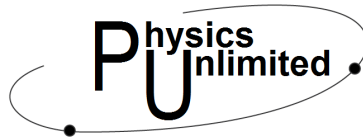


Physics Unlimited Explorer Competition

Assignment packet

Submissions due: April 16, 2023 11:59 pm EST



Guidelines

Student teams will have a total of **up to two weeks** to work on the 2023 Explorer Competition, and teams registering later than the assignment release date may begin to work at any time. For successful completion of this assignment, we recommend that teams set aside at least 10 hours of time, cumulatively. Please refer to the submission explanation below for details on both formatting and the submission process.

Scoring

Students are encouraged to work on as much of the assignment as possible. The award structure will be as follows:

1. Certificate awards will be given to the four teams with the highest scores, per scoring rubric that would allocate points for questions and exercises based on their difficulty level as determined by the assignment creator.
2. There will be medalist certificates granted for first place, second place, and third place, respectively.
3. There will be an honorable mention certificate granted to the fourth-highest scoring submission.

Collaboration Policy and External Resources

Students participating in the competition **may only correspond with members of their team**. Absolutely and unequivocally, **no other form of human correspondence is allowed**. This includes any form of correspondence with mentors, teachers, professors, and other students. Participating students are barred from posting content or asking questions related to the exam on the internet (except where specified below), and moreover, they are unequivocally barred from seeking the solution to any of the exams' parts from the internet or another resource. Students are allowed, however, to use the following resources for purposes of reference and computation:

- **Internet:** Teams may use the internet for purposes of reference with appropriate citation. Again, teams are in no way allowed to seek the solution to any of the exams' parts from the internet. For information about appropriate citation, see below.
- **Books and Other Literature:** Teams may use books or other literature, in print or online, for purposes of reference with appropriate citation. As with the use of the Internet, teams are in no way allowed to seek the solution to any of the exams' parts from books or other literature.
- **Computational Software:** Teams may use computational software, e.g. Mathematica, Matlab, Python, whenever they deem it appropriate. Of course, teams must clearly indicate that they have used such software. Additionally, the judges reserve the right to deduct points for the use of computational software where the solution may be obtained simply otherwise.

Citation

All student submissions that include outside material must include numbered citations. We do not prefer any style of citation in particular.

Submission

All submissions, regardless of formatting, **should include a cover page listing the title of the work, the date, and electronic or scanned signatures of all team participants.** The work must be submitted as a single **PDF document** with the “.pdf.” extension. All other formatting decisions are delegated to the teams themselves. No one style is favored over another. That being said, we recommend that teams use a typesetting language (e.g. LATEX) or a word-processing program (e.g. Microsoft Word, Pages). **Handwritten solutions are allowed**, but we reserve the right to **refuse grading of any portion of a team's submission in the case that the writing or solution is illegible.**

All teams must submit their solutions document to the 2023 Explorer Competition by **emailing directors@physicsu.org by 11:59 pm Eastern Time (UTC-5) on Sunday, April 16, 2023.** Teams will not be able to submit their solutions to the Explorer Competition at any later time. The team member who submitted the team registration form should send the submission; in case they are unable to, another team member may do so. The title of the submission e-mail should be formatted as **“PUEC 2023 SUBMISSION - Team Name”**, without quotation marks, where **Team Name** is to be replaced with your actual team's name, as registered. All teams may make multiple submissions. However, we will **only read and grade the most recent submission submitted before the deadline.** Teams will receive confirmation once their submission has been received within at most two days. **In the case of extraordinary circumstances, please contact us as soon as possible.**

Microcrystalline Organic Solar Cells

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Learning Goals

Through the course of this assignment, you will learn some basic concepts and ideas about quantum mechanics and apply it to consider principles of designing a solar cell made of micro-

crystalline organic semiconductors. We want you to get an idea of the way fundamental physics concepts form the foundations of modern, cutting-edge technologies, and for you to see that even a little bit of physics knowledge can help you understand these devices a whole lot better.

Those of you who have worked on the 2018 Explorer assignment or looked over it while reviewing might find some of the content familiar. However, rest assured each question will be different.

Topic Format and Grading

This document consists of a few sections of expository material with exercises and questions interspersed along that lead you to considering several ideas related to laser design. Exercises will typically ask students to mathematically derive or demonstrate a result useful to the discussion. They can also ask students to explain crucial concepts. Questions will ask students to, in their own words, interpret stated results. We are looking to see how well you understand the subject, so to receive full credit, all work shown must be complete and properly justified.

Expected Amount of Work

Do not expect to understand the concepts in this document after only one read through; these concepts take time to absorb. While it may feel like you are not getting much accomplished as you try to understand the reading, persevere. It may be necessary to read some passages several times in a row before understanding them completely. Because there are not too many questions in this document, you should have time to complete the readings. We have made every attempt to be rigorous in our presentation, but simplifications have been made when appropriate. Students are welcome to investigate the subject in more detail outside of this document.

I Introduction

This exam assumes a familiarity with atomic structure and electron configuration. If you are unfamiliar with these concepts, feel free to check out these Khan Academy resources on these topics or Google the topics yourself to familiarize yourself with the necessary concepts.

The following sections present some background on semiconductors and solar cells to orient and contextualize the exam and its content for you. Refer to the relevant sections of Chenming Hu's Modern Semiconductor Devices for Integrated Circuits or any other resource of choice for more info or better explanations if needed. I would recommend Sections 1.3 and 1.4 for II, Sections 1.2, 1.7.1, 1.7.2, 4.1.1, and 4.1.2 for II.6,. You do not need to know all of the equations in these sections unless specified in the exam, but you should understand the basic ideas and concepts behind semiconductors versus metals and insulators, doping, Fermi levels, p-n junctions, thermal equilibrium versus non-equilibrium in semiconductors, drift versus diffusion for carrier motion within semiconductors, and the basic operating principle of a solar cell from a semiconductor device perspective.

II Semiconductors

II.1 Semiconductors, Metals, and Insulators

When thinking about the electronic properties of materials, such as conductivity (which measures how well they conduct electricity), there are three main categories of materials:

- Metals: conduct electricity "easily" (i.e. at room temperature, without adding impurities to the material, needing to shine light on the material, etc.)

- Insulators: conduct electricity poorly under most conditions
- Semiconductors: can be manipulated into conducting electricity by various means (eg. adding impurities, shining light on them, etc.)

The difference, in practice, comes down to the **electronic band structures** of these materials. When atoms form bonds with each other in a material, their orbitals overlap, and individual orbitals become continuous bands within which electrons can reside. All shells with energies at or below the valence shell form the **valence band**. The higher-energy orbitals, which are empty when the atoms are in their lowest energy states, form the **conduction band**. The conduction band is like a highway with no traffic, so if electrons can make their way into the conduction band somehow (more on that later), then they can easily move. The valence band is more like a Los Angeles highway during rush hour – electrons can barely move within it. The conductivity of a material depends on the setup of these bands. Below is a comparison of the band structures of metals, semiconductors, and insulators:

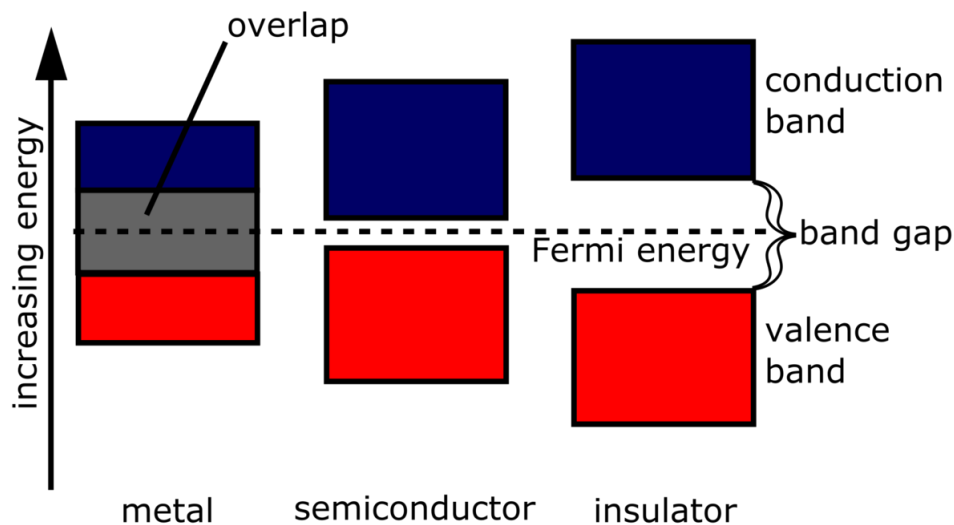


Figure 1: Comparison of the band diagram of metals, semiconductors, and insulators. The key difference lies in the energy separation between the valence and conduction bands.

In metals, the valence bands and conduction bands overlap, so electrons can effortlessly move from the valence to the conduction band, where they can conduct electricity when, say, a voltage is applied to the material.

On the other end of the spectrum, an insulator, like glass, has such a large energy difference between its conduction and valence states that it is practically impossible for electrons to jump into the conduction state from the valence state under "normal" circumstances. For example, SiO_2 has a bandgap of > 7 eV, which is in the UV part of the electromagnetic spectrum. When heated to around 1340°F, or 730°C, glass can conduct electricity well enough to light a lightbulb. This is because the high temperatures provide electrons with sufficient thermal energy to jump into the conduction state in significant enough quantities to measure a current flow through the device. The exact behavior of the electrons is probabilistic due to quantum mechanics, but on a macroscopic level we can measure electric conduction even in insulators under such extreme conditions.

Semiconductors are somewhere in between. Silicon, for instance, has a bandgap of 1.12 eV, which is in the infrared part of the electromagnetic spectrum. This means that these materials can conduct electricity more easily than insulators at elevated temperatures or under illumination. An electron in silicon that absorbs a visible-light photon, for instance, can jump from the valence to the conduction band. We can switch the material from being conductive to being

nonconductive with relatively quick modifications such as switching illumination or turning a moderate voltage on and off. This property makes it incredibly useful for optoelectronic devices such as lasers, LEDs, solar cells, and transistors. Modern electronic devices like your phone and computer are made possible by this property of semiconductors!

Modern optoelectronic devices, however, generally do not use pure semiconductors to perform this conductivity switching. Instead, they use something called **p-n junctions**, which will be discussed more in the next section. These rely on deliberately inserting different impurities in different parts of the semiconductor to make them conductive under certain voltages or illumination levels.

Silicon is the most common semiconductor around. It is an inorganic semiconductor, and can be crystalline, polycrystalline, or amorphous. Modern electronics are mostly made of crystalline silicon, while solar cells can be made of all three types, although each has its advantages and disadvantages as noted in the link above. Other inorganic semiconductors include gallium arsenide (GaAs) and indium phosphide (InP), which are **compound semiconductors** made of two elements rather than one. Semiconductors can get even more complicated, containing three or more elements, such as indium aluminum arsenide (InAlAs). Organic semiconductors, which will be the focus of this exam, are composed of long hydrocarbon molecules. Only some of them can be crystallized. But they all can be used to manipulate electrical conductivity to make devices like solar cells.

II.1.1 Exercise

Indium tin oxide (ITO) typically has a bandgap of at least 3.5 eV.

