligned} &3 + 2\cos(\mathbf{K} \cdot \tilde{\mathbf{a}}_1) + 2\cos(\mathbf{K} \cdot \tilde{\mathbf{a}}_2) + 2\cos(\mathbf{K} \cdot (\tilde{\mathbf{a}}_1 - \tilde{\mathbf{a}}_2)) \\ &+ 2\boldsymbol{\kappa} \cdot \tilde{\mathbf{a}}_1 \sin(\mathbf{K} \cdot \tilde{\mathbf{a}}_1) + 2\boldsymbol{\kappa} \cdot \tilde{\mathbf{a}}_2 \sin(\mathbf{K} \cdot \tilde{\mathbf{a}}_2) + 2\boldsymbol{\kappa} \cdot (\tilde{\mathbf{a}}_1 - \tilde{\mathbf{a}}_2) \sin(\mathbf{K} \cdot (\tilde{\mathbf{a}}_1 - \tilde{\mathbf{a}}_2)) \\ &- (\boldsymbol{\kappa} \cdot \tilde{\mathbf{a}}_1)^2 \cos(\mathbf{K} \cdot \tilde{\mathbf{a}}_1) - (\boldsymbol{\kappa} \cdot \tilde{\mathbf{a}}_2)^2 \cos(\mathbf{K} \cdot \tilde{\mathbf{a}}_2) - (\boldsymbol{\kappa} \cdot (\tilde{\mathbf{a}}_1 - \tilde{\mathbf{a}}_2))^2 \cos(\mathbf{K} \cdot (\tilde{\mathbf{a}}_1 - \tilde{\mathbf{a}}_2)) \end{aligned}} \quad (6.86)$$

Next, we note some identities:

$$\cos(\mathbf{K} \cdot \tilde{\mathbf{a}}_1) = \cos(\mathbf{K} \cdot \tilde{\mathbf{a}}_2) = \cos(\mathbf{K} \cdot (\tilde{\mathbf{a}}_1 - \tilde{\mathbf{a}}_2)) = -\frac{1}{2} \quad (6.87)$$

$$\sin(\mathbf{K} \cdot \tilde{\mathbf{a}}_1) = -\sin(\mathbf{K} \cdot \tilde{\mathbf{a}}_2) = -\sin(\mathbf{K} \cdot (\tilde{\mathbf{a}}_1 - \tilde{\mathbf{a}}_2)) \quad (6.88)$$

From these identities Eq. (6.86) reduces to

$$\varepsilon = \alpha \pm \beta \sqrt{\frac{1}{2}(\boldsymbol{\kappa} \cdot \tilde{\mathbf{a}}_1)^2 + \frac{1}{2}(\boldsymbol{\kappa} \cdot \tilde{\mathbf{a}}_2)^2 + \frac{1}{2}(\boldsymbol{\kappa} \cdot (\tilde{\mathbf{a}}_1 - \tilde{\mathbf{a}}_2))^2} \quad (6.89)$$

Solving this (see the Problem Set) gives the approximate dispersion relation for graphene:

$$\varepsilon = \alpha \pm \frac{3}{2} \beta a_0 |\boldsymbol{\kappa}| \quad (6.90)$$

Since the speed of the charge carrier is given by the group velocity: $v = \hbar^{-1} \partial \varepsilon / \partial k$, we get

$$v = \frac{3}{2} \frac{\beta a_0}{\hbar} \quad (6.91)$$

For $a_0 = 1.42 \text{ \AA}$ and $\beta = 2.5 \text{ eV}$, $v = 10^6 \text{ m/s}$.

