How Light Interacts with Matter

The everyday objects around us are white, colored or black, opaque or transparent, depending on how the electrons in their atoms or molecules respond to the driving force of electromagnetic radiation

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The overwhelming majority of things we see when we look around our environment do not emit light of their own. They are visible only because they reemit part of the light that falls on them from some primary source, such as the sun or an electric lamp. What is the nature of the light that reaches our eyes from objects that are inherently nonluminous?

In everyday language we say that such light is reflected or, in some cases, transmitted. As we shall see, however, the terms reflection and transmission give little hint of the subtle atomic and molecular mechanisms that come into play when materials are irradiated by a light source. These mechanisms determine whether an object looks white, colored or black, opaque or transparent. Most objects also have a texture of some kind, but texture arises largely from the interplay of light and shadow and need not concern us here. I shall restrict my discussion mainly to the effect of white light on materials of all kinds: solids, liquids and gases.

White light, as it comes from the sun or from an artificial source, is a mixture of electromagnetic radiation, with wavelengths roughly between 400 and 700 nanometers (billionths of a meter) and an intensity distribution characteristic of the radiation from a body that has a temperature of about 6,000 degrees Celsius. When such light impinges on the surface of some material, it is either reemitted without change of frequency or it is absorbed and its energy is transformed into heat motion. In rare instances the incident light is reemitted in the form of visible light of lower frequency; this phenomenon is termed fluorescence. In what follows I shall take up the commonest forms of secondary light emission. I shall undertake to answer such familiar questions as: Why is the sky blue?

Why is paper white? Why is water transparent? What causes objects to appear colored? Why are metals shiny?

The answers are all based on the fact that the electrons of atoms are made to perform tiny vibrations when they are exposed to light. The amplitudes of these vibrations are extremely small: even in bright sunlight they are not more than 10⁻¹⁷ meter, or less than 1 percent of the radius of an atomic nucleus. Nevertheless, all we see around us, all light and color we collect with our eyes when we look at objects in our environment, is produced by these small vibrations of electrons under the influence of sunlight or of artificial light.

What happens when matter is exposed to light? Let us go back to the simplest unit of matter and ask what happens when an isolated atom or molecule is exposed to light. Quantum theory tells us that light comes in packets called photons; the higher the frequency of the light (and the shorter the wavelength), the more energy per packet. Quantum theory also tells us that the energy of an atom (or a system of atoms such as a molecule) can assume only certain definite values that are characteristic for each species of atom. These values represent the energy spectrum of the atom. Ordinarily the atom finds itself in the ground state, the state of lowest energy. When the atom is exposed to light of a frequency such that the photon energy is equal to one of the energy differences

between an excited state and the ground state, the atom absorbs a photon and changes into the corresponding excited state. It falls back to a lower state after a short time and emits the energy difference in the form of a photon [*see illustration on page 63*].

According to this simple picture the atom reacts to light only when the frequency is such that the photon energy is equal to the difference between two energy levels of the atom. The light is then "in resonance" with the atom. Actually the atom also reacts to light of any frequency, but this nonresonant reaction is more subtle and cannot be described in terms of quantum jumps from one energy level to the other. It is nonetheless important, because most of the processes responsible for the visual appearance of objects are based on responses to nonresonant light.

Fortunately the interaction of light with atoms can be described rather simply. One obtains the essential features of that interaction-in particular the reemission without change of frequencyby replacing the atom with electron oscillators. An electron oscillator is a system in which an electron vibrates with a certain frequency designated ω_0 . One can imagine the electron bound to a center with a spring adjusted so that there is a resonance at the frequency ω_0 . The electron oscillators we are using to represent an atom are designed so that their frequencies ω_0 correspond to transitions from the ground state to higher states.

LIGHT AND COLOR were brilliantly manipulated by the medieval artisans who created the stained-glass windows of the Gothic cathedrals. The photograph on the opposite page shows a detail of the Passion Window, in the west façade of the Cathedral of Notre Dame at Chartres. The window was made in the 12th century. Stained glass is given its color by adding metal oxides directly to molten glass or by burning pigments into the surface of clear glass. Both coloring methods are evident in the example on the opposite page. The details in the faces and in the folds of the garments were produced by painting the glass with an opaque brown pigment, which was then permanently fused to the glass.





