Scribed lecture notes
15-849C lecture 1/28/2002
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<u>Background for Molecular Rectifiers paper</u>

<u>Intro:</u>
This lecture is background for A. Aviram and M. A. Ratner, "Molecular Rectifiers", *Chem. Phys. Lett.* **29**, 277 (1974). The paper is the first to propose that individual molecules could be used as elements in circuits.

<u>Slide 1: Quantum Mechanics</u>
Schrodinger's equation is the fundamental equation of quantum mechanics:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

It is needed to describe the motion of light particles, such as electrons. The vibrational and rotational motion of molecules must be treated with quantum mechanics, while the translational motion may typically be treated with classical mechanics. The wave nature of the Schrodinger equation leads to particles with wave-like properties. The solutions of the above equation are standing-waves. For electrons, these standing waves are call orbitals. The Schrodinger equation also allows particles to "tunnel" through barriers that, in classical mechanics, would be too high in energy to allow a particle to pass through.
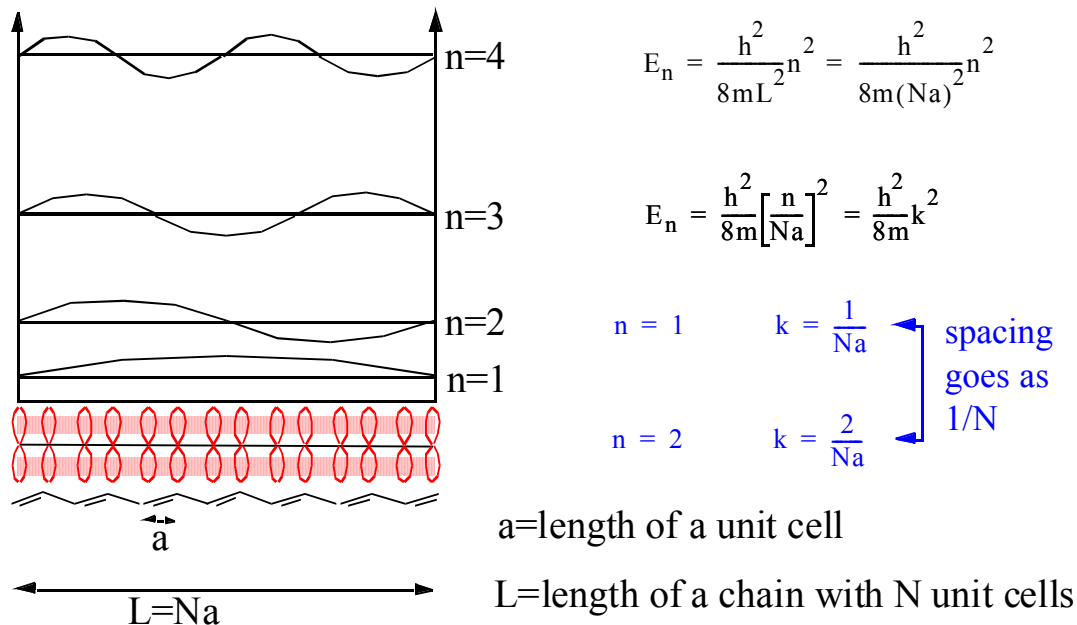
<u>Slide 2: The particle in a box</u>
The particle-in-a-box model illustrates many consequences of quantum mechanics. In this model, a single particle is constrained to move in one dimension in a potential well as shown in the figure below. The potential energy is zero inside the box (0<x<L) and is infinitely large outside the box (x<0 or x>L).

The particle in a box
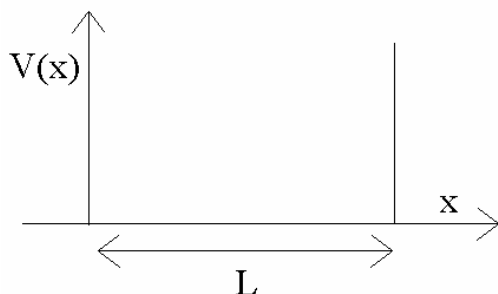
The standing-wave solutions, or "wavefunctions", of Schrodinger's wave equation for this system are quantized by the boundary conditions imposed by the box. The quantization is precisely analogous to the quantization of macroscopic bound standing waves, such as the standing waves in a

plucked guitar string. A guitar string strung across a length L can have standing waves with wavelength L/2, L, 1.5L... {(n/2)*L | n=1,2,3...}. These are also the wavelengths allowed for a quantum-mechanical particle in an infinite box of length L. One particle in a box of length L can exist in any of the states shown in the diagram: the n=1 state, the n=2 state, and so on. The number n is called a quantum number, since it labels the quantum mechanical state of the particle. The particle's energy, momentum, and probable positions are all functions of its state, n.

$$E_n = \frac{h^2}{8mL^2}n^2 = \frac{h^2}{8m(Na)^2}n^2$$

$$E_n = \frac{h^2}{8m}\left[\frac{n}{Na}\right]^2 = \frac{h^2}{8m}k^2$$

$n = 1 \qquad k = \frac{1}{Na}$

$n = 2 \qquad k = \frac{2}{Na}$

spacing goes as 1/N

a=length of a unit cell

L=length of a chain with N unit cells

The *square* of the wavefunction gives the probability of finding the particle at the point x. For example, if a particle-in-a-box is in the n=1 state, and you measure its position, you will never find it at the node in the middle of the box (a node is where the wavefunction passes through 0).

Energy:
        In quantum mechanics, the energy of a particle is inversely proportional to its wavelength.[1] Thus, a particle-in-a-box can only have a discrete set of allowed energies, corresponding to the wavelengths allowed inside the box and proportional to 1/n. This can be seen in the figure above: the four wave functions are spaced along the vertical access according to their energies.
        Energy quantization is general in quantum mechanics: *bound particles have discrete allowed energies.* In addition, it can be shown quite generally that the energy always increases monotonically with the number of nodes.