Introduction to Nanoelectronics

Now, for carbon nanotubes, the periodic boundary condition on the circumference is

$$(\boldsymbol{\kappa} + \mathbf{K}) \cdot \mathbf{w} = 2\pi l, \quad l \in \mathbb{Z} \quad (6.92)$$

Let's consider each K point in turn:

$$\text{For } \mathbf{K} = \left(\frac{4\pi}{3\sqrt{3}a_0}, 0 \right)$$

$$\begin{aligned} (\boldsymbol{\kappa} + \mathbf{K}) \cdot \mathbf{w} &= \boldsymbol{\kappa} \cdot \mathbf{w} + \mathbf{K} \cdot (n\tilde{\mathbf{a}}_1 + m\tilde{\mathbf{a}}_2) \\ &= \boldsymbol{\kappa} \cdot \mathbf{w} + n\mathbf{K} \cdot \left(-\frac{\sqrt{3}}{2}a_0, \frac{3}{2}a_0 \right) + m\mathbf{K} \cdot \left(\frac{\sqrt{3}}{2}a_0, \frac{3}{2}a_0 \right) \\ &= \boldsymbol{\kappa} \cdot \mathbf{w} + \frac{2\pi}{3}(m-n) \end{aligned} \quad (6.93)$$

Rearranging gives:

$$\boldsymbol{\kappa} \cdot \mathbf{w} = 2\pi l + 2\pi \frac{(n-m)}{3} \quad (6.94)$$

$$\text{For } \mathbf{K} = \left(\frac{2\pi}{3\sqrt{3}a_0}, \frac{2\pi}{3a_0} \right)$$

$$\begin{aligned} \boldsymbol{\kappa} \cdot \mathbf{w} &= 2\pi l + 2\pi \frac{(2n+m)}{3} \\ &= 2\pi l + 2\pi \frac{(3n-(n-m))}{3} \\ &\equiv 2\pi l - 2\pi \frac{(n-m)}{3} \end{aligned} \quad (6.95)$$

$$\text{For } \mathbf{K} = \left(-\frac{2\pi}{3\sqrt{3}a_0}, \frac{2\pi}{3a_0} \right)$$

$$\begin{aligned} \boldsymbol{\kappa} \cdot \mathbf{w} &= 2\pi l + 2\pi \frac{(n+2m)}{3} \\ &= 2\pi l + 2\pi \frac{((n-m)+3m)}{3} \\ &\equiv 2\pi l + 2\pi \frac{(n-m)}{3} \end{aligned} \quad (6.96)$$

The other K points follow by symmetry, and we can conclude that

$$\boldsymbol{\kappa}_\perp = \frac{2\pi}{|\mathbf{w}|} \left(l + \frac{(n-m)}{3} \right) \quad (6.97)$$

where we have separated $\boldsymbol{\kappa}$ into two components parallel, $\boldsymbol{\kappa}_\parallel$, and perpendicular, $\boldsymbol{\kappa}_\perp$ to the tube axis. From Eq. (6.90) we get

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$$\varepsilon = \alpha \pm \frac{3\beta a_0}{d} \sqrt{\left(l + \left(\frac{n-m}{3}\right)\right)^2 + \left(\frac{\kappa_{\parallel} d}{2}\right)^2}. \quad (6.98)$$

where the tube circumference is $|\mathbf{w}| = \pi d$. Interestingly, Eq. (6.98) predicts that tubes are metallic when $[(n-m)/3] \in \mathbb{Z}$. Assuming that n and m are generated randomly, we expect that $1/3$ of tubes should be metallic. Indeed, this seems to be the case in practice. Note also that for semiconducting tubes the band gap is inversely proportional to the tube diameter.