COLOR-QUALITY MAP, technically known as a chromaticity diagram, indicates how closely the colors of printing inks, color film and color television can approach the fully saturated colors of the visible spectrum, represented by the boundaries of the white horseshoe-shaped curve. The numbers around the curve indicate wavelength in nanometers. The straight line at the bottom of the horseshoe marks the boundary of the nonspectral colors from bluish purple to purplish red. When mixed with the spectral color at the opposite end of the axis, these "c" (for "complementary") colors form white. Inward from the horseshoe colors decrease in saturation, meaning that they contain more than one wavelength. The area printed in color shows the range of hues and saturations attainable with inks of three colors: magenta ("red"), yellow and cyan ("blue"). The open circles at the perimeter indicate the pure inks at full density. The open circle in the center is the white of average daylight. The colored area is actually a continuum; the steplike structure simplified the specification of ink combinations. An optimum set of dyes for color film (*white triangles*) can reproduce all the printing-ink colors plus all the more saturated tones that lie between the colored area and the broken white outline. The red, green and blue phosphors (*black dots*) used in color television picture tubes can re-create all the colors inside the black triangle. The x axis specifies the proportion of red in a particular color, the y axis the proportion of green. The rest is blue and need not be specified.

They represent the resonance frequencies of the atom in the ground state. Each of these oscillators has a certain "strength," a measure of the probability of the transition it represents. Usually the first transition from the ground state has the largest strength; that being so, we can replace the atom with a single oscillator.

Another quantity that characterizes these oscillators is their resistance coefficient, or friction. Friction causes a loss of energy in the oscillating motion. It describes a flow of energy away from the vibration into some other form of energy. It indicates that energy is being transferred from the excited state by some route other than the direct transition back to the ground state. Thus whenever the excited state can get rid of its energy by means other than reemission of the absorbed quantum, the corresponding oscillator must be assumed to suffer some friction. This is an important point in our discussion, because excited atoms in solids or liquids transmit their excitation energy mostly into heat motion of the material. Unlike the isolated atoms found in rarefied gases, they have only a small chance of returning directly to the ground state by emission of a light quantum.

Henceforward I shall discuss the effect of light on atoms in terms of this oscillator model. We can now forget about photons and excited quantum states because one obtains correct results by considering the incoming light as a classical electromagnetic wave acting on classical electron oscillators. The effects of quantum theory are taken care of by the appropriate choice of oscillators to replace the atom. One can interpret the results of the oscillator model in such a way that under the influence of light the motion of the oscillators is superposed on the ordinary state of motion of the electron in the ground state. Whenever a light wave passes over the atom, a general vibration is set up in the ground state of the atom, a vibration of a kind and strength equal to the vibrations the oscillators of our model would perform if they were exposed to the light wave. The electron cloud of each atom vibrates under the influence of light. The cloud vibrates with the same frequency as the incoming light and with an amplitude corresponding to that of one of the model oscillators. It is this vibration, amounting to less than $10^{\cdot 17}$ meter in amplitude, that reemits the light by which we see the objects around us.

The light from the sun or from artificial sources is a mixture of light of many frequencies. The motion of an oscilla-



INTERACTION OF LIGHT WITH MATTER involves the absorption of a photon, or quantum of light, by an atom or a molecule. If the photon has the required energy, the atom or molecule will be raised from a low energy state to one of higher energy. After a short time the atom or molecule falls back to a lower state and the energy difference is emitted as a photon. Two simple pictures of the interaction are presented here. At the left a photon (*wavy arrow*) interacts with a Bohr model of an atom with five electrons (*top*). The photon raises an electron from the second, or 2s, orbit to the third, or 2p, orbit (*middle*). When the excited electron drops back to its former orbit, a photon is emitted (*bottom*). At the right the sequence is depicted in terms of energy-level diagrams. The photon supplies exactly the energy (ΔE) required to raise an electron from the 2s to the 2p level. These simple pictures are inadequate, however, for describing the typical interaction of visible light with matter, dealt with in this article. First, photon energy usually does not correspond to the energy difference between orbits. Second, when atoms in bulk matter are excited, they normally get rid of their energy by means other than the emission of a photon.

tor exposed to such a mixture is simply a superposition of all the motions it would perform if exposed separately to light of each frequency contained in the mixture. Hence all one needs to know for the study of atoms under the influence of light is the motion of oscillators driven by an electric wave of a specific frequency.