Intro to basis functions:
        The solutions of Schrodinger's equation can be expressed as a superposition of a set of standard, "basis" functions. The use of basis sets simplifies the solution of the Schrodinger equation, by converting it to a linear algebra problem, the solution of which gives the amplitudes of the various basis functions. Basis functions can be plane waves, Gaussians, or any set of convenient functions. Chemists often express molecular wave functions as a superposition of exact solutions of the one-electron atom. (Discussed at length below, slide 5.) This is what's going on with the string of little blobs at the bottom of the figure. These represent the atomic basis functions of a 14-atom molecule of

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[1] For a non-constant potential, V(x), the wavelength changes with x and so is not unique. However, the local wavelength, or curvature, of the wavefunction at the point x is directly proportional to the particle's kinetic energy.

length L. An electron constrained to move along the backbone of this molecule, and through this line of basis functions, will behave as if it were in a one-dimensional box.

Useful applications of the energy level concept include band theory and molecular orbital ("MO") theory. Band theory describes bulk-scale metals and semiconductors as "bands" of closely-spaced energy levels (see next slide). Molecular orbital theory describes individual molecules in terms of conjugated particles using wave functions obtained from simple one-body calculations.

Tunneling in the particle in a box:

Another useful point to be made from the particle-in-a-box model is the case of a finite potential barrier in the middle of the box:
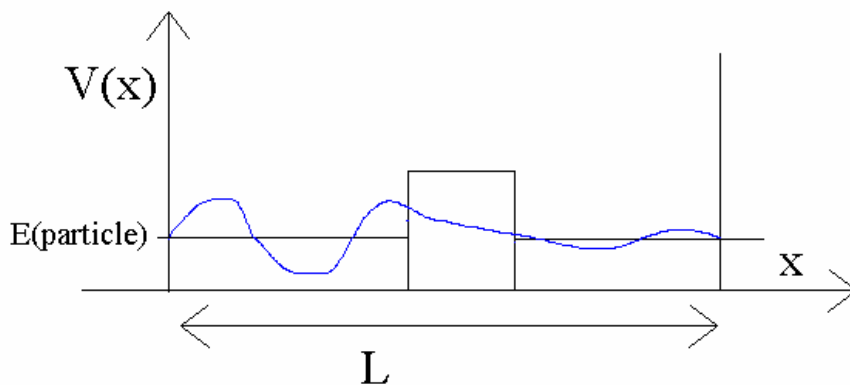
Suppose the particle starts on the left, and does not have enough energy to go over the barrier. If one solves the Schrodinger's equation for this system, the resulting wave functions have some amplitude inside the barrier, and some amplitude (wiggliness) on the right side of the box. This means that the particle has some chance of going from the left side of the box to the right side of the box, *even though it doesn't have enough energy to go over the barrier in the middle.* (The blue line is a qualitative representation of the wave function of a particle of energy E in the left of the box.) This phenomenon is called "tunneling" through a potential barrier, and is discussed in slide 16 of this lecture:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}y(x) + V(x)y(x) = Ey(x)$$

$$\frac{d^2}{dx^2}y(x) = \frac{2m}{\hbar^2}\left(V(x) - E\right)y(x)$$

$$E > V(x) \quad \frac{d^2}{dx^2}y(x) = (\text{negative}\#)y(x) \quad \text{Þ} \quad y(x) = e^{icx}$$

$$E < V(x) \quad \frac{d^2}{dx^2}y(x) = (\text{positive}\#)y(x) \quad \text{Þ} \quad y(x) = e^{-cx}$$

The first 2 equations above (from slide 16) are 2 versions of Schrodinger's equation. The 3rd is the solution (wavefunction) in regions where the total energy is greater than the potential energy (classically allowed regions, left and right of the potential box shown above.) Solutions to Schrodinger's equations in these regions have exp(i x) dependence, and therefore are oscillating functions (as shown by the wave functions in the left and right parts of the box above).

The 4th equation is the solution of Schrodinger's equation in the middle of the box (classically forbidden region) where the total energy is less than the potential energy. Here, the wavefunction follows an exponential decay, with the decay rate being faster for higher barriers.

One important fact: The figure above shows the electron as having the same energy in the left and right halves of the box. If this is not an allowed state, the electron can tunnel into a state at the right with lower energy than it had on the left, but it must give the excess energy to the surroundings as heat. . The probability of tunneling between the two states is largest when the energies are equal, and becomes less likely as the energy mismatch increases.

Take home message:

Electrons can go through a potential barrier.
Tunneling probability is highest between two states of the same energy.

Slide 3: Band theory
The formulas on the previous slide show that the spacing between the energy levels of a particle-in-a-box decreases as the box length L increases. In the limit of a macroscopic "box" the energy levels are close enough together to form a continuum. The energy-versus-wavenumber relation for a continuum is shown below:

$$E = \left[\frac{h^2}{8m}\right]k^2$$
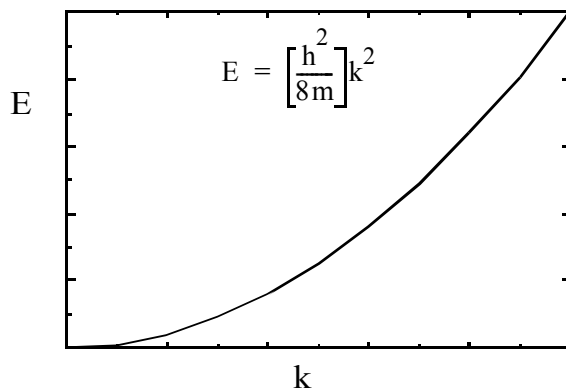
The wavenumber k corresponds to $\pi n/L$, where n is the quantum number (#of nodes-1) of the current wave function and L is the length of the box.