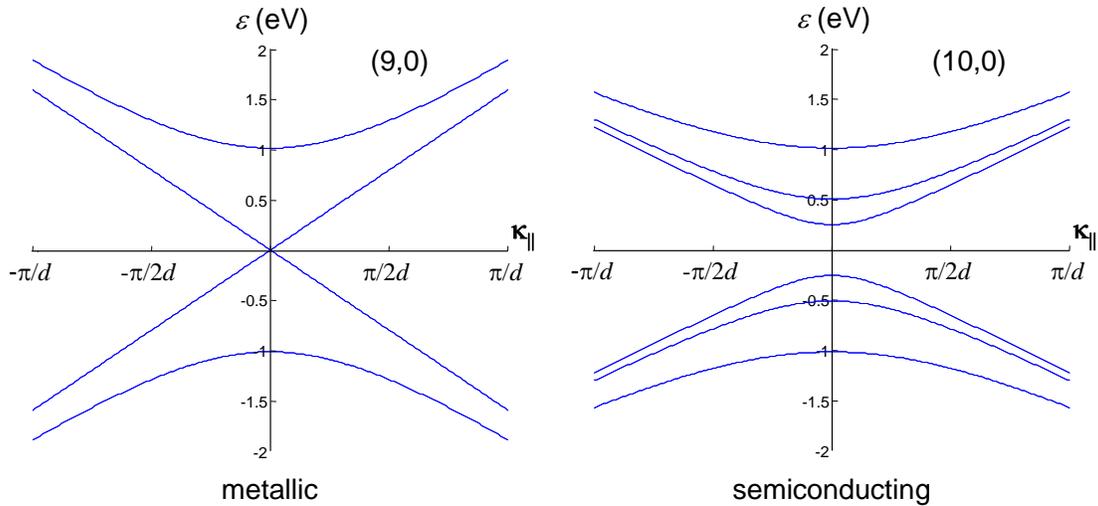


Fig. 6.36. Approximate band structures for metallic and semiconducting zigzag tubes.

Bandstructure of bulk semiconductors

As stated above, most of the common semiconductors are constructed from sp^3 -hybridized atoms assembled in the diamond crystal structure.

Unfortunately, sp^3 -hybridization makes the bandstructure calculation much harder. In our earlier sp^2 -hybridized examples, we were able to ignore all of the atomic orbitals involved in σ bonds, and we considered only the π -bonding electrons from the unhybridized p atomic orbital. Since sp^3 -hybridized materials only contain σ bonds, we can no longer employ this approximation and our calculation must include all four sp^3 -hybridized atomic orbitals. In fact, to obtain reasonable accuracy, bandstructure calculations usually include the next highest unfilled orbital also.

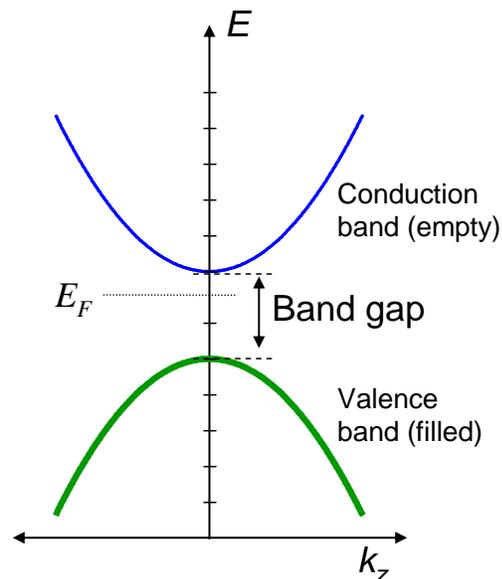
For a diamond structure, with a two atom unit cell, this means that we must consider 10 atomic orbitals per unit cell (one set of five per atom in the unit cell).

The calculation itself follows the procedures we described for graphene. But now we must solve a 10×10 matrix. We will draw the line here in this class.

Band Gaps and Conduction and Valence bands

As shown in Fig. 6.37, if the Fermi energy separates two bands of allowed electron states, the upper band is empty and the lower band is full. The energy difference between the top of the filled band and the bottom of the empty band is known as the *band gap*. Empty bands that lie above the Fermi energy are known as *conduction bands*. Filled bands that lie below the Fermi energy are known as *valence bands*. In this class, we have mostly considered charge transport through the conduction band. Charge may also move through vacancies in the normally full valence band. These vacancies are known as holes. Holes are effectively positively charged because the semiconductor no longer has its full complement of electrons. Consequently, a MOSFET that conducts through its valence band is known as p-channel MOSFET. It requires a negative V_{GS} to turn on.

Fig. 6.37. The energy difference between the top of a filled (valence) band and the bottom of an empty (conduction) band is known as the band gap.



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Band diagrams

Often the dispersion relation is simplified to show just the bottom of the conduction band, and the top of the valence band. This simplification is useful because usually the density of states is sufficiently large in a bulk semiconductor that the gate is prevented from pushing the Fermi level into the band. Plots showing the band edges as a function of position are known as a band diagrams.