If an electromagnetic wave of frequency ω passes over an electron oscillator, the electric field exerts a periodic force and leads to certain characteristic responses [*see illustration on next page*]. First of all the periodic electric field induces a vibration of the oscillator so that it oscillates with the frequency ω of the field, not with its own resonance frequency ω_0 . The amplitude and the phase of this motion depend on the relative values of ω and ω_0 . If ω is much

smaller than ω_0 , the oscillation is weak and in phase with the driving electric force of the light. If ω is much larger than ω_0 , it is also weak but opposite in phase to the driving force. If ω is in resonance (in which case ω equals ω_0), the oscillation is strong and out of phase. That is, when the driving force is at its crest, the oscillation goes through the zero point. The amplitude of the oscillation follows a fairly simple mathematical formula that need not concern us here. The formula shows that if ω is much smaller than ω_0 , the amplitude is small but is almost independent of the driving frequency ω . If ω is much larger than ω_0 , the amplitude decreases with increasing ω at a rate proportional to $1/\omega^2$. Only the resonance case ($\omega = \omega_0$) corresponds to the simple picture of a transition to another quantum state.

What are the resonance frequencies in different atoms and molecules? Most of the simple atoms such as hydrogen, carbon, oxygen and nitrogen have resonances with frequencies higher than visible light; they lie in the ultraviolet. Molecules, however, can perform vibrations in which the atoms move with respect to one another within the molecule. Because of the large mass of the nuclei, such vibrations have very low frequencies; the frequencies are lower than those of visible light, in the infrared region. Hence most simple molecules such as O₂, N₂, H₂O and CO₂ have resonances in the infrared and ultraviolet and no resonances in the visible region. They are transparent to visible light. Nevertheless, visible light has an influence on them, which can be described by our oscillator picture. We replace the molecules by two kinds of oscillator, one representing the ultraviolet resonances, the other the infrared resonances. The latter are not really electron oscillators; they are "heavy" oscillators in which the mass of the oscillating charge is as large as the mass of the vibrating atoms, since they are supposed to represent the

motions of atoms within the molecule.

We are now ready to understand one of the most beautiful colors in nature: the blue of the sky. The action of sunlight on the molecules of oxygen and nitrogen in air is the same as the action on the two kinds of oscillator. Both oscillators will vibrate under the influence of visible sunlight. The amplitude of the infrared oscillators, however, will be much smaller than the amplitude of the ultraviolet oscillators because of their higher vibrating mass. Accordingly we need to consider only the oscillators with ultraviolet resonance. When the oscillators are under the influence of visible sunlight, the force that drives them is below the resonance frequency. Therefore they vibrate with an amplitude that is roughly equal for all visible frequencies [see illustration on opposite page].

We must now take into account the fact that a vibrating charge is an emitter of light. According to a principle of electrodynamics an electron oscillating with an amplitude A emits light in all directions with an intensity given by a formula in which the intensity of the radiation is proportional to the fourth



RESPONSE OF OSCILLATOR TO PERIODIC DRIVING FORCE serves as a model of how the electrons of an atom respond to the driving force of light. The response of each oscillator (b, c, d, e) depends on its particular resonance frequency, ω_0 . The driving force (a) has a frequency of ω . When ω_0 is much greater than ω , the oscillator responds in phase but only weakly (b). When ω_0 equals ω , the response reaches a maximum and is 90 degrees out of phase (c). When ω_0 is much less than ω , the response is again weak and 180 degrees out of phase (d). This weak response closely resembles the response of a free electron (e).

power of the frequency. (The formula is $1/3(e^2/c^3)\omega^4 A^2$, where e is the charge of the electron, c the velocity of light and ω the frequency of oscillation.) Hence the molecules of air emit radiation when they are exposed to sunlight. This phenomenon is known as Rayleigh scattering. It is called scattering because part of the incident light appears to be diverted into another direction. Whenever we look at the sky but not directly at the sun, we see the light radiated by the air molecules that are exposed to sunlight. The scattered light is predominantly blue because the reradiation varies with the fourth power of the frequency; therefore higher frequencies are reemitted much more strongly than the lower ones.

The complementary phenomenon is the color of the setting sun. Here we see solar rays that have traveled through the air a great distance. The higher-frequency light is attenuated more than light of lower frequency; therefore the reds and yellows come through more strongly than the blues and violets. The yellowish tint of snowy mountains seen at a distance is a similar phenomenon. The stronger attenuation of higher frequencies is a consequence of the conservation of energy: the energy for the reradiation must come from the incident sunlight, and because there is stronger reradiation at the higher frequencies more energy is taken from the sunlight at higher frequencies.