1. Please show your calculations – simply listing a number will **NOT** receive any credit!
 - (a) What wavelength light is needed to excite ITO's electrons from the valence to the conduction band?
 - (b) In what part of the electromagnetic spectrum does this light fall? (eg. gamma ray, radio, etc.).
2. Sketch a graph of the solar radiation spectrum versus wavelength, being sure to label your axes, and label the wavelength at which this graph peaks. Label the boundaries of the visible spectrum and the wavelength from #1a above on this solar spectrum graph.
 - (a) In what part of the electromagnetic spectrum does the peak fall?
3. For reasons that will be clearer later, the ideal bandgap for a basic solar cell is 1-1.5 eV, depending on various factors (such as whether the solar cells will be on Earth or in space).
 - (a) What is the wavelength of light corresponding to this ideal bandgap?
 - (b) In what part of the electromagnetic spectrum does this light fall? (eg. gamma ray, radio, etc.).
 - (c) Will the ideal solar cell material absorb a meaningful amount of light with a longer wavelength than what you found in part 3a? Why or why not?
 - (d) Given that a solar cell needs to absorb photons to generate electricity, what regions of the electromagnetic spectrum should a solar cell absorb to function?
 - (e) Will ITO absorb a meaningful amount of light at the ideal solar cell wavelength that you found in part 3a? Why or why not?
 - (f) Will ITO absorb a meaningful amount of light at the peak solar spectrum wavelength that you labeled? Why or why not?

- (g) Antireflection coatings (ARCs) are often used to improve solar cell efficiency by reducing the amount of reflection from the surface and allowing greater absorption of this incoming sunlight. A good antireflection coating will be transparent to the wavelengths that we want the solar cell itself to absorb.

Based on this, would ITO make a good ARC? Why or why not?

II.2 p vs. n-type Semiconductors

Modern optoelectronic devices rely on semiconductors with impurities deliberately introduced into the core material. The resulting impurity-infused semiconductor can be referred to as either a **p-type semiconductor** or an **n-type semiconductor**.

A **p-type semiconductor** has an impurity with fewer valence electrons than the core material, while the **n-type semiconductor** has an impurity with more valence electrons than the core material. For example, silicon has 4 valence electrons. A p-type silicon layer contains atoms like boron, which has 3 valence electrons, while an n-type silicon layer contains atoms like phosphorous, which has 5 valence electrons (see this periodic table for reference). This means that if you put a p-type and n-type semiconductor layer next to each other, the n-type side will have an excess electron concentration while the p-type side will have a reduced electron concentration. For the purposes of calculations, this missing electron concentration is treated like an excess concentration of a positively-charged "particle" called a **hole**. A hole is not a physical positively-charged particle that can move, but it can be treated as such for the purposes of calculating a system's electrical properties. When an electron from a neighboring atom moves into the empty spot represented by a hole, it leaves behind its own empty spot, which is effectively equivalent to a hole having moved from one atom to another. Figure 2 below illustrates this phenomenon of electron and hole motion:

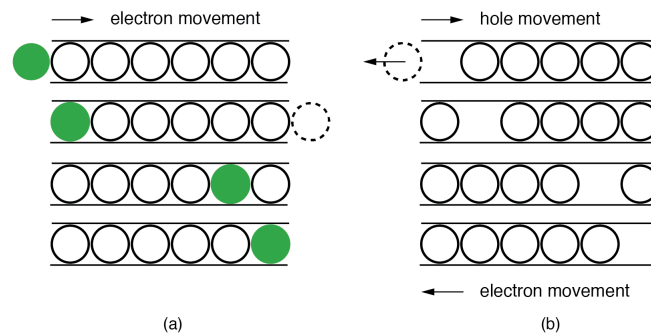


Figure 2: Illustration of electron and hole motion. In both cases, electron motion is the physical mechanism for particle motion, but for calculation's sake, holes are treated like physical particles.

The act of deliberately inserting impurity atoms into a material is called **doping**, and the impurity atoms themselves are referred to as **dopants** to distinguish them from unintentional impurities.

Physically, an n-type dopant has valence electrons at a higher energy compared to the semiconductor's valence electrons, while a p-type dopant has holes at a lower energy compared to the semiconductor's conduction band (which remember, is relatively empty for a semiconductor at room temperature). This makes it MUCH easier for electrons from an n-type dopant to be excited into the semiconductor's conduction band and for holes from a p-type dopant to be excited into the semiconductor's valence band, so much so that for calculation simplicity we can effectively assume this to occur with 100% efficiency. Below is a diagram representing the physical mechanism behind doping:

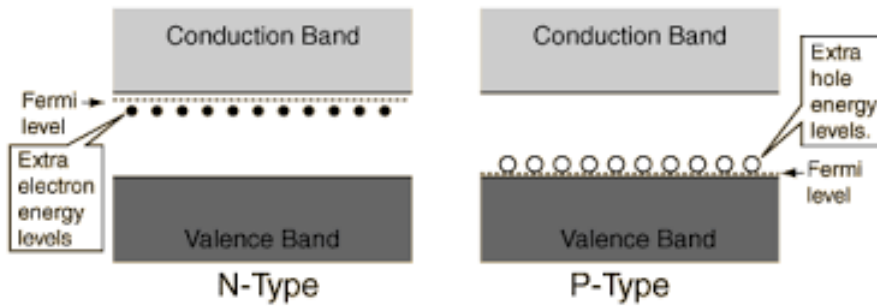


Figure 3: Illustration of dopant energy levels in n-type and p-type semiconductors (extra electrons and extra holes, respectively).

The Fermi level will be discussed later in this section, so you can ignore that for now. For a Refer to Section 1.2 of Hu’s book for more detail.

II.2.1 Exercise

Consider indium phosphide (InP), a compound semiconductor.

1. To what column of the periodic table does indium (In) belong? To what column of the periodic table does phosphorous (P) belong?
2. From what column(s) of the periodic table would you want to choose a doping element to create p-type InP? From what column(s) would you want to choose a doping element to create n-type InP?

II.3 Density of States

All you need to know for this idea is that quantum mechanics dictates the states a particle or system can be in. For electrons in a semiconductor, the density of states is zero in between the conduction and valence bands, while it is nonzero above the conduction bands and below the valence bands. The density of states is useful in calculating carrier concentrations within semiconductors. You can find more quantitative information in Section 1.6 of Hu’s book if you would like. A derivation of the density of states requires knowledge of quantum mechanics, but can be found here for interested readers.

II.3.1 Exercise

As you can see in the references in this section,

$$D_c(E) \propto m_n^{3/2} \text{ and } D_v(E) \propto m_p^{3/2}$$

where m_n is the **effective electron mass** and m_p is the **effective hole mass**. These are quantities that simplify the effects of local electron and ion interactions on carrier motion equations by pretending that that the electron or hole is an object with mass m_n and m_p , respectively. The exact values of m_n and m_p vary from material to material, and most are measured experimentally.

1. Consider silicon, which has $m_p = 0.59m_e$ at a temperature of 4 K and $m_p = 1.15m_e$ at a temperature of 300 K, and an electron effective mass of $m_n = 1.06m_e$ (m_e is the rest mass of an electron in free space).
 - (a) At a given energy E below the valence band energy E_v , at which temperature will the density of states be higher? Justify your answer.
 - (b) At a temperature of 4 K, will the conduction band or valence band have a higher density of states? Justify your answer.

II.4 Fermi Levels

Thoroughly understanding this section from first principles requires an understanding of statistical thermodynamics. This section will take the Fermi-Dirac distribution as a given for electrons.

The **Fermi-Dirac distribution function** describes the probability that a **fermion** (particle with half-integer spin) occupies a state with a particular energy. An electron, with a spin of $\pm 1/2$, is a fermion (as would a particle with spin $\pm 3/2$, etc., but not a particle with spin 0, ± 1 , etc.). It is given by the following function:

$$f(E) = \frac{1}{1 + e^{(E-E_F)/(kT)}} \quad (1)$$

where E is the energy of the fermion, typically defined with respect to the top of the valence band (so $E = 0$ at the top of the valence band). E_F is dictated by the total number of particles in the system. Notice that this function does not depend on the properties of the material – it applies for any system of non-interacting, indistinguishable particles with half-integer spin (like non-interacting electrons). Notice also that for an electron with energy $E = E_F$,

$$f(E) = f(E_F) = \frac{1}{1 + e^0} = \frac{1}{2}$$

Thus, for any system described by the Fermi-Dirac distribution, the probability of an electron having energy $E = E_F$ is $1/2$ (there's discontinuity issues at $T = 0$, but we will not concern ourselves with this for the sake of the exam).

In the conduction band, we are concerned with the probability of an electron occupying a particular state, which is given by $f_C(E)$ (Fermi-Dirac distribution in the conduction band). In the valence band, we care about holes for calculation purposes, and therefore are concerned with $1 - f_V(E)$, the probability that an electron DOES NOT occupy a particular state in the valence band.

Because the Fermi energy is dictated by the total number of electrons and holes, the Fermi energy of a system in equilibrium (no applied voltage, no light shining on it, etc.) is *constant* throughout a system. When a semiconductor is doped p-type or n-type, this shifts the Fermi level because the dopant impurities increase the probability that an electron will occupy the conduction band or that a hole will occupy the valence band.

Interested readers can refer to this forum for an explanation of the **Boltzmann distribution**, a building block of statistical thermodynamics, and this derivation of the Fermi-Dirac distribution.

II.4.1 Exercise

1. Consider a state in the conduction band that is 0.6 eV above the Fermi level E_F .
 - (a) What is the probability that an electron at room temperature $T = 300$ K will occupy this state? What about at $T = 0.1$ K? Please show your work to get credit.
2. Now consider a state in the valence band that is 0.6 eV below the Fermi level E_F .
 - (a) What is the probability that an **electron** (NOT a hole!) at room temperature $T = 300$ K will occupy this state? What about at $T = 0.1$ K? Please show your work to get credit.
3. Based on the previous two questions, sketch graphs of the occupation probabilities $f(E)$ as a function of the state energy E at both $T = 300$ K and $T = 0$ K (yes, the $T = 0$ K case is a limiting case for a physical system, even though mathematically you can't just plug in $T = 0$ K to figure this out). Label $f(E_F)$ on both graphs.

II.5 Electron and Hole Concentrations in Semiconductors

Check out Section 1.8 of Hu's book for a derivation of electron concentrations n and hole concentrations p in semiconductors as a function of energy E above or below the valence band. In summary, the concentration of electrons (electrons per unit volume) occupying a state between energy E and $E + dE$ is given by

$$D(E) * f(E) dE$$

since there are $D(E) dE$ state between E and $E + dE$. You need both the density of states and the probability of a carrier occupying said state. If there are no available and allowed states at a particular energy E , then the electron cannot occupy them and actually reside at that energy even if $f(E) \neq 0$. The relevant formulas for carrier concentration to remember from Section 1.8 of Hu's book are

$$n = N_c e^{-(E_c - E_F)/(kT)} \text{ where } N_c \equiv 2 \left(\frac{2\pi m_n kT}{h^2} \right)^{3/2} \quad (2)$$

for electron concentration **in the entire conduction band** (all energies $E \geq E_c$) and

$$p = N_v e^{-(E_F - E_v)/(kT)} \text{ where } N_v \equiv 2 \left(\frac{2\pi m_p kT}{h^2} \right)^{3/2} \quad (3)$$

for hole concentration **in the entire valence band** (all energies $E \leq E_v$).