A box made from a chain of N elements (like the chain of 14 elements in the figure on the previous slide, or the chain of 7 elements shown below) has at most N different wave functions:

$$E = 2\beta\cos(k)$$
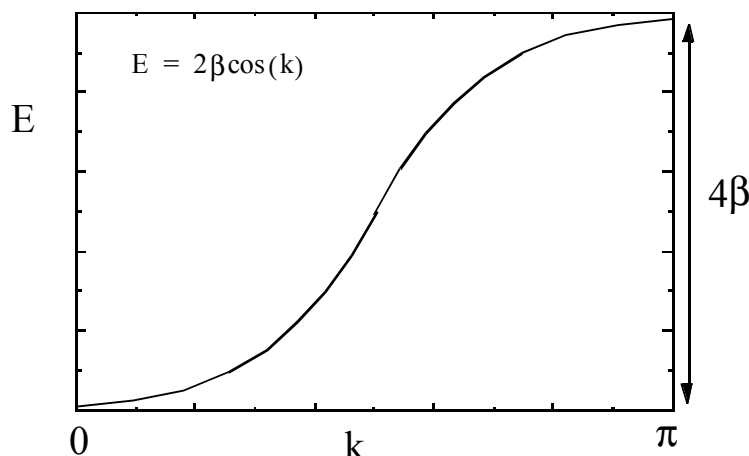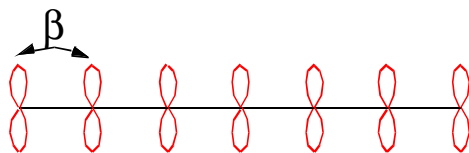
In this case, the variable k in the energy formula corresponds to $\pi n/(N*a)$, where n is the quantum number of the current wave function, N is the number of elements in the chain, and a is the length of the chain. Normalization factors ensure that k for a site model varies

between 0 and pi, as shown. (Question: Are there more states available at higher energies, or at lower energies?)
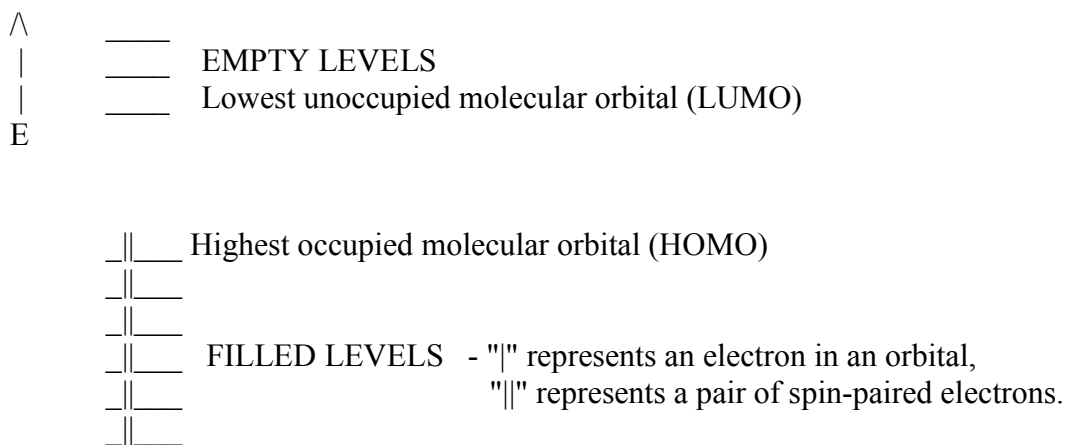
Hopping:

The beta between the elements of the chain on the figure to the right is an off-diagonal Hamiltonian matrix element between the adjacent orbitals. Beta gives the amount of coupling between the orbitals, and is related to the strength of the bond between them. This will be covered in more detail later.

Electron momentum:

In both cases, the quantum number k is a measure of the momentum of an electron in that wave function. Energy levels with higher index (# of nodes +1) n have higher energies. Thus, particles in energy levels with higher k have larger total energies and larger momentum. ("Particle momentum" is most useful for a quantum mechanical particle in a continuum.)

Energy level diagrams:

Band theory allows us to think of all of the electrons in a chunk of metal or semiconductor as existing inside of a very large, 3-D version of the one-dimensional box described above. The energy levels of this large box are closely spaced, as described above. We can describe the electron configuration of the metal or semiconductor by assigning all the electrons to the calculated wave functions of the system, starting with the lowest-energy wave functions and working up. A fundamental symmetry-based result of multi-particle quantum mechanics says that no two particles can exist in the same state at the same time. Electron spin means that we can put two electrons in each of our energy levels. Thus, the lowest-energy ("ground-state") electronic configuration of a metal or semiconductor in the large-box model described is as shown:

```
/\        ____
|         ____     EMPTY LEVELS
|         ____     Lowest unoccupied molecular orbital (LUMO)
E


          _||___  Highest occupied molecular orbital (HOMO)
          _||___
          _||___
          _||___   FILLED LEVELS   - "|" represents an electron in an orbital,
          _||___                     "||" represents a pair of spin-paired electrons.
          _||___
```

This energy-level diagram is how chemists think of metals or semiconductors. The energy difference between the HOMO and the LUMO represents how easily an electron may be excited from the filled band to the empty band. We will see that charge is transported through materials by excited carriers, so the HOMO-LUMO gap has a lot to do with whether a given material can conduct electricity.

The main point is that the quantized energies seen in small systems map to an energy continuum in the limit of large systems.