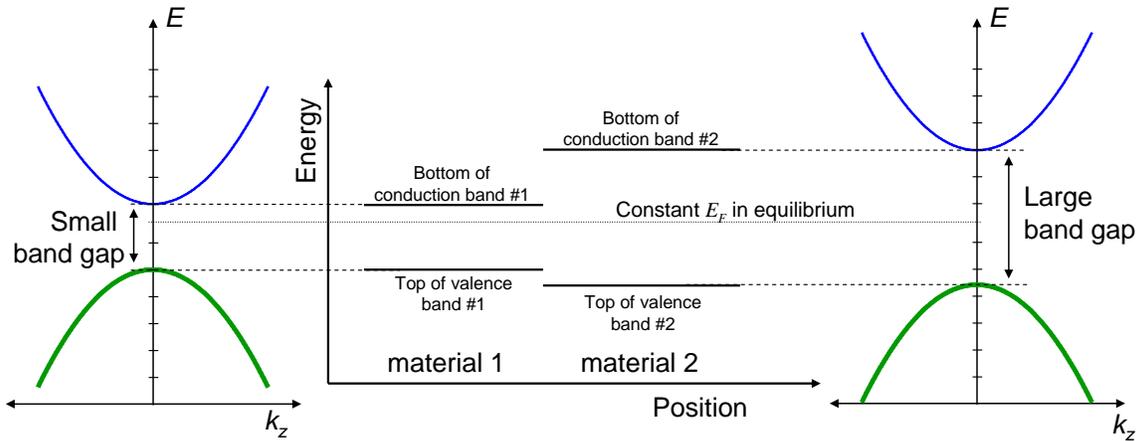


Fig. 6.38. An example of a band diagram. Here two insulators with different band gaps are connected. Note that the Fermi level must be constant in the two materials in equilibrium.

Semiconductors and Insulators

We have seen that insulators do not conduct because there are no uncompensated electrons. Considering both the conduction and valence band in the form shown in Fig. 6.38, it is evident that the material is an insulator when the Fermi energy lies in the bandgap. But if we introduce electrons to the conduction band, or remove electrons from the valence band, what was once an insulator can be transformed into a conductor. In fact if the Fermi energy is *close* to either band edge, then even a small movement in the Fermi energy can significantly modulate the conductivity. Such materials are known as *semiconductors* because it is easy to modulate them between the metallic and insulating regimes.

Sometimes, it can be difficult to distinguish between insulators and semiconductors. But insulators tend to have band gaps exceeding several electron-Volts and a Fermi energy close to the center of the band gap.

Introduction to Nanoelectronics

Problems

1. Consider the interaction of two carbon atoms each with one electron in a frontier $2p_z$ atomic orbital. Assuming the positions of the atoms are fixed, the Hamiltonian of the system consists of a kinetic energy operator, and two Coulombic potential terms: one for the central atom and one for its neighbor:

$$H = T + V_1 + V_2$$

Assume the wavefunction in this two atom system can be written as

$$\psi = c_1\phi_1 + c_2\phi_2$$

where ϕ_1 and ϕ_2 are the $2p_z$ atomic orbitals on the first and second carbon atoms, respectively, and c_1 and c_2 are constants.

The self energy is defined as

$$\alpha_r = \langle \phi_r | T + V_r | \phi_r \rangle$$

The hopping interactions are defined as

$$\beta_{sr} = \langle \phi_s | V_s | \phi_r \rangle$$

Earlier, we assumed that the *overlap integral* between frontier orbitals on atomic sites s and r could be approximated as

$$S_{sr} = \langle \phi_s | \phi_r \rangle = \delta_{sr}.$$

Do not make that assumption here and show that the electron energies of the system satisfy

$$\det(H - ES) = 0 \tag{6.99}$$

where H is a 2×2 Hamiltonian matrix and S is a 2×2 overlap matrix and E is a constant.

(a) Write each matrix in Eq. (6.99) in terms of the self energies, hopping integrals and overlap integrals.

(b) Under what conditions can you safely ignore the overlap integrals?

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2. (a) Consider the potential $V(x) = -V_0\delta(x)$, sketched below.