In actuality Rayleigh scattering is a very weak phenomenon. Each molecule scatters extremely little light. A beam of green light, for example, goes about 150 kilometers through the atmosphere before it is reduced to half its intensity. That is why we can see mountains at distances of hundreds of miles. Lord Rayleigh exploited the phenomenon of light scattering to determine the number of molecules in a unit of volume in air. In 1899 he was admiring the sight of Mount Everest from the terrace of his hotel in Darjeeling, about 100 miles away, and he concluded from the dimness of the mountain's outline that a good part of its light was scattered away. He determined the scattering power of each molecule from the index of refraction of air, and he found the number of air molecules per cubic centimeter at sea level to be 3×10^{19} , which is very close to the correct value.

Now we know why the sky is blue. Why, then, are clouds so white? Clouds are small droplets of water suspended in air. Why do they react differently to sunlight? The water molecule also has resonances in the infrared and in the ultraviolet, resonances not much different from those of oxygen and nitrogen molecules. Water molecules should react to sunlight in a similar way. There is, however, an essential difference. We determined the scattering of sunlight in air by assuming that each molecule reradiates independently of the others, so that the total scattered intensity is the sum of the individual molecular intensities. That is correct for a gas such as air because gas molecules are located at random in space, and thus there is no particular interference among the individual radiations of the molecules in any direction other than the direction of the incident sunlight.

That is no longer the case when the molecules or atoms take on a more orderly arrangement, as they do in solids and liquids and even in the droplets of a cloud. In order to understand the effect of light on matter in bulk, we must study how electromagnetic waves react to a large number of more or less regularly arranged oscillators, when the average distance between the oscillators is small compared with the wavelength of visible light. As we have seen, under the influence of incident light every oscillator emits a light wave. Because the oscillators are no longer randomly spaced, however, these waves tend to interfere with one another in a definite way: there is constructive interference in the forward direction (the direction of the light path) and destructive interference in all other directions. The individual waves build up to a strong wave called the refracted wave; in any other direction the waves tend to cancel one another. If the oscillators are in a regular array, the cancellation is complete [see illustration on next page].

The refracted wave travels with a velocity v that differs from the ordinary light velocity c. The ratio c/v is called the refractive index n of the medium. There is a simple relation connecting the value of n with the amplitude A of the oscillator vibrations. The greater this amplitude is under the influence of a given and fixed driving force, the more n departs from unity. Knowing the refractive index of air, Lord Rayleigh used this relation to find the amplitude in sunlight of the oscillators representing the air molecules.

In a regular and uniform arrangement of atoms the reemitted waves build up to a single refracted wave. There is no individual, or incoherent, scattering by each oscillator, as occurs in a gas such as air. As long as a crystal or a liquid contains heat it cannot be



OSCILLATOR AMPLITUDE is a function of the ratio between the frequency of the driving force, ω , and the oscillator's resonance frequency, ω_0 . This ratio, ω/ω_0 , is expressed in the horizontal scale, which is logarithmic. The amplitude approaches a constant value (*left*) when the driving frequency is much below resonance. This is the situation when molecules of nitrogen and oxygen in the atmosphere are exposed to visible light. When the driving frequency is much above resonance, the amplitude decreases as the square of ω/ω_0 .

completely regular. The atoms or molecules are constantly vibrating, and in addition there are always some irregularities and imperfections in the crystal structure. These irregularities scatter some of the light away from the direction of the refracted wave. This scattering, however, is much weaker than the scattering in air, assuming equivalent numbers of atoms. For example, water is 1,000 times denser than air, but its incoherent molecular scattering is only five times greater per unit volume than the scattering in air that makes the sky blue.

Now let us see what happens when light impinges on the surface of a liquid or a solid or a cloud droplet. Again we replace each atom by an oscillator. These oscillators vibrate under the influence of the incident light and emit light waves. In the bulk of the material all these light waves, apart from the weak incoherent scattering, add up to one strong refracted wave. This is not so, however, near the surface of the material. There is a thin layer of oscillators at the surface (about as deep as half a wavelength) for which the back radiation is not completely canceled by interference. The radiations backward of

these oscillators add up to a "reflected" wave [see illustration on page 67].

What is the color of this reflected light if the incident light is white? One might perhaps conclude that it should be as blue as the sky, since it too comes from the reradiation of oscillators and we have learned that the intensity of this reradiation is proportional to the fourth power of the frequency. Actually it is as white as the incident light. The intensity of the reflected light with respect to the incident light in water, glass or crystals is practically independent of the frequency.