The product np in a semiconductor at equilibrium (no potential bias or illumination) can be written as

$$np = n_i^2 \quad (4)$$

where n_i represents the concentration of the electrons in the conduction band and holes in the valence band for an intrinsic semiconductor in equilibrium (no potential bias or illumination). For an intrinsic semiconductor, $n = p = n_i$ because for a positive temperature T , electrons and holes form in pairs when an electron is excited into the conduction band and leaves behind a hole. Note, however, that $np = n_i^2$ even for doped samples! This is because the excess carriers from doping the sample (eg. excess electrons in an n-doped semiconductor) recombine with some of the intrinsic holes, and the recombination rate is proportional to np .

II.5.1 Exercise

1. Based on the above (including Section 1.8 of Hu's book), what is the electron concentration **at the Fermi energy** E_F of a semiconductor in which E_F is between E_V and E_C (true for almost all semiconductors in use)? Justify your answer.
2. Consider a sample of gallium arsenide (GaAs), with effective electron mass $m_n = 0.063m_e$ (where remember, m_e is the rest mass of an electron in vacuum).
 - (a) Calculate $D(E)$ and $f(E)$ at $E = 1.47$ eV where $E_C = 1.42$ eV and $E_F = 0.71$ eV.
 - (b) Calculate the electron concentration n in the conduction band of GaAs using Equation 1.8.5 and Table 1-4 in the book.
 - (c) When a semiconductor is doped p -type or n -type, the concentration of impurity atoms added (donors or acceptors) is typically at least $10^{16} / \text{cm}^3$.

How does this compare to the electron concentration calculated in 2b? Do you expect that doping would enhance conduction in a sample relative to an undoped sample?

Think about the orders of magnitudes of the values you calculated in Question 2. Does it make sense that the electron concentration in the conduction band, n , would be what you calculated? (Not graded, just for your own understanding).

3. The density of GaAs is 5.32 g/cm^3 . Its molar mass is 144.645 g/mol ($1 \text{ mol} = 6.022 \times 10^{23}$ atoms).

(a) Calculate the atom density per cubic centimeter for GaAs.

(b) How does this compare to the electron concentration you calculated in 2b?

Do you think you would observe significant conduction in GaAs under these conditions? (Not graded, just for self-reflection).

4. Examine Equations 2 and 3.

(a) Using those equations, calculate the product np . Does np depend on the position of the Fermi energy E_F ? What (other) factor(s) affect np ? Note that N_c and N_v are constant for a given semiconductor at a temperature T .

(b) Calculate n_i .

(c) Now consider a sample of n-type InP with donor concentration $N_d = 10^{16} \text{ cm}^{-3}$. Undoped InP has an intrinsic carrier concentration of $n_i = 1.3 \times 10^7 \text{ cm}^{-3}$. Assuming complete donor ionization, $n = N_d + n_i$.

Calculate the hole concentration p in this n-type InP sample. How does this compare to the electron concentration in the n-type InP? How does it compare to the hole concentration in undoped InP?

(d) Using the information about InP from question 4c, calculate the bandgap of InP ($E_c - E_v$). Show your work.

II.6 p-n Junction

This section will explain the concept of a p-n junction using silicon for simplicity. The concepts translate to more complicated semiconductors as well, but various details, such as those surrounding the desired impurity types and properties, will be different.

A **p-n junction** consists of a p-type and n-type semiconductor next to each other. In Section II, the valence and conduction bands were straight because they were for a pure (crystalline) material. When impurities are introduced, these valence and conduction bands bend within the material. Below is a diagram of the band structure of p and n-type semiconductors as well as a p-n junction:

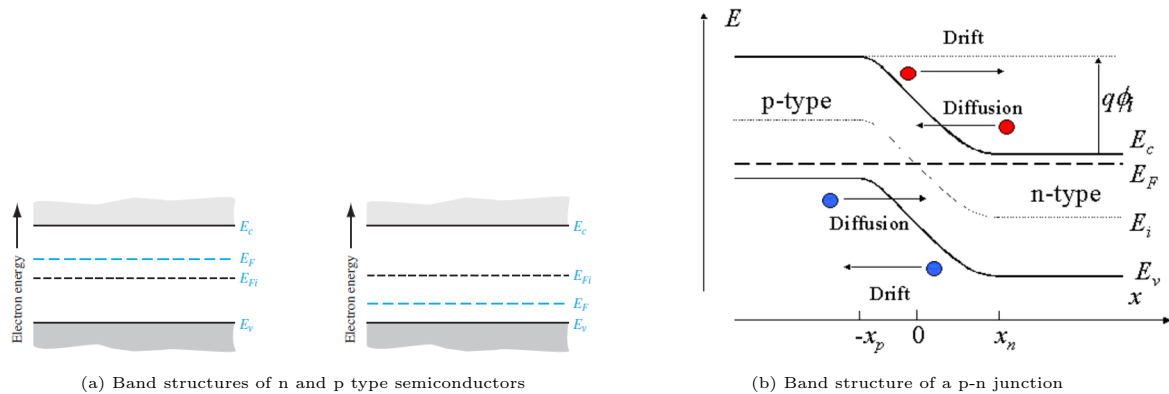


Figure 4: A comparison of the band structures of p and n type semiconductors that are far apart (4a) and next to each other (4b).

Don't get too confused by the diagram – there's a lot going on here that hasn't yet been discussed! Additionally, note that the n-type semiconductor is on the left and the p-type on the right in Figure 4a, but it's flipped around for Figure 4b. Keep in mind that the band diagram

illustrates electron energies, so a higher-energy hole is actually *lower* in the diagram than a lower-energy hole because of its opposite charge.

For this example, let's say the p-type side represents silicon with boron impurity atoms inserted, while the n-type side is silicon with phosphorous impurity atoms inserted. At equilibrium (no applied voltage, no sunlight shining on the sample, etc.), the Fermi level needs to be constant throughout the sample. This is because once equilibrium is achieved, the number of free carriers in question remains the same, and the derivation of the Fermi-Dirac distribution specifies that the position of E_F relative to the valence band is dictated by the total number of carriers. To achieve this, the conduction and valence bands must "bend" when a semiconductor has a p-type and n-type region adjacent to each other. Achieving this requires a flow of electrons from the n-type to p-type region and a flow of holes from the p-type to the n-type region until equilibrium is achieved.

In this initial stage, the **diffusion** of majority carriers (electrons from n-type, holes from p-type) dominates. However, as this diffusion occurs, electrons leave behind positively-charged ions while holes "leave behind" negatively-charged ions. See Figure 4-6 in Hu's book for a diagram illustrating this charge buildup in the p-n junction. Neither of the left-behind ions are able to move through the sample, so this creates a build-up of positive charge in the n-type region and a build-up of negative charge in the p-type region. This results in an electric field that opposes the diffusion of the majority carriers, since the negative charge in the p-type region will attract the holes back while the positive charge in the n-type region will attract the electrons back. This results in a **drift** current that opposes the diffusion current. At equilibrium, the drift and diffusion currents balance each other out.

The width of this region of left-behind charges, called the **space-charge region**, is given by

$$W_{dep} = \sqrt{\frac{2\epsilon_s\phi_{bi}}{q} \left(\frac{1}{N_a} + \frac{1}{N_d} \right)} \quad (5)$$

Note that for $N_a \gg N_d$, $W_{dep} \rightarrow |x_N|$ and for $N_d \gg N_a$, $W_{dep} \rightarrow |x_P|$.

The amount of band-bending in a p-n junction under equilibrium is given by the **built-in potential**:

$$\phi_{bi} = \frac{kT}{q} \ln \left(\frac{N_d N_a}{n_i^2} \right) \quad (6)$$

where q is the electron charge and N_d and N_a are the donor and acceptor concentrations, respectively. See Chapter 4 of Hu's book for a derivation of this expression.

Under a potential bias or illumination, however, the system is out of equilibrium, and the Fermi energy E_F is no longer constant within the sample. See Section 2.8 of Hu's book for a more thorough and quantitative treatment of this Fermi level splitting, with concepts such as **quasi-equilibrium** and **quasi-Fermi levels**. From that section, we can express the electron concentration in the entire conduction band, and the hole concentration in the entire valence band, using these new quasi-Fermi levels as

$$n = N_c e^{-(E_c - E_{Fn})/(kT)} \quad (7)$$

and

$$p = N_v e^{-(E_{Fp} - E_v)/(kT)} \quad (8)$$

where E_{Fn} is the electron quasi-Fermi level and E_{Fp} is the hole quasi-Fermi level.

For now, I will focus on a qualitative explanation of the physical mechanisms governing free carrier behavior in these various deviations from an unbiased p-n junction in the dark.

Below is a diagram illustrating the p-n junctions under forward, zero, and reverse bias:

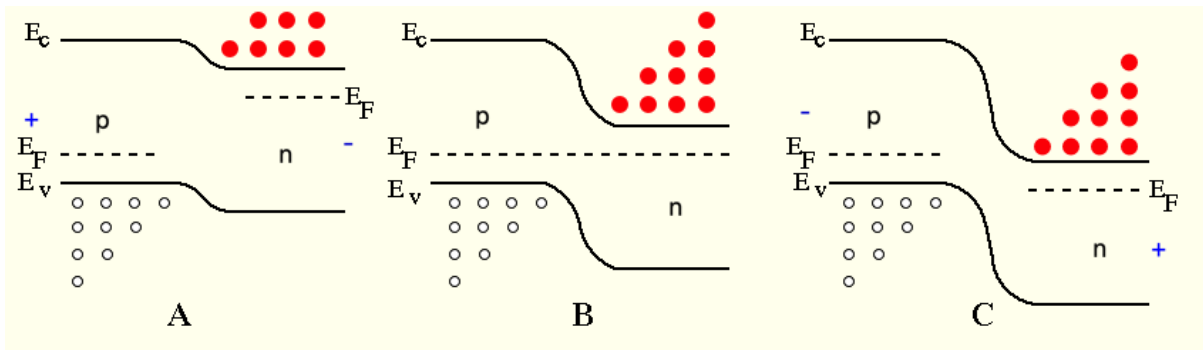


Figure 5: Schematic of a p-n junction under forward bias (A), no bias (B), and reverse bias (C).

The p-type side is on the left and the n-type side is on the right. In (A), the p-type side is positively biased while the n-type side is negatively biased. In (C), the p-type is negatively biased while the n-type side is positively biased.

The red circles represent the electron distribution in the conduction band and the white circles represent the hole distribution in the valence band (numbers not to scale – they simply serve an illustrative purpose). In (B), when the drift and diffusion currents balance, there's a certain number of electrons from the n-type side with energy above E_c in the valence band – it is ONLY these electrons that can diffuse to the p-type side, since they are above the energy barrier formed by the band-bending in the conduction band. The red circles with energy less than the E_c on the p-type side cannot make it over this barrier, and therefore cannot diffuse to the p-type side. A similar logic applies for the holes in the valence band which are or are not able to diffuse to the n-type side.