Slide 4: Orbitals
As mentioned before, the mathematics of wave mechanics allows you to express the wave functions of a system as a superposition (adding and subtracting) of simple functions. Chemists typically express electronic wave functions as a superposition of the functions shown below:
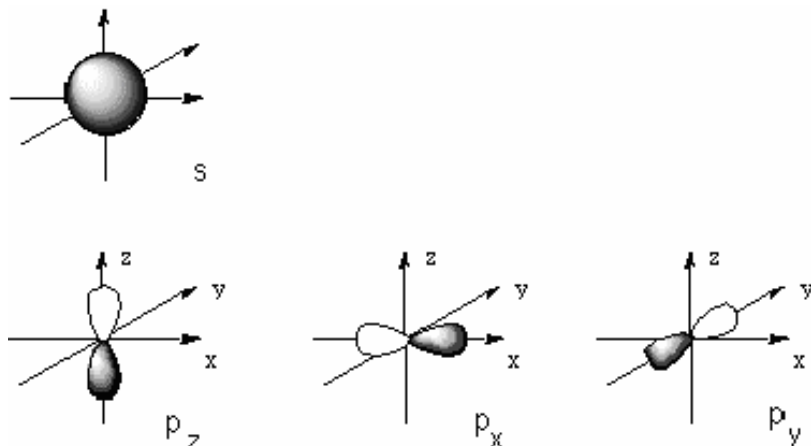
These functions are the solutions to Schrodinger's equation for a one-electron atom. (They are also the standard shapes of waves in a spherical piece of rubber: hitting a sheet of rubber will produce standing waves that are 2-D analogues of the atomic orbitals.)

Describing systems with orbitals:

The figure below shows the orbital description of the chemical bond:
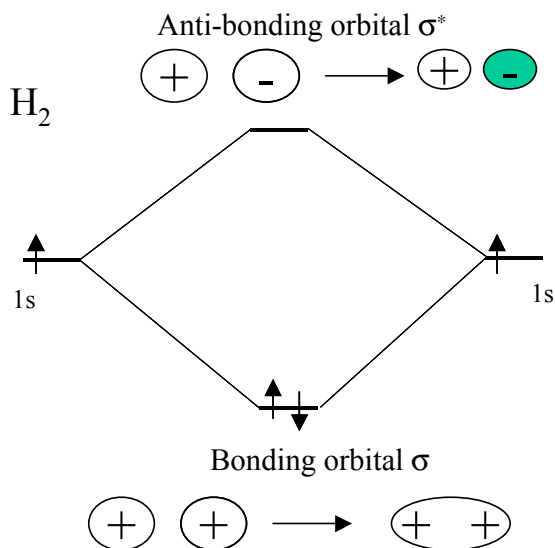
The energy levels at the left and right represent a pair of atomic orbitals, each on a different atom. If the two atoms are close together, adding and subtracting the atomic orbitals creates two new functions, the two center "molecular orbitals" at the top and bottom of the figure. The lower bonding (+ +)

molecular orbital is lower-energy than the two atomic orbitals. The higher, anti-bonding orbital is made by subtracting the two atomic orbitals. It contains a node between the nucleii and is higher-energy than the nonbonding orbitals. A chemical bond between the two atoms is described by having two electrons in the bonding orbital and zero in the antibonding orbital.

Energy ordering:

        Electrons like to be around nucleii, due to electrostatic interactions. Electrons in antibonding orbitals spend less time beside the nucleii, and very little time in the region of the node between the two nucleii. This gives them less electrostatic stabilization and higher energy.

        The picture above shows the case of two hydrogen atoms, each with a single electron whose wave function is described by an s (spherically-symmetric) orbital centered on the hydrogen nucleus. If we bring these two hydrogen atoms next to each other, we can add and subtract our atomic orbitals to generate bonding and antibonding molecular orbitals. If we assign two electrons to the bonding orbital and zero to the antibonding, the system's overall energy is lower (as electrons in the bonding orbital are lower-energy than electrons in the atomic orbitals.)

        We can also understand the case of two adjacent helium atoms, each with two electrons. Since there are four total electrons, we need to assign two electrons to a bonding orbital and two to an antibonding orbital. The total electronic energy is the same as in the unhybridized case. (In the real world, hydrogen atoms form hydrogen molecules containing two atoms. Helium atoms do not.)

Chemists use Lewis structures as a simple short-hand notation for the quantum-mechanical rules of chemical bonding. They operate based on the "octet rule": heavy atoms (not H or He) are most stable when they have 8 electrons around their outside.

For the light atoms, the octet rule is replaced by the pair rule: H and He prefer to have either zero or two electrons around them. This is another way of saying that hydrogen is most stable as H-H, and that helium is most stable in atomic (unbound) form. (If you understand the bonding example in the last slide, you have a pretty good idea of why the octet rule works.)

The periodic table (look at one) is organized based on the number of valence electrons that the different species have. All species in the same column have the same number of valence electrons. {For example, H, Li, Na, K, Rb, Sr all have a single valence electron, which means that they all behave kind of like hydrogen.} H and He can have up to 2 valence electrons, and all other elements can have up to eight. A chemical bond involves a sharing of electrons between two species (see previous H-H example).

For example, a carbon atom has six total electrons. Two of them are paired in a 1S orbital. These "core" electrons behave just like two electrons in helium, and are never involved in bonding. ("chemically inert"). The other four are valence electrons. Carbon needs 4 more electrons to obtain an octet. So, if you react carbon atoms and hydrogen atoms, what compound will you get?

Answer: Four hydrogen atoms contribute their valence electrons to each carbon atom, giving each hydrogen 2 shared electrons and each carbon 8 shared electrons:

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   H                    H
   ..                   |
 H : C : H    or      H - C - H
   ..                   |
   H                    H
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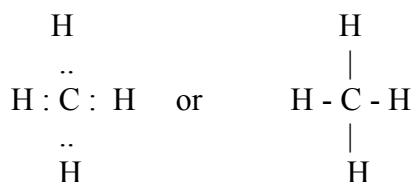
"Organic" chemistry is the chemistry of carbon compounds. Most of the molecules that we look at in this course will only contain carbon, hydrogen, oxygen, nitrogen, fluorine and sulfur.