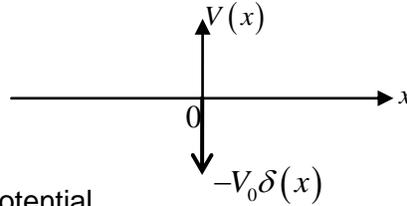


Fig. 6.39. A delta function potential.

(i) Show that the wavefunction is given by $\phi_1(x) = \sqrt{k}e^{-k|x|}$ where $k = \frac{mV_0}{\hbar^2}$

(ii) Show that the energy of the bound states ($E < 0$) is $E_1 = -\frac{mV_0^2}{2\hbar^2}$.

(b) Now add a second delta function potential at $x = a$.

i.e. if the previous Hamiltonian was $H_1 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - V_0\delta(x)$, the new Hamiltonian is

$H = H_1 + V$ where $V = -V_0\delta(x-a)$

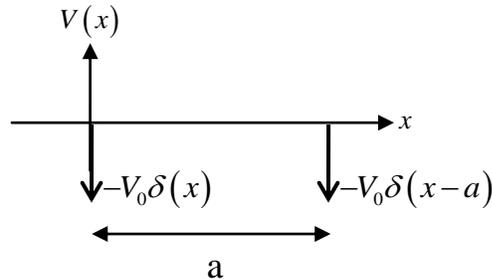


Fig. 6.40. Two delta function potentials.

Let the wavefunction of the new system be approximated by $\psi = c_1\phi_1 + c_2\phi_2$ where $\phi_2 = \phi_1(x-a)$ and c_1 and c_2 are constants.

The self energy is $\alpha = \langle \phi_1 | H_1 | \phi_1 \rangle$

The hopping interaction is $\beta = \langle \phi_2 | V | \phi_1 \rangle$

In addition, define the overlap integral $S = \langle \phi_1 | \phi_2 \rangle$, and $\gamma = \langle \phi_1 | V | \phi_1 \rangle$

By evaluating the expressions

$$\langle \phi_1 | H | \psi \rangle = E \langle \phi_1 | \psi \rangle$$

and

$$\langle \phi_2 | H | \psi \rangle = E \langle \phi_2 | \psi \rangle$$

show that

$$\begin{pmatrix} \alpha + \gamma & \alpha S + \beta \\ \alpha S + \beta & \alpha + \gamma \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Now show that $\alpha = \frac{-mV_0^2}{2\hbar^2}$, $\beta = \frac{-mV_0^2}{\hbar^2} e^{-ka}$, $S = (1+ka)e^{-ka}$, and $\gamma = \frac{-mV_0^2}{\hbar^2} e^{-2ka}$

Dropping terms containing e^{-2ka} , show that the matrix reduces to $E \approx \alpha \pm \beta$

3. For molecules where each carbon atom contributes at least one delocalized electron to a π orbital, we can use the perimeter free electron orbital theory approximation, which is described below.

Assume that the molecule in question is a circular ring of atoms and assume an infinite square well potential.

(a) Show that the energy levels of a molecule under this approximation are

$$E = \frac{\hbar^2 m_l^2}{2m_e L^2},$$

where where m_l is an integer, and L is the perimeter of the molecule.

Hint: The Hamiltonian in polar coordinates is given by:

$$\hat{H} = \frac{\hbar^2}{2m_e} \left(\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} + \frac{1}{r^2} \frac{d^2}{d\phi^2} \right)$$

(b) According to the perimeter free electron orbital theory approximation, the energy level structure of anthracene is shown in Fig. 6.41, below.