The explanation is that the reflected wave is a coherent composite of many individual reradiations. The oscillators, since they are not randomly distributed, reradiate in unison. That by itself would not yet explain the difference; it would only tell us that the reradiated intensity is high. In a coherent radiation it is the amplitudes that add up and not the intensities. Hence N coherent oscillators give N^2 times the intensity of one individual radiation. It still would seem that the reradiation should be blue, inasmuch as the radiation intensity of each oscillator increases strongly with frequency. What happens, however, is that the



REFRACTED WAVE IN CRYSTAL consists of a parallel series of plane waves (*dark color*) formed by the crests of many spherical waves (*black circles*). The spherical waves depicted here represent

light reemitted by the atoms (*black dots*) in a crystal that is exposed to a light beam entering from the left. The refracted wave is traveling to the right. The situation in glass and water is similar.

number of oscillators acting in unison also depends on the frequency: the layer that gives rise to reflection is half a wavelength deep, and the area of the layer whose reflected light arrives in step, or with the same phase, at a given point in space is also proportional to the wavelength. (This area is known as the first Fresnel zone. The radiations from all other parts of the surface interfere with one another, so that they give no light at that point.) Hence the number \tilde{N} of oscillators producing light in unison is proportional to the square of the wavelength. The intensity of this light is proportional to N^2 . The net effect is to cancel the fourth power of the frequency, because higher frequency means smaller wavelength and a smaller value of N. As a consequence the reflected-light intensity is independent of frequency. Therefore clouds are white: the incident sunlight is reflected at the surface of the water droplets without change in spectral composition.

On the same basis we can understand the transparency of water, of glass and of crystals such as salt, sugar and quartz. If light impinges on these substances, it is partially reflected at the surface but without preference for any color. The rest of the light enters the substance and propagates as a refracted wave within it. Therefore these objects look colorless. Their outlines are nonetheless visible because of the reflection of the light at the surfaces.

Sometimes such objects may exhibit color under special circumstances. Reflection and refraction are only approximately independent of frequency. Both increase slightly at higher frequencies because such frequencies are a little closer to the natural resonance of the atom. Although these differences amount to only a few percent, they can become important if the details of refraction and reflection are critically involved in the way the light returns to the observer. Then, as in the case of a rainbow, these small differences may spread white light into its constituent colors.

Transparent substances with a large smooth surface reflect part of the incident light in a fixed direction according to the familiar laws of reflection. Therefore extended plane surfaces of colorless substances (windowpanes, water surfaces) can produce mirror images. If such colorless substances are in the form of small grains, each grain being larger than the wavelength of light, the substances appear white, like clouds. The incident white light is partially reflected in many directions, depending on the orientation of the grain surfaces. The light that penetrates the grains is again partially reflected at the inside surfaces, and after several reflections and refractions it comes back to the eye of the observer from various directions. Since none of these processes discriminates against any color, the returning light will be white and diffuse. This explains the color of snow, of salt and sugar in small grains and of white pills and powders: all consist of small crystals of molecules with resonances only in the infrared and in the ultraviolet. The whiteness of paper has the same origin. Paper consists of an irregular weave of transparent fibers [see illustrations on next page]. The molecules of the fibers also have no resonances in the visible region. The fibers reflect and refract light in the same way as fine grains of salt or snow. If the grains are smaller than the

gion. The fibers pale mixture of white and blue—far from the same way the deep, rich blue that prevails where the air is clear.

Although water is transparent because

wavelength of light, there are not

enough oscillators in the grain to estab-

lish ordinary reflection and refraction.

The situation is then more as it is in a

gas of independent molecules, and the

substance looks bluish. One can see this

on a dry day when a cloud disappears.

What often happens is simply that the

droplets become smaller and smaller by

evaporation until the cloud appears blue.

The blue color of cigarette smoke is also

evidence that the particles are smaller

than the wavelength of visible light. The

color of the sky above our cities is largely

determined by the way sunlight is scat-

tered by particles of smoke or dust, some larger than the wavelength of light, some

smaller. That is why the city sky is a



REFLECTION OF LIGHT from the surface of a solid or liquid involves only the oscillators (electrons) located in a small, pillbox-shaped volume at the surface of the material. When light (1) impinges on a smooth surface, part of the light proceeds into the material as a refracted wave (R) and part is reflected toward the observer (P) makes up the reflected wave originates in a thin layer whose thickness is about half the wave-length of the incident light. The oscillators whose radiation adds up coherently at P are contained in a flat cylinder whose top surface is about λd in area, where λ is the wave-length of the light and d is the distance from the surface to the observer. This area is called the first Fresnel zone. For a spherical surface of radius R the area of the first Fresnel zone is equal to $\pi\lambda R$, provided that the distance to the observer is large compared with R.

it has strong resonances only in the infrared and the ultraviolet, it does have a slight color of its own. This is not the wonderful deep blue one often sees on the surface of a lake or an ocean. That blue is the reflected color of the sky. The intrinsic color of water is a pale greenish blue that results from a weak absorption of red light. Because of its strong electric polarity the water molecule vibrates readily when it is exposed to infrared radiation. Indeed, its infrared resonances are so strong that they reach even into the visible red [*see top illustration on page 70*].