Under a forward bias, this potential barrier, this difference between the conduction band energies is reduced since the positive bias on the p-type side drags the bands down and the negative bias on the n-type side pushes the bands up. Thus, a greater fraction of the carriers now have sufficient energy to overcome the lower energy barrier between the two halves of the p-n junction, increasing the diffusion current. Meanwhile, the drift current (effectively) doesn't change (relative to the diffusion current) because drift current is linearly proportional to electric field, which is linearly proportional to carrier concentration, while the carrier distribution above the conduction band and below the valence band is exponential. Thus, there is a greater net current flow, with electrons flowing to the p-type side and holes flowing to the n-type side.

Under a reverse bias, on the other hand, the negative bias on the p-type side pushes the bands up while the positive bias on the n-type side pushes the bands down, which increases the energy barrier between the bands. Now, fewer carriers are able to diffuse over this energy barrier. The greater potential drop between the p and n-type sides of the junction, as evidenced by the steeper slope between these regions, does slightly increase the drift current in the "reverse" direction.

Finally, under illumination (which is relevant for a solar cell), the band diagram (once the illuminated system is in equilibrium) looks like this:

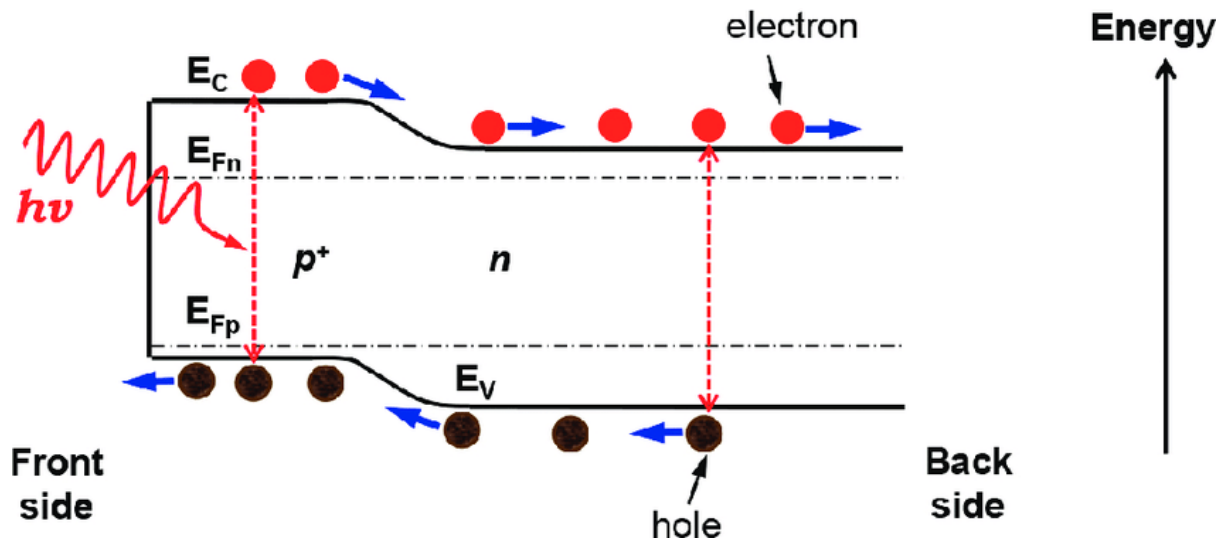


Figure 6: p-n junction under illumination

Illumination excites electrons from the valence band into the conduction band, which generates both excess electrons and excess holes (in pairs) compared to the number of free carriers before. This increase in the number of free carriers causes Fermi level to split (since the old Fermi level was based on the previous number of free carriers). Because of the generation of new electron-hole pairs, rather than just a movement of carriers (like in the biased case discussed previously) the electrons and holes have their own Fermi levels that reflect the new concentration of each in the conduction and valence bands, respectively.

Once electron-hole pairs form by absorbing this energy (in this case, from the incoming light's photons), they can also recombine. This happens when the electron falls back down from the conduction band into the valence band and occupies a hole again. This makes the free electron and hole "disappear" (since the electron that returned to the valence band is no longer "free", and the hole previously there has now been occupied). This occurs because the electron is then in a lower-energy state. However, the continued illumination will keep exciting electrons into the conduction band when it absorbs a photon, so eventually there is an equilibrium between electron-hole pair generation and recombination. Check out Section 2.6 in Hu's book for more information on carrier recombination.

See Figure 4-6 in Hu's book for diagrams relating to the rest of this paragraph. The depletion region already has fewer dopant carriers (fewer donor electrons in the n-type half of the depletion region, fewer donor holes in the p-type half of the depletion region), so electron-hole pairs won't really form IN the depletion region. However, near the boundary between the depletion and neutral regions, electron-hole pairs can be excited by incoming photons. The electrons in the conduction band of the p-type region will be swept into the conduction band of the n-type region because of the electric field that causes the conduction band to slope down from the p-type region through the depletion region into the n-type region. Similarly, the holes that form at the edge of the n-type region will be swept up into the valence band of the p-type region because of the potential difference illustrated by the sloping valence band through the depletion region (remember, for holes, higher up the energy curve is "lower energy" because of their opposite charge from electrons). This means that under illumination, there is a non-zero **reverse** current when there is no potential bias applied to the system.

II.6.1 Exercise

1. Show that when the p-n junction IS in equilibrium (i.e. $np = n_i^2$), that $E_{Fn} = E_{Fp}$ using Equations 7 and 8

2. How does increasing the donor concentration affect ϕ_{bi} ? How does increasing the acceptor concentration affect ϕ_{bi} ?
3. Based on your answer to question 2 and the dependence of W_{dep} on dopant concentration (and / or Section 4.2.1 from Hu's book), how does increasing the doping concentration affect the electric field in the depletion region?
4. The drift current referred to in this section is proportional to the electric field:

$$J_{drift} \propto E \propto \frac{dV}{dx}$$

where V is the electric potential. Based on this,

- (a) How would increasing the dopant concentration affect the drift current?
- (b) How would this affect the current of a p-n junction under illumination?
- (c) Based on this information alone (and ignoring other effects of doping), is a higher or lower p-n junction doping more desirable for a well-functioning solar cell (one that generates as much electricity as possible from incoming light)? Justify your answer.

II.7 Current-Voltage Behavior

Please refer to Chapter 4 in Hu's book for information on the derivations relevant to the formulas that will be introduced in this section.

For a p-n junction in the dark under bias, the net current (density) flow can be quantified as a function of applied voltage with the equation

$$J(V) = J_0(e^{qV/(kT)} - 1) \quad (9)$$

where J_0 is a parameter that quantifies the current density under infinite reverse bias, in which regime drift current dominates. This is also called the **saturation current** (density). **NOTE:** the book will write these formulas in terms of current rather than current density, and I may occasionally use these terms interchangeably (though I'll try to avoid it) – the only difference is that using current density divides out area – I don't need to repeatedly read about the dependence of device current on its area. That's effectively meaningless – it's like saying bigger galaxies have more mass.

A positive current (density) reflects "forward" current flow, in which diffusion current is greater than drift current, while negative current (density) reflects "reverse" current flow, in which drift current is greater than diffusion current (in other words, the direction of diffusion current, the current flow from the n -type to the p -type region, dictates "positive" current flow). Notice that the diffusion current term, which is the first term, is exponential while the drift current term, which is the second term, is effectively constant as a function of voltage.

For a p-n junction under illumination, the net current (density) flow can be quantified as a function of voltage as

$$J(V) = J_0(e^{qV/(kT)} - 1) - J_{sc} \quad (10)$$

which almost resembles the equation of a p-n junction in the dark except for the J_{sc} term, which reflects the additional drift current that results from the extra electron-hole pairs that form under illumination and are swept up by the electric field of the depletion region. The value of J_{sc} depends on the photon flux density (# of incoming photons per unit area at a particular photon energy $\hbar\nu$) and the bandgap of the semiconductor, assuming perfect, complete absorption and harnessing of every incoming photon at or above the band-gap energy. To quantify this, we can write

$$J_{sc}(E_g) \propto \int_{E_g}^{\infty} \frac{E^2}{e^E - 1} dE \quad (11)$$

where E is the photon energy. This expression arises because the integrand is proportional to the solar spectrum (assuming the sun is an ideal blackbody).

II.7.1 Exercise

1. Using Sections 4.9, 2.5, and 2.2 of Hu's book,
 - (a) What does J_0 depend on? (**NOTE:** one of the variables you'll find in Section 4.9 that affects J_0 depends on other parameters that are described in Section 2.5, which then depend on factors mentioned in Section 2.2). Explain thoroughly what each of these parameters is where needed.
 - (b) At a given, fixed temperature (eg. room temperature), which of these variables can be manipulated / improved to achieve a higher J_0 ? For each of those, describe whether you would want to increase or decrease its value and how you can achieve this.
2. Along with J_{sc} and J_0 , another parameter that tells us about solar cell performance is called **open-circuit voltage** (V_{oc}). This is the value of V at which the current density through the solar cell is 0:

$$J(V_{oc}) = J_0(e^{qV_{oc}/(kT)} - 1) - J_{sc} = 0$$

- (a) Derive an expression for V_{oc} in terms of J_0 and J_{sc} . First, don't make any approximations, and then make the approximation that $J_{sc} \gg J_s$.
- (b) A higher V_{oc} usually points to a better solar cell efficiency, all else equal.

Is a higher or lower short-circuit current (density) J_{sc} desired for a better V_{oc} ? Is a higher or lower saturation current (density) J_0 desired for a better V_{oc} ? Justify your answers.
- (c) Do you think a smaller or larger semiconductor bandgap E_g would improve the J_{sc} in the desired direction (based on your answer for the previous part) for higher V_{oc} ? Justify your answer.
- (d) Do you think a smaller or larger semiconductor bandgap E_g would improve the saturation current J_0 ? Justify your answer. (**HINT:** Section 4.9 of Hu's book contains the expression for I_0 , and remember the saturation current I_0 is the same for all potential biases and illumination conditions, including a dark system at $V = 0$).
- (e) Using Equation 11 and the expression you found in part 2d,
 - i. Calculate $J_{sc}(E_g)$ and plot it as a function of E_g using Wolfram Alpha (eg. from $E_g = 0$ to $E_g = 5$ in these units).
 - ii. Then, sketch a plot of J_0 vs. E_g (**HINT:** set all of the constants equal to 1 to simplify the expression, since we are concerned with the dependence of J_0 on E_g)
 - iii. Now, sketch a plot of $V_{oc}(E_g)$ as a function of E_g using the previous two parts. All in all, does V_{oc} depend on band gap E_g ? If so, how does increasing or decreasing the band gap affect the V_{oc} ?
- (f) Is there a trade-off inherent in optimizing the bandgap of a semiconductor for maximizing solar cell efficiency? (A proxy for this is maximizing both J_{sc} and V_{oc} simultaneously). Justify your answer. (**NOTE:** You must get your answers to both parts 2c and 2d to get credit for this part.

3. The power (energy per unit time) generated by a solar cell is given by

$$P(V) = I(V) * V$$

Note that since $I(V) < 0$ for $V < V_{oc}$, which means the power is "negative" – this sign convention indicates that power is being generated, rather than consumed, in this voltage range.

Derive an expression for V_{mp} , the voltage at which the generated power is maximized, as a function of V_{oc} . (**HINT:** calculate the derivative of $P(V)$ and set it equal to 0: $dP/dV = 0$, and then use the approximation used in the second part of 2a). Show your work.