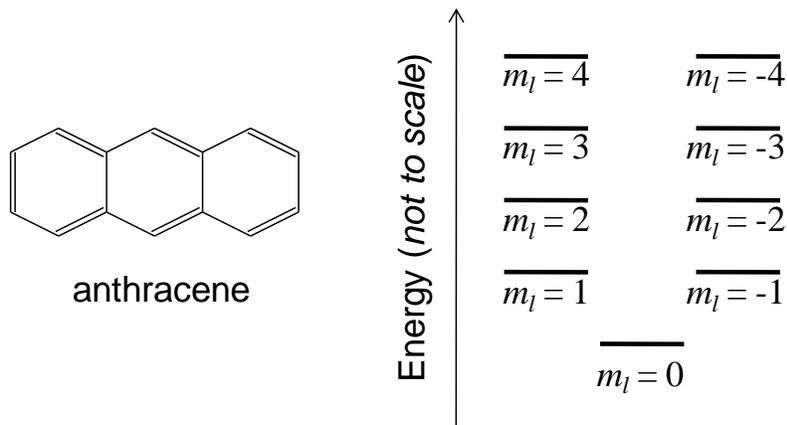


Fig. 6.41. The molecular and energetic structure of anthracene.

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Continued on next page....

(i) Why is there a solution for $m_l = 0$ in anthracene but no solution for $n = 0$ in the infinite quantum well?

(ii) Why are there solutions for negative m_l in anthracene but no solutions for negative n in the infinite quantum well? *Hint:* consider the Pauli exclusion principle.

(c) Calculate the molecular orbitals and HOMO-LUMO gap of anthracene. Take $a = 1.38\text{\AA}$ as the C-C bond length. Assume each C atom donates 1 electron to the frontier orbitals.

4. Consider the periodic molecule consisting of two different alternating atom types illustrated below (frontier orbitals are shown).

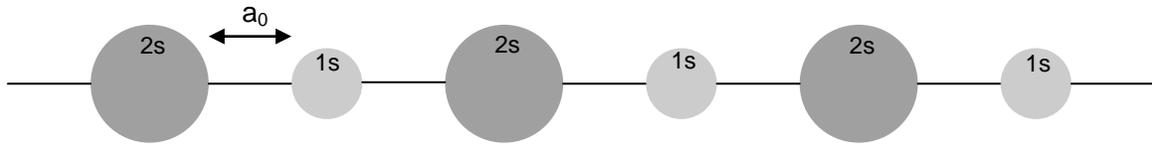


Fig. 6.42. A periodic array of two different atoms.

(a) How many atoms are in the unit cell in this molecule? Using periodic boundary conditions and assuming molecular wavefunctions of the Bloch form, find the energy levels.

(b) Find the density of states.

5. The band structure of molecular crystals

Let $\phi(\mathbf{r})$ be the HOMO of a typical molecule. As in most stable molecules, $\phi(\mathbf{r})$ is fully occupied and contains two electrons.

Unlike conventional crystalline semiconductors such as Si, the unit cells in a molecular crystal are held together by weak van der Waals forces. A typical value for the interaction between nearest neighbors in a van der Waals bonded solid is

$$\beta = \langle \phi(\mathbf{r} + \mathbf{R}) | H | \phi(\mathbf{r}) \rangle \approx -10 \text{ meV}$$

where H is the Hamiltonian for the interaction between nearest neighbors and \mathbf{R} is the set of lattice vectors connecting the molecule at \mathbf{r} to its nearest neighbors.

(a) Calculate the 'valence' band structure of a cubic molecular crystal of this molecule. Let $\langle \phi(\mathbf{r}) | H | \phi(\mathbf{r}) \rangle = \alpha$. (See Fig. 6.43 below).

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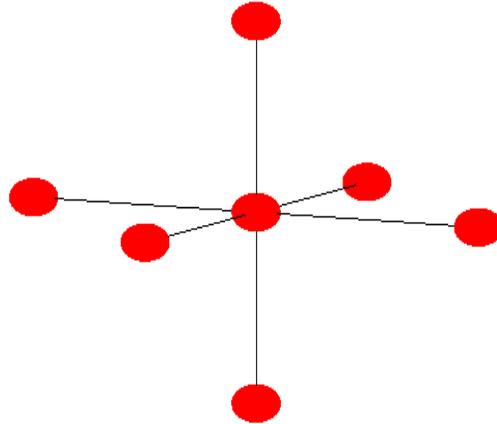


Fig. 6.43. The structure of a simple cubic molecular crystal

(b) Show that all molecular crystals with filled HOMOs are insulators.