These resonances represent true ab-

sorptions of light because the energy of the light quantum absorbed is transformed into heat motion. The weak resonances in the visible red therefore cause a slight absorption of red light in water. Fifteen meters of water reduces red light to a quarter of its original intensity. Practically no red sunlight reaches a depth below 30 meters in the sea. At such depths everything looks green. Many deep-sea crustaceans are found to be red when they are raised to the surface. In their normal environment they appear black. The selection mechanisms of evolution could not distinguish between black and red under such conditions.



ORDINARY PAPER consists of a random mesh of translucent cellulose fibers. This 125diameter magnification was made with a scanning electron microscope by Consolidated Papers, Inc. In such a micrograph the object appears to be tilted at an angle of 45 degrees.



REFLECTION OF LIGHT FROM PAPER SURFACE involves many refractions and reflections as the rays of incident light perform a random walk through a mesh of translucent fibers, represented here in cross section. The multiple refractions of a single entering beam are traced in dark color; beams reflected from various surfaces are shown in light color.

The greenish-blue color of water is different in kind from the blue color of the sky. It is a color produced by the preferential absorption of the red and not by the preferential reemission of the blue, as it is in the sky. One way to be convinced of this difference between air and water is to look at a white object under the surface of water: it looks bluish green. On the other hand, a snowy slope seen through many miles of air looks yellowish. In the first instance the red light was absorbed; in the second the blue light was scattered away.

 M ost of the colors we see around us are due to preferential absorption: the colors of leaves, flowers, birds, butterflies, rubies, emeralds and the whole gamut of paints and dyes. What accounts for the preferential absorption in such a diverse range of things and substances? Most atoms and molecules have resonances only in the infrared and the ultraviolet. In order to produce a resonance in the visible region the excitation energy must be between 1.5 and three electron volts. These are rather small values for electron excitations and large values for molecular vibrations. There are, however, atoms and molecules that do have excited states in that region. They are atoms with several electrons in incomplete shells and certain organic compounds: the dyestuffs. Such atoms can be excited by rearranging the electrons in the incomplete shell, which requires less energy than excitation to a higher shell. The dyestuffs are chain or ring molecules in which the electrons move freely along the chain or the ring. They are spread out, so to speak, over larger distances than electrons in ordinary atoms and molecules. The excited states in such a system are of lower energy than they are in atoms, because larger size gives rise to longer electron wavelengths, and this in turn is associated with lower frequency and thus lower excitation energy. Thousands of chemists have devoted their professional lives to the synthesis of organic molecules that have resonances in one part or another of the visible spectrum [see illustration on opposite page].

Although low-lying excited states give rise to resonance frequencies in the visible region, other conditions must be fulfilled before a molecule will serve as a dye. First, one must be sure that the light quantum is not simply reemitted after its absorption has lifted the molecule into the excited state. One wants the energy of the excited state to be transformed preferentially into heat motion. This will be the case if we deal with matter in bulk, liquid or solid. Under such circumstances reemission of light is very improbable. Second, the resonance frequencies must be spread over a broad interval. A dye with a narrow absorption band would reflect most wavelengths and thus look practically white. Here again matter in bulk contributes to the desired effect. In liquids and solids the energy levels of atoms or molecules are expanded into broad energy bands, with the result that resonances are spread over broad ranges of frequency. For example, a red dye absorbs light of all visible frequencies except the red. A green paint absorbs red and yellow as well as blue and violet. The absorption of a dye covers the visible spectrum with the exception of the actual color of the material. Some people may have wondered why a mixture of paint of all colors gives rise to a dirty black, although we are told that white is the sum of all colors. Colored paints function not by adding parts of the spectrum but by subtracting them. Hence a mixture of red, green and blue paints will absorb all wavelengths and look virtually black.