III Organic Semiconductors

Organic semiconductors and devices were developed more recently than their inorganic counterparts, and record organic solar cell performance still lags behind record inorganic solar cell performance [1]. Despite their lower efficiencies, organic solar cells have several features that make them more attractive than their inorganic counterparts: they are cheaper, flexible, and lightweight [2]. Their flexibility and low weight make them easy to integrate into existing infrastructure [2]. These advantages are possible because organic semiconductors have absorption coefficients 1000 times those of polycrystalline silicon and have lower densities, which allows thin, light layers of active materials to absorb photons efficiently.

III.1 Physics of Electron Arrangement in Atoms

Organic semiconductors have a somewhat different energy structure than inorganic semiconductors. The formation of electronic bands, which allow charge transfer, in organic molecules can be understood by orbital hybridization theory. Electrons that orbit atoms come in different orbitals, each of a different energy level. Below is an image that shows the shapes of the orbitals that are present in carbon atoms:

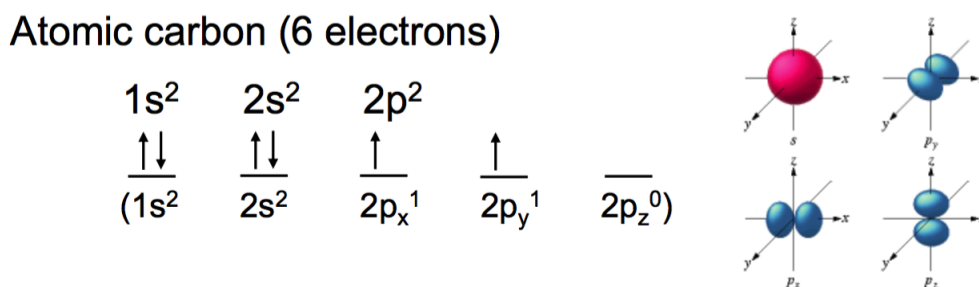


Figure 7: Schematic representation of electron orbitals in a carbon atom [3]. The arrows represent the arrangement of electrons and their spins in different orbitals.

The 1s and 2s orbitals, which are represented by the pink sphere in Figure 7 above, are filled first [3]. Each has two electrons, one of each spin. Then, the higher-momentum 2p orbitals are filled, but this time, each orientation (p_x, p_y, p_z) is filled with one spin-up electron before being filled with any spin-down electrons. This is due to a combination of the **Pauli exclusion principle** and **Hund's rule of maximum multiplicity** [4].

Pauli Exclusion Principle

The Pauli exclusion principle states that each electron must have a unique quantum description – this means that each electron must be in its own energy level and orbital (so either 1s, 2s,

$2p_x$, $2p_y$, or $2p_z$), and that two electrons in the same orbital must have different spins (up or down). This results because electrons are part of a class of indistinguishable particles called *fermions*, for which multi-particle wavefunctions change in sign when particles are renamed [5]. In other words, a two-electron system's wavefunction $|\psi\rangle$ is represented as such:

$$|\psi\rangle_{n_1, n_2} \equiv c(|n_1\rangle|n_2\rangle - |n_2\rangle|n_1\rangle) \quad (12)$$

where c is a proportionality constant that helps normalize the wavefunction [5]. Note that the first $|\rangle$ represents the "first particle" and the second $|\rangle$ represents the "second particle", while the n_1 and n_2 refer to the **state** the particle is in. The indistinguishability of the particles makes the total wavefunction a superposition of the states $|n_1\rangle|n_2\rangle$, in which the first electron is in the n_1 state and the second electron is in the n_2 state, and $|n_2\rangle|n_1\rangle$, in which the first electron is in the n_2 state and the second electron is in the n_1 state [5]. The wavefunction of a fermion is **antisymmetric** because

$$|\psi\rangle_{n_2, n_1} = c(|n_2\rangle|n_1\rangle - |n_1\rangle|n_2\rangle) = -c(|n_1\rangle|n_2\rangle - |n_2\rangle|n_1\rangle) = -|n_1, n_2\rangle$$

when I switched the order of the state labels n_1 and n_2 in the wavefunction. The wavefunction for a **distinguishable** pair of particles, in which you can tell the difference between the first and second particle, is simply given by

$$|\psi\rangle_{n_2, n_1} = |n_1\rangle|n_2\rangle \quad (13)$$

when the first particle is in state n_1 and the second particle is in state n_2 . In general, $|n_1\rangle|n_2\rangle \neq |n_2\rangle|n_1\rangle$, so Equation 13 does not work for fermions.

The particles obeying the equation

$$|\psi\rangle_{n_1, n_2} \equiv c(|n_1\rangle|n_2\rangle + |n_2\rangle|n_1\rangle) \quad (14)$$

for indistinguishable particles are called **bosons**. Bosons have a **symmetric** wavefunction:

$$|\psi\rangle_{n_2, n_1} = c(|n_2\rangle|n_1\rangle + |n_1\rangle|n_2\rangle) = c(|n_1\rangle|n_2\rangle + |n_2\rangle|n_1\rangle) = |n_1, n_2\rangle$$

A quick aside: a wavefunction, at the end of the day, exists to predict the probability of obtaining various measurements (in quantum mechanics, the values of observables like particle energy are technically probabilistic). The result is that the square of the magnitude of its integral across all of the relevant independent variables dictating its behavior (eg. position, time) should evaluate to 1. In the notation used here, this can be written as

$$\langle n_1|n_1\rangle = 1 \text{ and } \langle n_1, n_2|n_1, n_2\rangle = 1 \quad (15)$$

where $\langle \dots | \dots \rangle$ represents a multiplication of a wavefunction by its complex conjugate (called an **inner product**). For distinguishable particles, for example, we would say that

$$\langle n_1, n_2|n_1, n_2\rangle = \langle n_1|\langle n_2|n_1\rangle|n_2\rangle = \langle n_1|n_1\rangle\langle n_2|n_2\rangle = 1 * 1 = 1$$

You can read more about this in pages like this Wikipedia link on bra-ket notation (used to write wavefunctions like $|\rangle$), paying special attention to the **Hermitian conjugation** section of that page. Additionally, this plus this link on complex conjugates will help (and your own Googling), but the important takeaway is Equation 15. If $|n_1\rangle = a + bi$ (where i is the imaginary number $i = \sqrt{-1}$), then $\langle n_1|n_1\rangle = (a - bi)(a + bi)$. I used this reference to clarify convention regarding label order and tensor product calculation. **PAY CAREFUL ATTENTION TO THIS ORDERING TO MAKE SURE YOU EVALUATE THESE EXPRESSIONS CORRECTLY IN THE EXERCISES!**

III.1.1 Exercise

Consider a pair of electrons.

1. What happens if you try to put both electrons in the same state (eg. n_1)? Evaluate Equation 12 in that case.
2. Could you possibly properly normalize this result? (i.e. can you use the result of the previous question to obtain Equation 15)? Show your work and / or justify your answer.
3. Based on this, do bosons follow the Pauli Exclusion Principle? Justify your answer using the previous two questions.

III.1.2 Exercise

Now consider a pair of bosons.

1. What happens if you try to put both bosons in the same state (eg. n_1)? Evaluate Equation 14 in that case.
2. Could you possibly properly normalize this result? (i.e. can you use the result of the previous question to obtain Equation 15)? Show your work and / or justify your answer.
3. Is this consistent with the Pauli Exclusion Principle for fermions? Justify your answer using the previous two questions.

III.1.3 Exercise

Determine an expression for c (in terms of inner products of $|n_1\rangle|n_2\rangle$) for

1. Fermions (starting with definition 12)
2. Bosons (starting with definition 14)

Read the following for more background on wavefunctions and symmetries and how they dictate electron arrangement in atoms such as hydrogen, helium, and lithium. Important takeaways include:

- To put two electrons in a single orbital (eg. $1s$, $2p_x$, etc.), their spins need to be opposite to construct an antisymmetric wavefunction
- If more than two electrons are in a given orbital (eg. $1s$, $2p_x$, etc.), it is impossible to construct an antisymmetric wavefunction

Hund's Rule

Meanwhile, Hund's rule states that electrons are arranged in orbitals to maximize spin [4]. Because electrostatic repulsion causes two electrons in the same orbital to have a higher energy than each electron in a different orbital, and the atom wants to minimize its energy, each orbital in a given energy level is filled with one electron before any orbital in that energy level is filled with another [4]. In this electron arrangement within a carbon atom, two p orbitals are partially filled, and one is empty.

Read the section Relative stability of $2p^2$ configurations in the linked PDF for a more detailed explanation below, but I'll summarize below.

There are five possible wavefunctions to represent the spin configurations in a carbon atom [5]:

$$\begin{aligned}\psi_{\uparrow_x\downarrow_x} &= 2p_x(1)2p_x(2) \times \left[\uparrow(1)\downarrow(2) - \uparrow(2)\downarrow(1) \right] \\ \psi_{\uparrow_x\downarrow_y} &= \left[2p_x(1)2p_y(2) + 2p_x(2)2p_y(1) \right] \times \left[\uparrow(1)\downarrow(2) - \uparrow(2)\downarrow(1) \right] \\ \psi_{\uparrow_x\uparrow_y} &= \left[2p_x(1)2p_y(2) - 2p_x(2)2p_y(1) \right] \times \uparrow(1)\uparrow(2) \\ \psi_{\uparrow_x\uparrow_x} &= \left[2p_x(1)2p_y(2) - 2p_x(2)2p_y(1) \right] \times \left[\uparrow(1)\downarrow(2) + \uparrow(2)\downarrow(1) \right] \\ \psi_{\uparrow_x\uparrow_y} &= \left[2p_x(1)2p_y(2) - 2p_x(2)2p_y(1) \right] \times \downarrow(1)\downarrow(2)\end{aligned}$$

All of the wavefunctions are formed as products of a symmetric and anti-symmetric wavefunction [5]. When the spatial wavefunction is symmetric, the spin wavefunction is antisymmetric and vice versa. Because of the arguments made in the PDF regarding electrostatic repulsion in these different cases, combined with the magnetic interaction being much weaker and thus not influencing the outcome, the last three wavefunctions $\psi_{\uparrow_x\uparrow_y}$ end up being the most stable.

III.2 Molecular Bonding

Just as with atomic orbitals, we can write Schrodinger's equations for electrons in molecules. Solutions to these equations can be approximated by writing wavefunctions that are linear combinations of atomic orbitals. For a diatomic molecule, this gives us

$$\Psi = c_a\psi_a + c_b\psi_b \quad (16)$$

where Ψ gives the molecular wavefunction, a and b denote the different atoms, and c_a and c_b are proportionality constants that affect the wavefunction normalization [4]. Molecular orbitals form when atomic orbitals overlap, yielding a relatively high probability that both atoms' electrons will be found in the overlap region between the nuclei [4]. Bonding requires three factors: orbitals must be symmetric such that regions with the same sign of ψ must overlap, atomic orbital energies must be similar so that the formation of molecular orbitals changes the electron energy to make bonding favorable, and the distance between the atoms must be short enough for good atomic orbital overlap but long enough that electron repulsion forces do not interfere [4]. If one of these three conditions is not true, then nonbonding orbitals tend to form when the atoms come together [4].