6. Consider the following polymer:

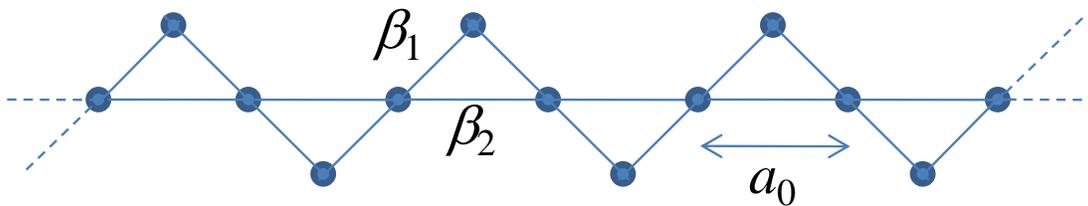


Fig. 6.44. A polymer.

Assume the spacing between atoms on the linear backbone is a_0 , as shown. Also, assume all atoms are the same element, β_1 and β_2 are the hopping interactions between atoms as shown, the self energy at each atom is α , and assume each atom contributes one electron.

(a) What is the primitive unit cell and primitive lattice vector?

(b) Show that the dispersion relation is given by

$$E = \alpha + \beta_2 \cos(ka_0) \pm \sqrt{\beta_2^2 \cos^2(ka_0) + 2\beta_1^2 (1 + \cos(ka_0))}.$$

(c) Is the polymer metallic or insulating?

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7. Graphene and carbon nanotube transistors

(a) With reference to the bandstructure of graphene shown below, explain why graphene when rolled up into nanotubes can be either metallic or semiconducting?

(b) Using the k -space plot shown below, determine whether the following (n,m) nanotubes are metallic or semiconducting. Recall that nanotubes are rolled-up graphene sheets with wrapping vector $\vec{w} = na_1 + ma_2 = (n,m)$.

i) (0,6)

ii) (N,N)

iii) (3,9)

iv) (3,5)

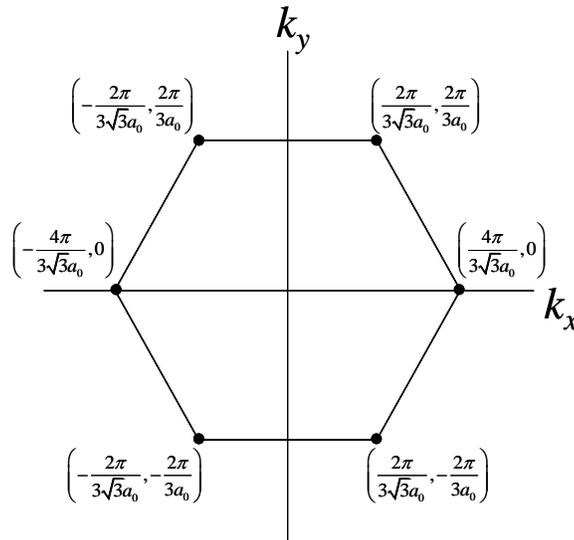


Fig. 6.45. The K points in graphene.

(c) At present, there is much interest in using graphene (as opposed to carbon nanotubes) as the channel material for field effect transistors. The idea is to fabricate entire chips on a single sheet of graphene.

First the graphene is deposited somehow (this is a technological challenge at present).

Next, the graphene is cut up.

Finally, contacts and gate insulators are deposited.

Why is the graphene cut up? Explain with reference to particle in a box models of conductors.

8. Carbon Nanotubes

(a) Prove the identities in Eq. (6.87) and Eq. (6.88).

(b) Derive Eq. (6.90) from Eq. (6.89).

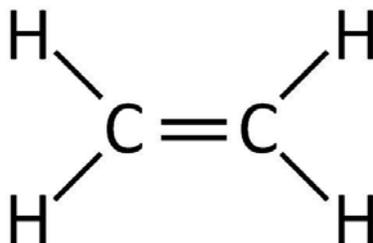
9. This question relates to the molecule shown below.



a) Write the Hamiltonian matrix for this molecule in terms of the tight binding parameters α , and β .

b) Write the energy for this molecular orbital in terms of α and β .

c) Compare the density of states of the HOMO and LUMO of the previous molecule to the one below.



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