The quantum mechanical description of electrons as waves implies a substantial amount of non-locality. Despite this, electrons in bonds are generally quite localized. Sigma bonds between atoms have most of the wavefunction amplitude between the atom centers, and are defined as being symmetric about the axis between the bound atoms. The H-H bonding orbital shown above is a sigma bonding orbital. Sigma bonds are NOT good at conducting. Conduction requires the transfer of electrons through a medium, and electrons in sigma bonds are too localized to be transferred very easily.

Another way to think about sigma-bond conduction is with a scattering model. The straightest path between two sigma bonds in a chain goes through an atomic nucleus. Moving electrons along a chain of sigma bonds implies scattering off of several atomic nucleii, which is not a good situation for conduction.

All conductive organic molecules conduct electrons through pi bonds. A pi-bond is a second bond between two atoms that are already bound (if you draw the Lewis structure for C2H4, you'll see that the only way to satisfy the octet rule on all atoms is to put two bonds between the carbons). Pi bonds are made by addition of adjacent p-orbitals (see orbital pictures above). They always have a

node along the axis between the bound atoms. Most of the electron density in a pi bond is above and below the plane of the connected atoms:

p-orbitals

$$\pi^*$$

$$E$$

$$\pi$$
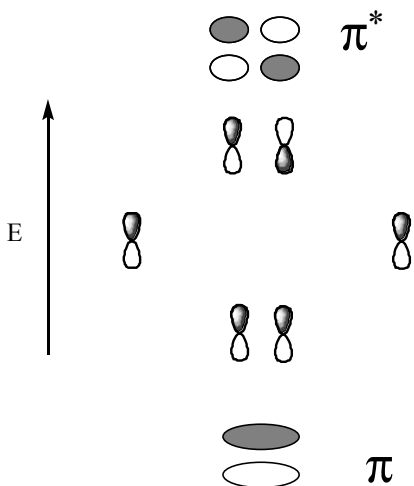
   Pi-bonds are formed from adding p-orbitals on adjacent atoms that are perpendicular to the bond axis (right figure). The bonding orbital (lower energy) has a node along the bond axis (pi orbital). It is formed when the phases of the two p-orbitals match. The antibonding (pi-star) orbital has a node along the axis and a node in the middle of the bond axis, between the two bound atoms.
   Note: The beta shown between p-orbitals in slide 4 is the splitting between the energy of their bonding-hybrid pi orbital and their antibonding-hybrid pi-star orbital.

Using a scattering model, it's easy to see why pi bonds are good conductors. The path between one pi-orbital and an adjacent pi-orbital is above and below the plane of the atomic nucleii. Electrons can move along the path of maximum electron density without being scattered off of the nucleii.

Distance effects:
   Two atoms that are linked by a sigma-bond and a pi-bond are more strongly bound to each other than if they were just sigma-bonded. This extra bonding brings them closer together. A C=C bond has a smaller distance between the carbon atoms than a C-C bond.

Question during class: "What about orbital hybridization"?
   A carbon atom in the gas phase has two electrons in a core s orbital, two electrons in a valence s orbital, and one electron in two of the three valence p-orbitals. However, a molecule of methane (CH4, see above Lewis structure) has tetrahedral symmetry. Neither s-orbitals nor p-orbitals have tetrahedral symmetry, so we describe the orbitals of methane carbon as a linear combination of the valence s and p orbitals. The 4 resulting "hybrid atomic orbitals" are similar to the molecular orbitals we made in H-H, but are all centered on the carbon. The orbitals have tetrahedral symmetry, and one points at each hydrogen nucleus in the methane.

Skip to...

Chemists use the octet rule to simplify drawings of molecular structures. For example, we know that every carbon atom in a structure must have 4 bonds to it, in order to obtain the 4 extra electrons it needs to get an octet. Thus, we can use

     C-C

as a shorthand for C3H6, as we know that each carbon needs to be bound to 3 other things.

The convention that unlabelled vertices are carbons means that, for example, the 3-edge 4-vertex graph:

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   =
     \
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stands for C4H8:

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   H        H  H
   |        |  |
H-C - C = C - C  - H
   |   |        |
   H   H        H
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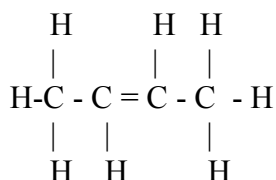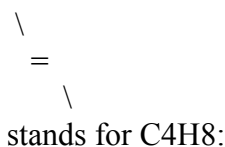
The discussion of the particle-in-a-box included a picture of a line with little blobs on it. Now we can say that that line represents: "a series of sigma-bound carbons, with alternating single-double-single bond character", and that the little blobs are "the unhybridized p orbitals on the carbons that participate in the double bonding". In other words, a system with alternating single-double bonds can have its double bonds ("pi-bond system") treated as a set of sites that the pi electrons can inhabit:
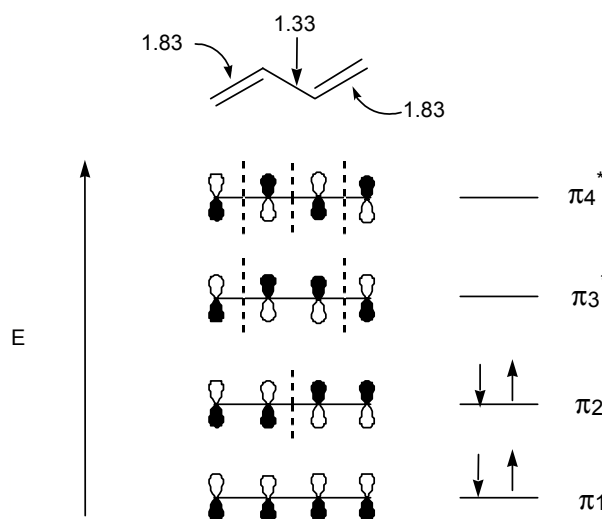
The upper figure is a line drawing of the 4-carbon molecule butadiene. It contains two double bonds, and therefore has 4 electrons in its pi system. The bonds are labeled with their experimentally-determined bond order (a pure single bond has order 1.0, a pure double bond has order 2.0). The experimentally-observed bond order of 1.3 between the central carbons implies that there is some double-bond character between them.