When two s orbitals overlap, as in a diatomic molecule like H_2 , then the resulting larger molecular electron clouds are linear combinations of the atomic orbitals:

$$\begin{aligned}\Psi(\sigma) &= N \left[c_a\psi(1s_a) + c_b\psi(1s_b) \right] \\ \Psi(\sigma^*) &= N \left[c_a\psi(1s_a) - c_b\psi(1s_b) \right]\end{aligned}$$

where N is a normalizing factor for Ψ while σ and σ^* indicate orbitals that are rotationally symmetric about a line passing through both nuclei [4]. The wavefunctions show that combining the atomic orbitals yields one lower-energy bonding molecular orbital, with an increased electron concentration between the nuclei and one higher-energy antibonding orbital, which yields a node with zero electron density between the nuclei [4]. In bonding orbitals, the electrons cluster between the nuclei and attract the nuclei towards themselves, which holds the molecule together [4].

Each p orbital, however, has separate regions whose wavefunctions have opposite signs. Once again, when two regions that overlap have the same sign, then the electron probability in the overlapping region is increased, but when two regions that overlap have opposite signs, then

the overlapping region has a reduced electron probability [4]. However, because of the shape and multiple orientations of the p -orbitals, we end up with not only σ and σ^* molecular orbitals but also π and π^* molecular orbitals [4]. Below are diagrams which demonstrate the bond formation:

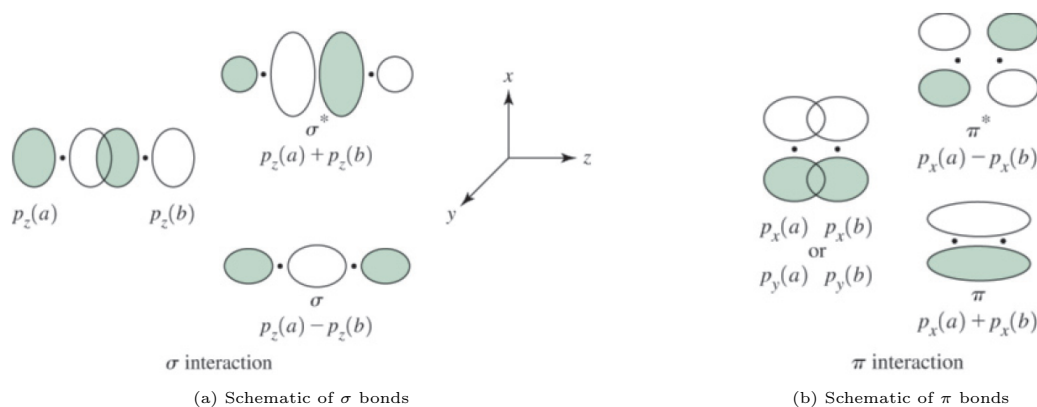


Figure 8: Schematic diagram demonstrating σ and π bonding and anti-bonding orbitals [4]. The white and green orbitals represent those having wavefunctions of the opposite sign.

As evident in Figure 8a, adding the p_z orbitals of the two atoms causes wavefunctions of the opposite sign to overlap, which leads to anti-bonding orbitals [4]. Meanwhile, subtracting the orbitals flips the sign of the second p_z orbital such that wavefunctions of the same sign are overlapping (the colors of $p_z(b)$ flip, so there's a same-colored "blob" that forms in the middle that demonstrates increased electron probability between the atoms, and thus "bonding") [4].

III.2.1 Exercise

1. Examine Figure 8b. Explain what happens (in terms of overlap of wavefunctions with the same sign vs. opposite sign), similar to my explanation above for p_z , for:

(a) $p_x(a) + p_x(b)$ (adding two p_x orbitals)

(b) $p_x(a) - p_x(b)$ (subtracting two orbitals)

2. Now think about the implications for bonding and antibonding:

(a) Bonding results for which one(s) of the two?

(b) Antibonding results for which one(s) of the two?

When orbitals of the same type overlap, then the result is a symmetric arrangement of orbitals such as below:

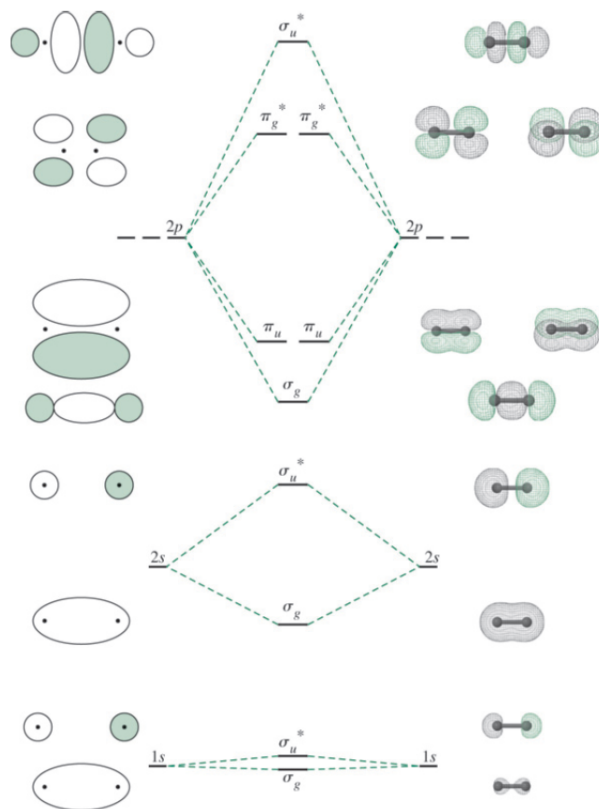


Figure 9: Schematic of molecular orbitals for atoms with atomic number up to 10 [4].

In the $2p$ orbitals of Figure 9 above, π molecular orbitals have higher energies than σ while π^* orbitals have a lower energy than σ^* [4]. Thus, the gap between the π orbitals is lower than that between σ orbitals.

Non-identical orbitals can mix if their energies are similar enough and they exhibit the same symmetries. For instance, the σ_g orbitals of the $2s$ and $2p$ energy levels can mix, as can the σ_u^* orbitals. Orbital mixing lowers the energy of the lower-energy orbital and raises the energy of the higher-energy orbital. Below is a diagram illustrating the effects of such orbital mixing:

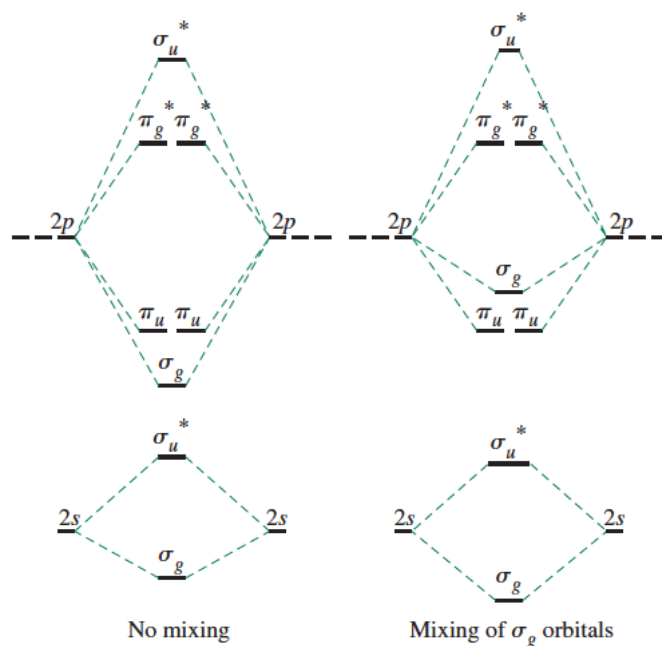


Figure 10: Schematic of the effects of σ_g orbital mixing between the 2s and 2p levels [4]. The $\sigma_g(2p)$ energy level is raised while the $\sigma_g(2s)$ energy is lowered [4].

After orbital mixing, the $\sigma_g(2p)$ energy level is now higher than the $\pi_u(2p)$. The exact orbital overlap dictates which of the orbitals is the highest occupied molecular orbital (HOMO), the highest-energy bonding orbital in a molecule mostly full of electrons, and which is the lowest unoccupied molecular orbital (LUMO), the lowest-energy anti-bonding orbital containing few (if any) electrons at room temperature. However, the HOMO will always be denoted by the highest-energy non-asterisk orbital (in Figure 10, the $\sigma_g(2p)$ orbital) while the LUMO will always be denoted by the lowest-energy asterisk orbital.

There are other molecular orbitals that form with the overlap of these orbitals with the d molecular orbitals, as well as nonbonding that occurs in the conditions described earlier, but the formation of σ and π bonds are the most important to understand organic semiconductors.

III.3 Energy Band Formation

Diatomic molecules contain bonding and anti-bonding orbitals within a single region in between the two atoms. In the case of organic polymers, the orbital formation leads to the presence of a quasi-continuous region of bonding and anti-bonding orbitals. Below is a schematic of this phenomenon:

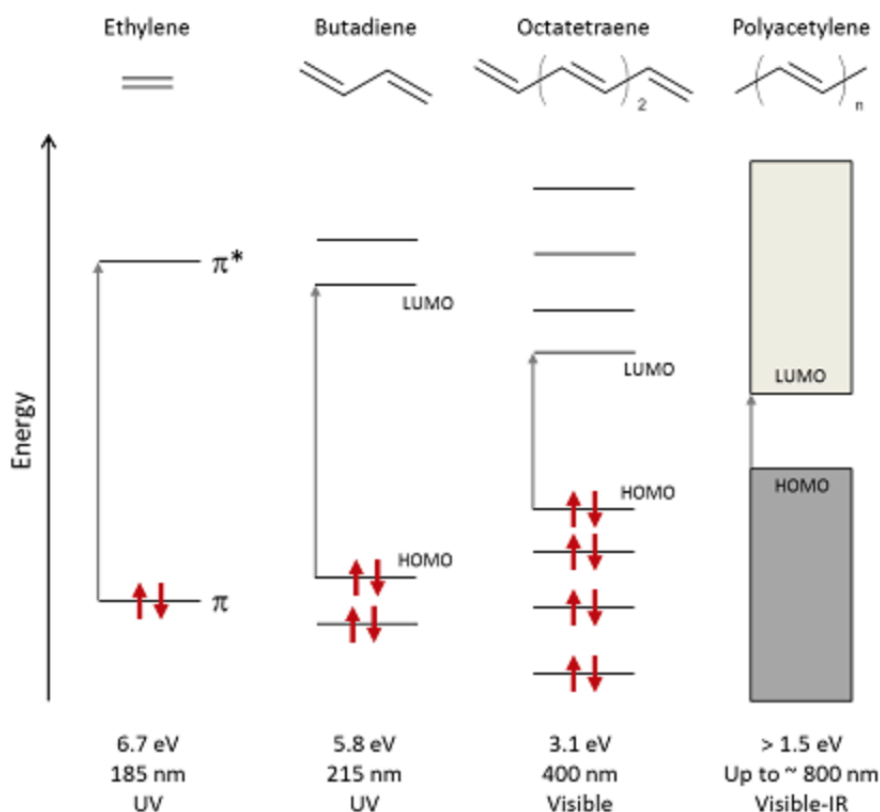


Figure 11: Schematic representing the formation of HOMO and LUMO levels as alkenes get longer [6]. The lowest energy optical transition lies between the top of the HOMO levels and the bottom of the LUMO levels.