simple and striking color effect is the one produced by a stained-glass window. The dyestuff is contained in the glass. When light falls on stained glass, it is partially reflected at the surface, just as it is by ordinary glass. Indeed, the reflection is a little stronger for those frequencies that are absorbed, because, as we saw earlier, the amplitude of vibration is larger when the frequency is in resonance with the system. This effect, however, is usually not very pronounced, since the main reflection comes from the oscillators with resonances in the ultraviolet, as it does in ordinary glass. The part of the light that penetrates the body of the glass-the refracted wave-is subjected to the absorbing effect of the dye. Accordingly only light of the frequency that is not absorbed will pass through the glass. That is why one obtains such impressive color effects when white light penetrates stained glass. The color of the glass is less strong when one looks at the side that is illuminated. The reflection from the surface is practically colorless; the principal color one sees is from light that has penetrated the glass and is reflected again by the second surface [see bottom illustration on next page].

A painted sheet of paper will serve as an example of ordinary painted objects. The paint causes the fibers of the paper to become impregnated with dye. When white light falls on paper, it is reflected and refracted many times before it comes back to our eyes. Whenever the



SPECTRAL CHARACTERISTICS of colored inks (*solid curves*) and of an optimum set of dyes for color film (*broken curves*) are plotted in these three panels. The inks and dyes are those represented in the illustration on page 62. There it can be seen that the dyes of color film can produce colors that are more highly saturated than those attainable with printing inks. The reason becomes clear in these curves: each of the color film dyes transmits more of the desired wavelengths than the corresponding printing ink is able to reflect.

light penetrates a fiber, the dye absorbs part of it: the fibers act as small pieces of stained glass. The best color effect is achieved when the reflecting power of the fiber is not too strong, so that most of the light enters the fiber. One remembers childhood experience with watercolors, which are most intense while the paper is still wet. The water reduces the difference in refraction between the fibers and the interstices, thereby reducing the reflection of the fiber surfaces.

Glossy colored paper has a smooth surface. Its irregularities are small compared with the wavelength of light. The incident light is partially reflected without much preference for one color over another, but it is reflected by the smooth surface at a fixed angle according to the familiar laws of reflection. At any other



LIGHT ABSORPTION BY WATER is negligible between 400 and 580 nanometers in the visible part of the spectrum. The absorption increases in the orange and red region and rises steeply in the near infrared. Absorption is also strong in the ultraviolet. The absorption is caused by resonances of the water molecule in response to various wavelengths.



COLOR OF STAINED GLASS depends on which wavelengths the glass absorbs. Here it is assumed that the glass absorbs the shorter wavelengths so that primarily red light is transmitted. Thus blue light, represented here by black, enters the glass and is absorbed; it is also partially reflected. Red light is reflected from the rear surface as well as from the front, so that the total reflected light is predominantly red. Thus red stained glass looks red by reflected as well as by transmitted light; the transmitted color is purer, however.

angle most of the light that reaches the eye will have made several passages through the fibers before leaving the paper. That is why the color of the light is clear and deep: it is free of any uncolored direct reflection. Sometimes glossy paper demonstrates the fact that being in resonance implies larger amplitudes and therefore stronger reflection. One often notices an increased reflection of the deeply colored parts of a glossy picture, but only when the dye is deposited in the uppermost layer. Examine the colored illustrations in this article.

Objects are black when there is absorption for all visible frequencies. Wellknown examples are graphite and tar. Black objects do not absorb all light that falls on them. There is always some reflection at the surface. Think of the reflection of the polished surface of a black shoe. A dull black surface reflects as strongly as a polished one but the reflected rays are distributed in all directions. A black surface with very low reflectivity can be produced by placing a few hundred razor blades in a stack. When the edges of the blades are viewed end on, they appear to be nearly dead black even though they are highly polished [see illustrations on opposite page]. The explanation is that light is trapped between the closely spaced edges and is absorbed after being reflected many times.

The most beautiful colors of all-the colors of plants, trees and flowers-are based on the same principle of preferential absorption. The cells of plants are filled with dyes: chlorophyll in green leaves and blades of grass, other dyestuffs in the petals of flowers. White light that falls on plants is reflected and refracted by the cells; a large part of the light enters the cells, in the same way it does the fibers of paper. When it returns to the eye, all the colors but one or two are strongly reduced by absorption. Only green light escapes from chlorophyllcontaining cells, only red light from the petals of red flowers.