The lower figure shows the wavefunctions of a 4-pi-orbital system (butadiene) treated by the particles-in-a-box model. The orbital diagrams on the left show the four possible wave functions. We use the convention that two adjacent p-orbitals are overlapping (bonding) if they have the same color at top and bottom, and that they have a node

between them (antibonding) if their colors alternate (see previous slide). The ground-state electron configuration is shown at the right of the figure: the n=1 and n=2 wave functions (zero nodes and one node, respectively, also referred to as the "pi" wave functions) are each doubly occupied, and the higher-energy n=3, n=4("pi-star") wave functions are unoccupied.

Note that one occupied orbital has a node between the central carbon, but that the other one does not. This implies that there is some double-bond character between the central carbons, which explains the bond orders shown above.

An extended pi system can be thought of as a "channel" for electrical conduction: the electrons can move above and below the chain of nucleii through the pi-system. The long-chain limit of an extended pi system is discussed below.

Slide 8: Conjugated Polymers
This is an extended pi system that is so long, we start being able to treat it with band theory (precisely like we treated a very long particle-in-a-box). In the long-chain limit, the conjugated polymer starts behaving as a semiconductor. The lower energy band is all of the pi orbitals, the higher-energy band is the pi-star orbitals. The widths of the bands depend on the size of the beta terms between adjacent p orbitals: beta-2 is coupling between the pi-system p orbitals of double-bound carbons, beta-1 is the coupling between the pi-system p orbitals of single-bound carbons. The alternation between double and single bonds in conjugated polymers leads to a band (HOMO-LUMO) gap. Other factors also contribute to the band gap. Conjugated polymers typically have gaps between about 1.8 and 3eV, although various groups are working on pushing the gap to larger or smaller values.

Slide 9: Benzene
To understand Ratner's paper, one needs to be aware that cyclic, planar C6H6 ("benzene") has a pi-system that behaves like those discussed above. A molecule of benzene has six p-orbitals and six electrons in its pi-system. The figure below shows cartoons of the six different molecular orbitals that can be made from the benzene pi-system orbitals:
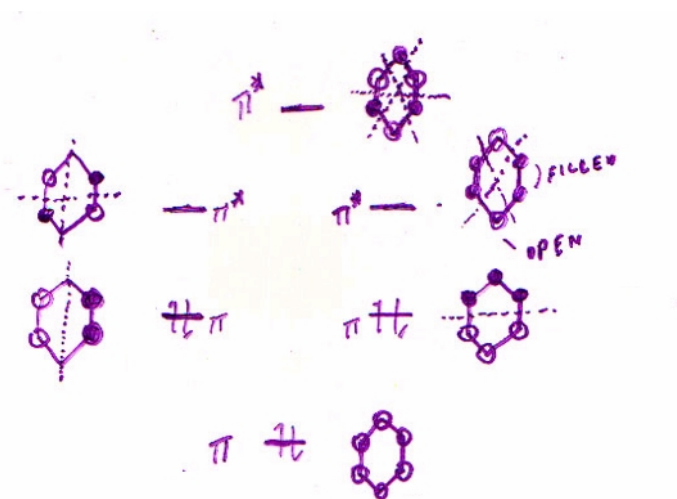
The lowest-energy orbital at the bottom of the figure has no nodes. There are two orbitals that contain only one node: these are identical in energy and are higher energy (more nodes=higher energy) than the first orbital. Going up, the highest-energy orbital has three nodes. While it is not shown on the

figure, the six unhybridized pi-system orbitals all have energies midway between the one-node and two-node orbitals. The ground state of benzene has the three lowest-energy orbitals doubly occupied.