As opposed to inorganic semiconductors, which are held together by stronger covalent bonds in a crystalline structure, organic semiconductors are made of molecules held together by weaker Van der Waals forces in chains and sheets. Van der Waals forces include the electron repulsion due to the Pauli exclusion principle explained earlier, the attractive and repulsive electrostatic interactions between ions, dipoles, quadrupoles, and other general multipoles [7]. As a result, the energy splittings actually reflect overlapping molecular orbitals, rather than the strong atomic orbital overlap present in inorganic semiconductors. The energy bands that form in organic semiconductors result from the overlap of π orbitals, as opposed to the bands that form due to the potentials of overlapping periodic lattices. The rest of the information in this subsection is a technical aside, and you can skip to subsection III.4.

Technical Aside

As the alkene chains get longer, the interactions between atoms and molecules becomes more complex [6]. Because of the Pauli exclusion principle, as established earlier, no two electrons can be in the same state [6]. As a result, the orbitals form at different energy levels but get closer together, becoming more “bunched up” as evident in the difference between the orbitals in butadiene and octatetraene in Figure 11. Eventually, for long polymer chains, the bonding orbitals become quasi-continuous, as do the anti-bonding orbitals. Then, the only significant gap left is that between the HOMO and the LUMO, which is the bandgap in an organic semiconductor.

Below is a schematic that demonstrates the band formation from overlapping π orbitals in benzene:

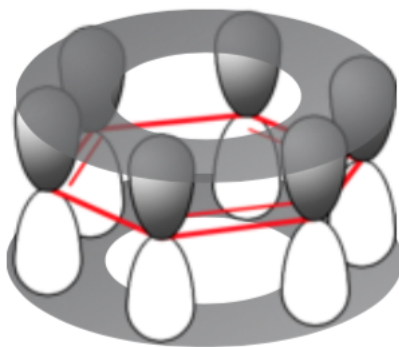


Figure 12: Schematic of band formation in a benzene molecule [3].

This electron delocalization makes sense in the context of molecular orbital theory discussed earlier. Going back to Figure 8b, the diagram shows the formation of delocalized bonding regions when p_x orbitals overlapped, such that regions of like signs combined to form a large region within which electrons could move. This is in contrast to the combined orbital shape in σ bond formation, where both σ and σ^* orbitals trap the electrons between atoms. Even if many σ or σ^* regions overlapped, electrons would always be trapped between two nuclei at best, but if many p_x orbitals overlapped side-by-side as shown in Figure 8b, then the delocalized regions would be larger and extend the length of the molecule, allowing for band-like transport.

In practice, some highly-crystalline organic semiconductors, like crystallized rubrene, have a regular enough structure to allow for such band-like transport. However, usually transport bands in organic semiconductors are not as smooth and straight in energy space as those of inorganic semiconductors. Thus, instead of a band transport model to describe carrier motion akin to that used to describe inorganic semiconductors, a “hopping transport” model involving phonon-assisted tunneling is used.

III.4 Absorption and Emission

For small and medium-sized organic semiconductor molecules, the conduction and valence energy levels do not really come in bands, but rather disjoint energy levels because the disorder in the semiconductor material yields uneven, unstructured molecular orbital overlap. Such molecules can be modeled as anharmonic oscillators, where the asymmetry results from the leveling off of the molecular energy due to the atoms being sufficiently far apart (accurately predicts electrons being able to dissociate from and escape their host atoms if they absorb enough energy, which a harmonic well would not allow for). The energy wells of interest in these anharmonic oscillators are formed by the energy level (HOMO or LUMO level) in question, and the energy levels within these oscillator potential wells are the vibrational levels in the molecule. Below is an energy schematic illustrating this [3]:

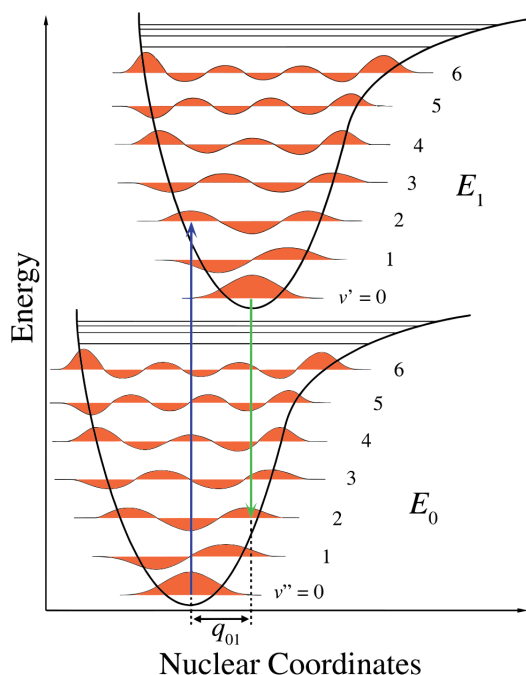


Figure 13: Illustration of the anharmonic oscillator model of vibrational energy levels in organic semiconductors. E_0 is the HOMO, E_1 is the LUMO in this case.

To properly understand this schematic, you need to understand that the anharmonic potential wells (the deformed parabolas) are plotted on these energy vs. nuclear coordinates axes, but the wavefunctions (sinusoid shapes within the potential wells) are NOT plotted on these axes – the curves reflect deviations of the wavefunction from 0, and both positive and negative deviations reflect a higher probability of electron being at a particular nuclear coordinate for a given vibrational level ν or ν' (which you can also see with the orange shaded regions).

Because optical transitions are on the timescale of 10^{-14} s, which is much shorter than the timescale of nuclear coordinate motion, optical transitions are portrayed as vertical in Figure 13 above. This is the justification for the **Franck-Condon principle**, which states that optical transitions are most likely when there is high vibrational wavefunction overlap for the different energy levels [3]. In this case, "wavefunction overlap" refers to the integral

$$\langle \psi_{\nu'} | \psi_{\nu''} \rangle = \int dq \psi_{\nu'}^*(q) \psi_{\nu''}(q) \quad (17)$$

which you can visualize partly by picturing the amount of overlap (of the the shaded orange regions) if the horizontal lines of the desired wavefunctions (eg. $\nu'' = 0$ and $\nu' = 1$) are laid on top of each other (in Figure 13, the vertical positions of $\nu'' = 0$ and $\nu' = 1$ reflect the energies of these levels, not the actual values of the wavefunctions – it's the deviation from the horizontal line that reflects the wavefunction). This overlap integral calculates the probability of a transition from state ν'' to ν' .

The consequence of this is that even photons with energy higher than the bandgap cannot always be absorbed. The higher the value of the overlap integral Equation 17, the more probable a given transition. Check out this link on the Franck-Condon principle for a more detailed explanation of the effects of overlap on the energy spectra.

III.4.1 Exercise

1. Graph $S_{00}/\sqrt{\pi}$ and $S_{01}/\sqrt{2}$ from this link (factors of $\sqrt{\pi}$ and $\sqrt{2}$ for normalization purposes) as a function of bond length change $R_e - Q_e$ with $\alpha = 1$ (you can do this by setting

$R_e - Q_e = x$ and graphing the result, as long as you remember that x is a CHANGE in bond length, and not a coordinate in absolute space).

2. What is the most likely change in bond length for the $\nu'' = 0$ to $\nu' = 0$ transition? (providing the value of x will suffice, and no need for units). Is this reflective of a vibration?
3. What is the most likely change in bond length for the $\nu'' = 0$ to $\nu' = 1$ transition? (providing the value of x will suffice, and no need for units). Is this reflective of a vibration?
4. If you consider the maximum possible values of $S_{00}(x)/\sqrt{\pi}$ and $S_{01}(x)/\sqrt{2}$ across all bond length changes, which transition is more likely?

III.4.2 Exercise

Earlier in the exam, you determined whether the J_{sc} and V_{oc} of a solar cell would depend on band gap or not, and if so then how raising or lowering said bandgap would affect each.

1. Based on Figure 13 and this page on the Franck-Condon principle, does a nuclear displacement between the ground and excited state of such a system effectively increase or decrease the bandgap? Justify your answer.

The Franck-Condon principle explains **Kasha's Rule**, which states that emission typically only happens from the lowest excited state, regardless of the excitation energy [8]. Because there is high spatial wavefunction overlap between the higher excited states and the lower excited state, such as between $\nu' = 2$ and $\nu' = 0$, such intra-energy-level transitions happen quite readily. The overlap is greatest when not only position but momentum overlap, which means that electrons in higher excited states will relax most readily into the lowest excited state before fluorescing by relaxing to a vibrational state in a lower energy level. As a result, for the most part the emission wavelength is independent of the absorption wavelength.

III.4.3 Exercise

One implication of Kasha's Rule is that carriers that are excited into a higher vibrational state (eg. from $\nu'' = 0$ to $\nu' = 1$) will likely relax down to the lowest excited state (i.e. $\nu' = 0$) before they can be collected to generate a solar cell current $J(V)$ at a given voltage.

1. How would this phenomenon affect solar cell efficiency, and why?
2. Which of the fundamental solar cell losses, as described in this paper, is represented by this phenomenon? Explain.

IV Excitons

When charge carriers are excited in organic semiconductors, they form excitons, which are electron-hole pairs bound by the Coulomb force. In this section, we will explore how excitons impact organic solar-cell efficiency compared to inorganic ones.

IV.1 Exciton Radii

Figure 14 shows diagrams of two different types of excitons – Wannier excitons and Frenkel excitons. An exciton consists of an electron orbiting a hole, which means to first order, we can semi-quantitatively treat the electron as if it is in a hydrogen atom. It can be shown that the most likely distance between the lowest-energy electron and the nucleus, in the quantum-mechanical description) of a hydrogen atom is

$$r_0 = a_0 \text{ where } a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \quad (18)$$

a_0 is the **Bohr radius**, the radius for a hydrogen atom that Bohr predicted (accidentally getting it right despite his quantum-mechanical description being wrong). μ is the reduced mass of the two-particle system (electron-proton for the hydrogen atom, electron-hole for the exciton). The Bohr radius is effectively dictated by the interplay between the Coulomb potential energy and the overall kinetic energy of the electron-proton system, although fully illustrating this would require quantum mechanics beyond the scope of this exam (but you can check out derivations of the hydrogen atom equations, energies, etc. for a full description).

The average electron distance, on the other hand, is calculated in quantum mechanics in a slightly different fashion:

$$\bar{r}_0 = \int_0^\infty \psi_{100}^* r \psi_{100} (4\pi r^2) dr \text{ where } \psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad (19)$$

where the $4\pi r^2$ term comes because we are integrating over spherical coordinates.

IV.1.1 Exercise

1. Calculate the integral in Equation 19 to evaluate \bar{r}_0
2. Is this value equal to the most probable electron distance calculated earlier? Does this make sense? Explain why or why not using the probability distribution sketched in this reference.



Figure 14: Side-by-side comparison of Wannier vs. Frenkel excitons [9].