We now turn to the visual appearance of metals. A metal is characterized by the fact that within the confines of the material there are many electrons –the conduction electrons–extending over many atomic diameters. These electrons are most important for the optical properties of metals. There is one, two or sometimes three electrons per atom among the conduction electrons. The rest of the atomic electrons remain bound to the atoms. The conduction electrons can be regarded as an electron gas that penetrates the crystal lattice





REFLECTIVITY OF "BLACK" OBJECTS can vary considerably. The light-absorption capability of three black surfaces is demonstrated above by allowing a bright, uniform band of light to fall on a piece of paper coated with black ink (*left*), a piece of black velvet (*middle*) and the ends of a tightly bolted stack of razor blades (*right*). Even though the edges of the razor blades are highly polished, they tend to absorb light rather than reflect it.

RAZOR-BLADE LIGHT TRAP consists of some two hundred blades bolted together. Light that enters the wedges between adjacent blades is reflected so many times that most of it is absorbed before it can escape.

without much hindrance. The reason for this quasi-free motion lies in the wave nature of the electron. Although it is true that an electron wave is scattered by each of the metal atoms, the regular arrangement of atoms in the lattice makes the scattered waves interfere in a definite way: the waves all add up to one undisturbed wave in the forward direction. The corresponding electron motion is therefore the motion of a free particle. This is a phenomenon closely related to the formation of a refracted wave when light penetrates a crystal.

The motion of the conduction electrons is not completely free, however. Thermal agitation of the crystal lattice and other lattice imperfections produce some scattering away from the main electron wave. This is closely analogous to the weak scattering of the refracted light wave in a crystal. The effect can be expressed as a kind of friction of the conduction electrons. It is the cause of the electrical resistance in metals. In the reaction of electrons to visible light, however, friction does not play an important role; we are allowed to consider the electrons as freely moving.

What is the behavior of a free electron under the influence of light? It performs vibrations of the same frequency as the frequency of the driving force but of opposite phase. When the force is moving in one direction, the electron moves in the other one. It is the same kind of movement an oscillator performs when the driving frequency is much higher than its resonance frequency. A free electron in plain sunlight performs vibrations with an amplitude about 10 times larger than the amplitude of electrons in water and in crystals, or several times 10⁻¹⁷ meter.

What happens when light impinges on a metallic surface? The answer is, very much the same as happens when light strikes the surface of a liquid or a crystal, but there is one important difference. Since the resonance frequencies of a liquid or a crystal are higher than the frequency of light, they vibrate in phase with the light. In a metal, however, the electrons vibrate in opposite phase. Under these conditions a refracted light wave cannot be propagated if the density of electrons and the amplitude of their vibration is above a certain limit. The limit can be expressed in terms of the "plasma frequency" ω_p , which is given by the equation $\omega_p = (Ne^2/m)^{\frac{1}{2}}$, where N is the number of electrons per cubic centimeter and m is the electron mass. This frequency usually is in the ultraviolet. Whenever the light frequency is less than ω_p , as it always is for visible light, no refracted wave can develop in the medium; there are too many electrons inside moving in phase opposite to the light.

Since no light energy can propagate into the material, all energy of the incoming light must go into the reflected wave. Just as with water or glass, the reflected light wave is produced in a thin layer at the surface of the metal, a layer no thicker than the wavelength of the light. A more exact calculation shows that in a metal this thickness is equal to the wavelength corresponding to the plasma frequency divided by 2π . This value is less than 10^{-7} meter. Unlike the wave reflected from water and glass, however, the wave reflected from a metal surface has almost the full intensity of the incoming wave, apart from small energy losses due to the friction of the vibrating electrons in the surface. This is why "white" metals such as silver and aluminum are so shiny: they reflect almost all visible light regardless of its frequency. Smooth surfaces of these metals therefore are ideal mirrors.

In colored metals such as copper or gold there are additional losses apart from the electron friction. These losses come from absorption by electrons other than the conduction electrons. Each atom in a metal is surrounded by shells of those electrons that remain with the atoms after the conduction electrons have detached themselves and formed the gas of free electrons. The resonance frequencies of the remaining electrons are usually in the ultraviolet and thus do not contribute to any color. In copper and gold, however, the bound electrons are part of an incomplete shell and do have resonances in the blue-violet that lead to absorption. As a result copper and gold have a reddish-yellow appearance.

Many color phenomena have not been treated here: the color of thin films, of fluorescent materials, of light emitted by flames, of electric discharges as produced in neon tubes and many others. We have taken up only the most common features of colored objects in order to provide some insight into the optical processes that occur on the surface of things when they are illuminated by light and seen by our eyes.