Below is an orbital-surface picture of the lowest-energy pi orbital of benzene. The C6H6 sigma system is drawn as a cartoon in gray (see lower picture). The red and blue blobs are the positive and negative phase lobes of the pi orbital. This picture emphasizes the idea that benzene is a planar ring with big blobs of electrons stuck to the ring faces.
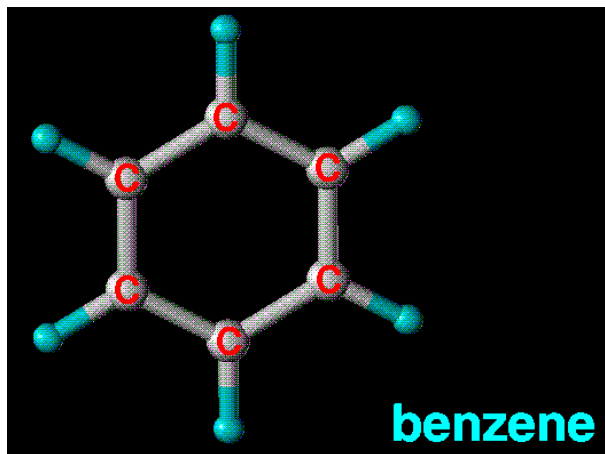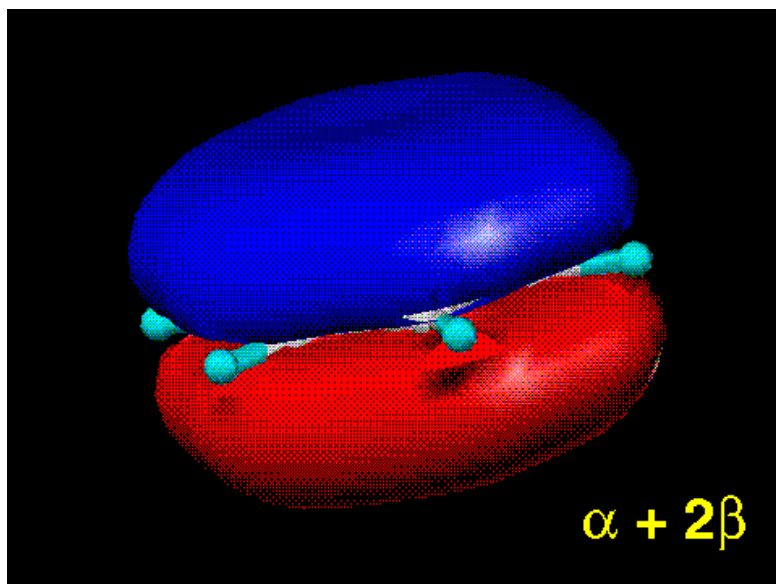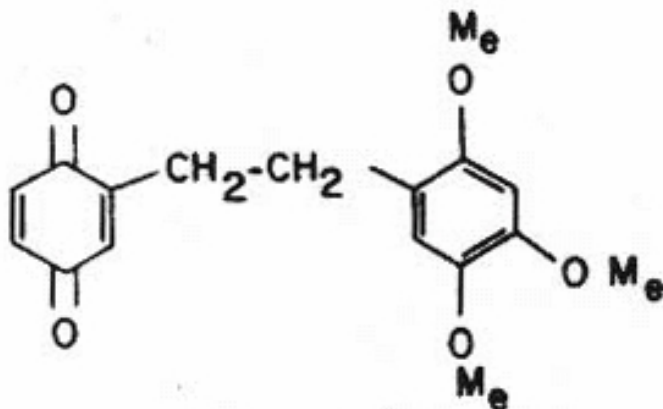
Fig. 1. An example of a hemiquinone.

The main molecule dealt with in the Ratner paper. (Slide 11 has a picture of a different proposed rectifier molecule.) The group on the left of the molecule is an electron-poor benzene derivative. It has more electron density than usual in the benzene ring, due to electron donation by the O= groups. (Electron donation and electronegativity are discussed below.) The group on the right is an electron-rich benzene derivative. The sigma-bonded segment in the middle has no pi-system, and effectively insulates the left and right groups from one another.

One good way to think about this molecule is to just consider the pi-systems of the left and right benzene derivatives. From this perspective, the molecule is two clumps of pi electrons, separated from each other by some space in the middle. The authors argue in the paper that the timescale of electronic motion through a sigma system is so slow relative to a pi-system that the sigma-system may be thought of as an insulator. (Recall the scattering theory explanation of sigma vs. pi conduction given above.)

In a device, the electron-rich group on the left will act to accept electrons from an electrode, and the right group will donate to an electrode. The molecule will be able to pass electric current from left to right, but not from right to left.

        Chemical substituents bound to a benzene ring can add electrons to, or take electrons from, the benzene pi-system. An atom's tendency to pull excess electrons onto itself is referred to as "electronegativity". One example of electronegativity in action is the compound hydrofluoric acid (HF). Hydrogen has a low electronegativity (2.1), and fluorine has a very, very high electronegativity (4.0). This means that fluorine will attract the electrons in the H-F sigma bond more strongly than hydrogen. The result is a polarization (permanent dipole moment) along the bond axis:
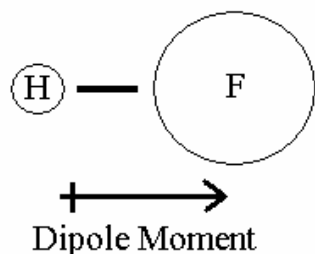
Oxygen, nitrogen, and fluorine are all more electronegative than carbon. Therefore, oxygen-substituted benzene rings tend to have less electron density in the ring than regular benzenes.
        Note that the -O-Me (-O-CH3) substituent is actually electron-donating.

Slide 14: Energy Level Diagrams
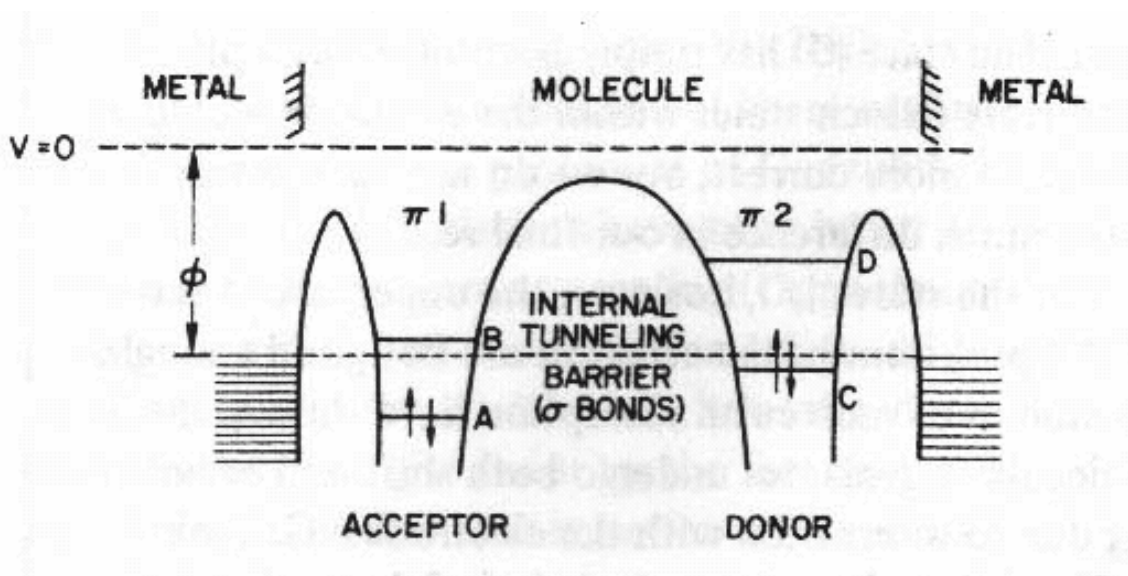
        This diagram is the heart of the paper, and pulls together all the topics discussed in the lecture. Briefly, the diagram represents a rectifier molecule (as in slide 10 or slide 11) strung between two metal electrodes. The horizontal axis is position, the vertical axis is energy. The manifolds of states at the left and right are continuum-pictures of the energy levels in the source and drain electrodes, respectively. Phi represents the energy difference between the HOMO of the metal electrodes and a free electron.
        Moving left-to-right, the left electrode is separated from the recitfier's acceptor pi-system by a potential barrier that represents the metal-organic junction. The electron-poor acceptor pi system has a very low HOMO and a low LUMO (high electron affinity) just above the HOMO of the electrode