Independent of your answers to the previous exercise, you should note that both $r_0 \propto a_0$ and $\bar{r}_0 \propto a_0$ (which should make sense from a dimensional analysis perspective). For an exciton, we have an electron-hole system within a material, rather than an electron-proton in free space. The electronic interactions with the material can be summed up by a modification of **dielectric constant** used to express the Coulomb potential energy in free space. We replace ϵ_0 with $\epsilon = \epsilon_r \epsilon_0$ where ϵ_r varies by material and can be measured. Then, the Coulomb potential of a hole in a semiconductor becomes

$$V(r) = \frac{e^2}{4\pi\epsilon r} \quad (20)$$

IV.1.2 Exercise

Based on the previous description about the radius of a hydrogen atom and the factors impacting it,

1. How does modifying this Coulomb potential, as done in Equation 20, change the radius of the exciton? Express the new radius a in terms of a_0 .
2. Since the dielectric constant ϵ reflects the extent to which atoms are polarized in the presence of an electric field, with higher dielectric constants indicating greater polarization, is it possible for $\epsilon_r < 1$? Explain.

The energy of such an exciton with radius a (analogous to the energy of the ground-state electron of a hydrogen atom) is given by

$$E = -\frac{\hbar^2}{2\mu a^2} \quad (21)$$

where the energy is negative because $E = 0$ is defined as the energy of an electron an infinite distance away from a positive charge.

Since the binding energy of an exciton depends on electron-hole distance, it is not tied to the material band gap per se. In particular, it can be (and often is) less than the band gap energy.

IV.1.3 Exercise

1. Using Equation 21, describe the dependence of the exciton binding energy on the relative permittivity ϵ_r .
2. Inorganic semiconductors like GaAs tend to have larger ϵ_r while organic semiconductors tend to have much smaller ϵ_r . Based on this,
 - (a) Are inorganic semiconductors more likely to have Wannier excitons or Frenkel excitons?
 - (b) Are organic semiconductors more likely to have Wannier excitons or Frenkel excitons?
 - (c) What does this say about the strength of the Coulomb interaction between electrons and holes in inorganic vs. organic semiconductors?
 - (d) Are exciton binding energies likely to be higher in organic or inorganic semiconductors?
3. Charge carriers should be able to move freely in order to be efficiently captured by a solar cell to generate power. Based on the answers to the previous questions about exciton binding energy, can charge carriers be more effectively captured in inorganic or organic semiconductors? Justify your response. (**HINT:** Excitons can absorb additional energy to excite the electrons and holes enough for them to separate from one another, but this additional energy absorption entails losses).

V Data Analysis Primer

When discussing the efficiency of solar cells, two different figures are used to better describe the device and highlight which factors cause the most significant deviations from 100% efficiency. The internal quantum efficiency (IQE) reflects the fraction of absorbed photons that generate current, while the external quantum efficiency (EQE) indicates the fraction of incident photons that give rise to current [10]. This means that a device with good charge transport properties but low absorption, either because the surface is very reflective or the material is very transparent, will have a high IQE but a low EQE. In this section, we will be looking at experimental data of EQE as a function of incoming photon energy to determine which photon energies give rise to a good amount of device current.

V.1 External Quantum Efficiency

Recent work has demonstrated that the interface between an organic donor of special interest, crystalline rubrene, and one particular organic acceptor, C₆₀ gives rise to photocurrent (i.e. current resulting from the excitation of charge carriers by light) that results from direct excitation of excitons [11]. Figure 15 shows the EQE at different photon energies in different systems. The graph shows the abrupt cut-off in EQE at 1.6 eV for C₆₀, which is its bandgap [11]. Figure

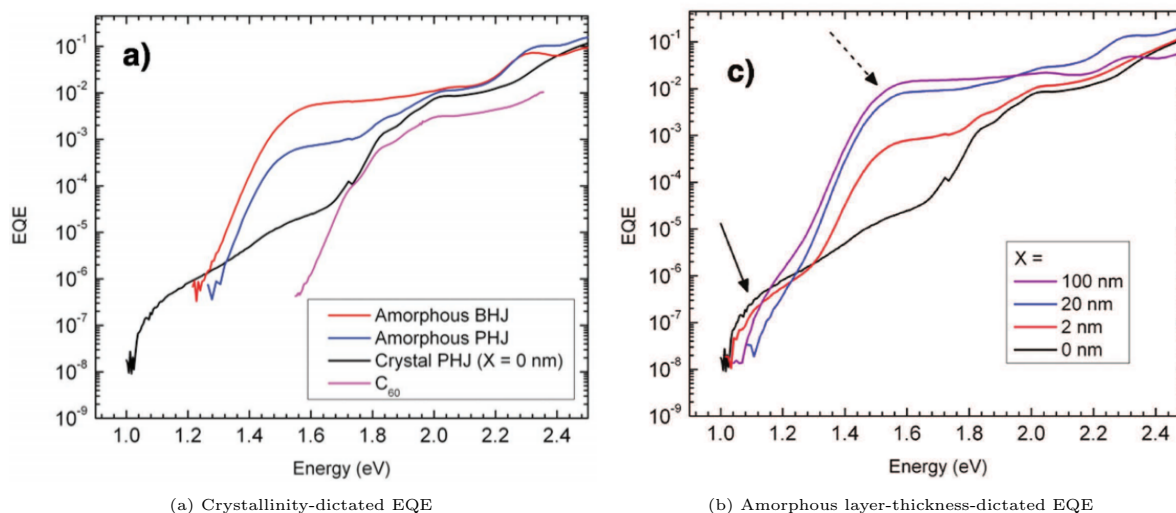


Figure 15: EQE as a function of the energy of incoming light. The crystal planar heterojunction has a nonzero EQE for energies as low as 1.05 eV. 15a shows how an absolute crystalline vs. amorphous device affects EQE, while 15b shows how varying the thickness of an amorphous rubrene- C_{60} layer on top of a crystalline layer of rubrene affects the CT state.

15 shows how factors such as using bulk (BHJ) vs. planar heterojunction (PHJ) structures, crystallization of a structure, and layer thicknesses can affect the EQE curves. Don't worry too much about these details, but pay special attention to the difference between the curves of amorphous vs. crystalline PHJs.

V.1.1 Exercise

Rubrene has a higher bandgap than C_{60} . Given that EQE measures the ability for electrons and holes to be excited and collected in the device at a given photon energy,

1. Would you expect a non-zero EQE at energies below 1.6 eV for a rubrene- C_{60} system? Why or why not?
2. Based on the answer to the previous part, how does the EQE data provide evidence of the excitation of exciton excitation?

The arrows in Figure 15b indicate the exciton binding energies, because the EQE starts leveling off a bit after these arrows. These "humps", therefore, represent a sudden jump in the ability of the device to harness charge carriers because the excitons have been excited, and the electrons and holes have been freed from each other.

VI Data Analysis

VI.1 Extracting Exciton Energies from EQE

Figure 16 contains plots of all of the EQE data collected:

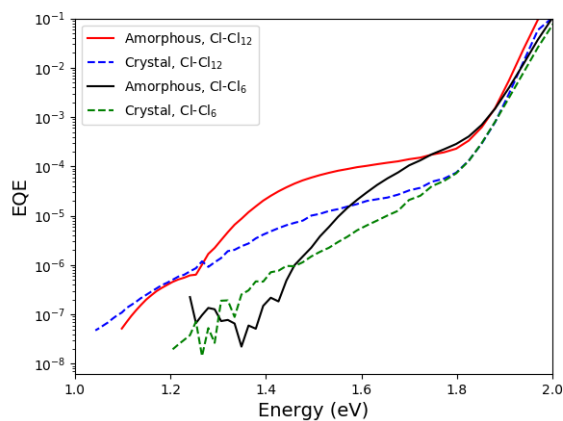


Figure 16: EQE vs. photon energy plot for crystalline and amorphous rubrene devices using Cl_6 -BsubPc-Cl and Cl_{12} -BsubPc-Cl as the acceptors.

Figure 17 illustrates data with curve fits to more accurately extract exciton energies (I don't remember why this data looks different from Figure 16 – bear with me here).

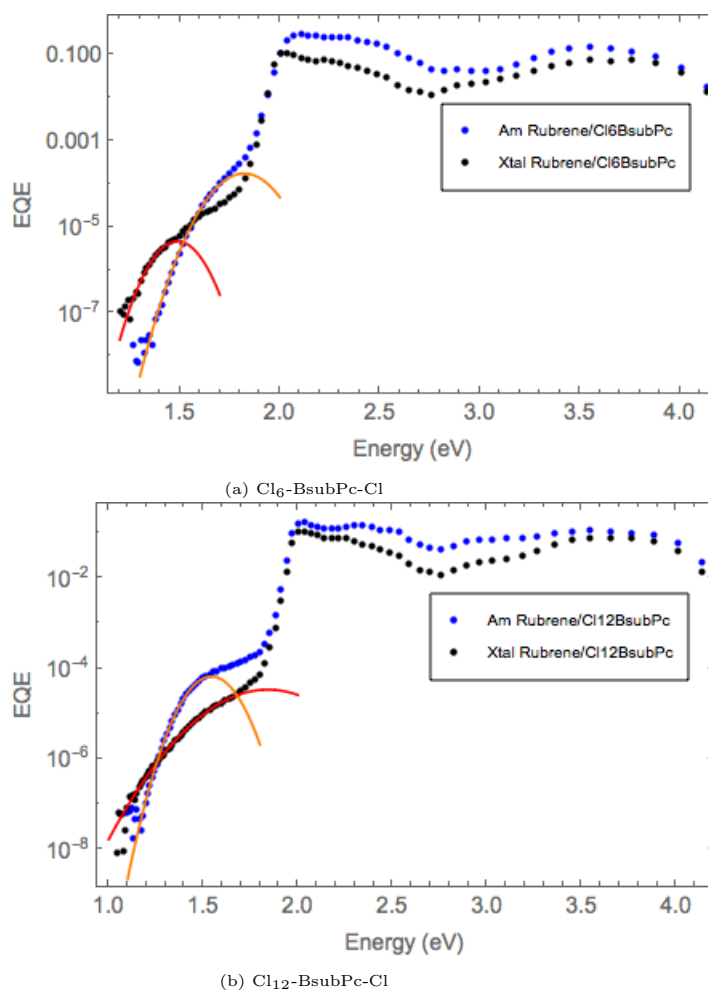


Figure 17: Comparison of curve fits for Cl_6 -BsubPc-Cl and Cl_{12} -BsubPc-Cl acceptor molecules.

I used my graduate student advisor's fitting script to quantify the differences in extracted exciton energies between systems using amorphous and crystalline rubrene for both the Cl_6 and the Cl_{12} -based acceptors. Figure 17 display the plots that show the EQE data as well as fitted

curves. The curve to which they were fit was

$$EQE = \frac{A}{x\sqrt{4\pi\lambda kT}} e^{-(E+\lambda-x)^2/(4\pi kT)} \quad (22)$$

where x is the incoming laser light energy in eV, E is the exciton energy, and λ reflects the broadness of the shape. Below is a table that gives the fitted exciton energies obtained by the scripts:

	Amorphous	Crystalline	Difference
Cl ₆ -BsubPc-Cl	1.59 eV	1.34 eV	0.25 eV
Cl ₁₂ -BsubPc-Cl	1.36 eV	0.98 eV	0.38 eV
C ₆₀	1.48 eV	1.1 eV	0.38 eV

The "amorphous" vs. "crystalline" columns reflect the use of amorphous vs. crystalline rubrene. So the top left entry reflects the exciton binding energy in a system containing amorphous rubrene and the Cl₆-based acceptor.

VI.1.1 Exercise

Based on the data in the table, does the choice of acceptor affect the reduction in exciton energy observed when going from amorphous to crystalline rubrene? Explain.

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