Next is another potential barrier, which represents the sigma-bonded "bridge" between the rectifier's acceptor and donor pi systems. In the hemiquinone in slide 10, this potential barrier is caused by the sigma-bonded segment (-CH2-CH2-) between the pi systems.

Next is the electron-rich donor pi system. The electron-donating groups attached to the benzene make it an inhospitable environment for more electrons to go to, as shown by the high HOMO and very high LUMO. The donor is separated from the drain electrode by another small potential barrier from the metal-organic junction.

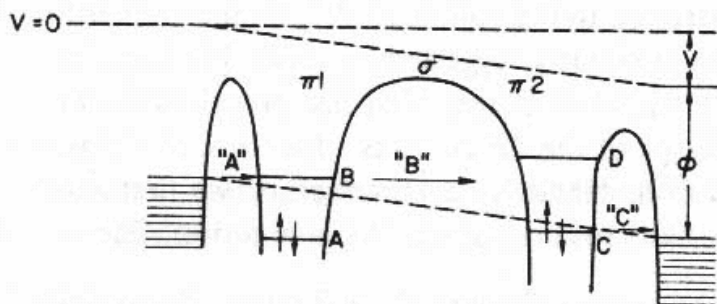Slide 15: Mechanism for Rectification

Fig. 4. Energy levels shift with applied voltage. "A", "B", and "C" are three tunneling processes.

Energy level diagram of a rectifier molecule under the influence of a small left-to-right potential difference. The potential brings the source (left) electrode's HOMO up to the level of the acceptor LUMO, allowing electrons to tunnel into the LUMO. The molecule will conduct electrons from left to right. The most important step is the transfer of injected electrons from the acceptor LUMO to the newly-emptied donor HOMO. These electrons must tunnel through the potential barrier in the middle of the rectifier molecule. Once they do so, they are in a donor energy above that of the donor HOMO, and the excess energy is lost as molecular vibrations (heat). Electrons therefore flow easily in this direction.
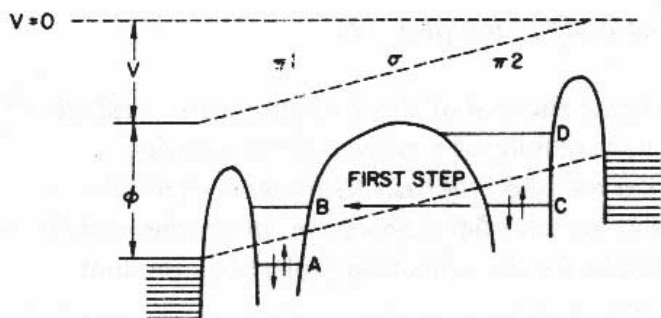

Fig. 6. Reverse applied voltage.

Under a reverse applied voltage, it takes a much larger potential to align the electron energy levels with D. The flow of current in this direction takes much larger applied voltage, and so the molecule acts as a rectifier.
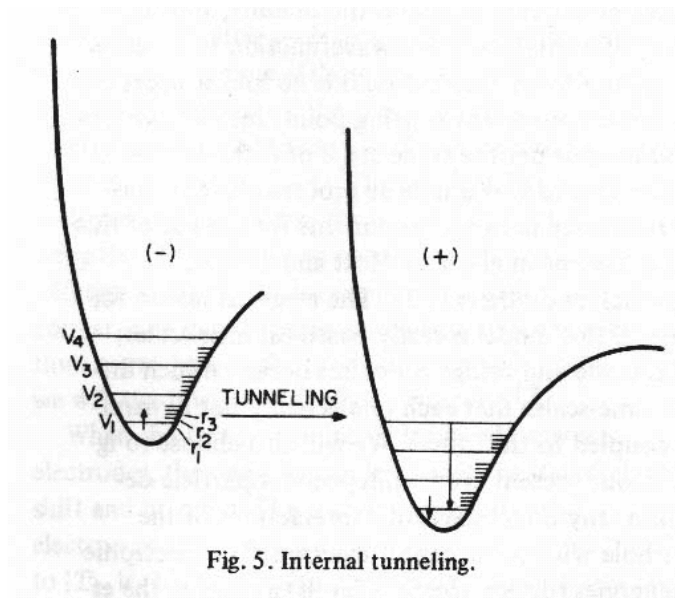
Slide 17: More on Tunneling and Electron Transfer

Fig. 5. Internal tunneling.

The two curves in slide 17 (above) are meant to represent electronic states in the rectifier's acceptor [left curve] and donor [right curve]. The curves represent atomic coordinates of the donor and acceptor. The main point of this graph is that an electron that jumps onto the donor is initially in an excited vibrational state. The vibrational energy with disperse as heat, and this is represented schematically by the downward-pointing arrow on the right curve.