

Quantum Mechanics and Spectroscopy for Mechanical Engineers

Overview

Classical mechanics, which is used to model the dynamics of macroscopic objects, is a limiting case of the more general theory of quantum mechanics. At present, quantum mechanics provides the most complete description of the behavior of a physical system.

At the core of quantum mechanics is the De Broglie relation for matter waves. It states, quite simply, that all matter has wave properties which correspond to a wavelength λ given by $\lambda = h/p$ where p is the momentum of the object, and h is Planck's constant (6.626×10^{-34} J·s). If matter is to have wave properties, then it must interfere constructively and destructively with other matter, and it must exhibit refraction and diffraction just like light and other waves do. However, due to the small size of h , the associated wavelengths of macroscopic objects are tiny, and thus these interference phenomena are only appreciable under circumstances in which the problem length scales (e.g. the distance between two particles) approaches the De Broglie matter wavelength. For example, when we talk about the electrons, protons, and neutrons in atoms, their behavior is almost always dominated by wave effects. A baseball, on the other hand, does have associated wave properties, but the wavelengths are so small as to be macroscopically not observable. Thus, a baseball trajectory remains describable to a high degree of accuracy by the approximate theory of classical mechanics.

The predictions of quantum mechanics are not, however, confined to the realm of the unobservably small system. In many problems, the interactions of atoms and subatomic particles (which must be treated with quantum mechanics) produce macroscopically observable effects. For example, a pure gas at high temperature emits only certain distinct frequencies of light, indicating that the atoms occupy only discrete energy levels. This is in stark contrast to other classical systems (e.g. a mass-spring system) in which the total system energy is a continuous variable. Some of these manifestations of quantum theory are essential in the derivation of macroscopic theories such as thermodynamics, where the results of quantum mechanics calculations are required to formulate a consistent and complete thermodynamic theory of matter.

Quantum mechanics has a complex mathematical formalism which makes predictions which are difficult to reconcile within human intuition. Indeed, the general interpretation of quantum mechanics is still an active issue of debate, a debate which includes philosophers as well as mathematicians. However, the mathematics of quantum mechanics are extremely well established and have been verified by numerous experiments to an extraordinary degree of accuracy. That is, the dynamics of atoms and subatomic particles can be completely described using quantum theory, and the predictions of the theory are complete, even if they seem to violate common sense at times.

Quantum mechanics tells us why the electron and proton, though oppositely charged, do not simply attract each other to the point where they collide and collapse the atom. It also explains why

atomic energy is a discrete variable. However, the form of the answers is as follows: physical systems obey the postulates of quantum mechanics, and these postulates make the following predictions..... The question of 'why is it so?' is never answered. It is just like asking why energy is conserved in a closed system. There is no underlying observable reason. It is simply an observation of the way nature works.

Those considerations aside, the rest of this handout is devoted to presenting the mathematical postulates of quantum mechanics, applying these to the behavior of simple systems, and, finally, to presenting the results necessary for a basic understanding of molecular structure and interactions.

Postulates of Quantum Mechanics

Like classical thermodynamics and all higher order theories, the postulate approach is used to define quantum mechanics. All predictions of the theory follow from the six basic postulates listed in this section.

POSTULATE 1: *Any physical system is most completely described by a wave function $\Psi(\{\mathbf{r}_i\}, t)$ which is a function of the spatial coordinates and time. The wave function is a complex, single-valued, and finite function which is continuous and differentiable where defined.*

This statement implies that the wave function is the quantity of interest for a physical system. We say the wave function Ψ defines the condition of the system at a given time. The set of all possible functions Ψ make up state function space, \mathcal{E} .

We can think of the wave function as a probability amplitude. For example, for a system consisting of one particle, we can write the wave function as $\Psi(x, y, z, t)$. The probability per unit volume of finding the particle at a certain point in space (x, y, z) at a given time t is given by $|\Psi(x, y, z, t)|^2 = \Psi^* \Psi$, where the * superscript denotes the complex conjugate.

With this interpretation of the wave function, we must have the normalization condition which applies to all wave functions: $\int \Psi^* \Psi d\mathbf{r} = 1$, since all probabilities must sum to 1.

The goal of most of quantum mechanics is to find the wave function for a given system. From it, all observable information at any chosen time may be extracted.

POSTULATE 2: *For any observable quantity A , there is an associated operator \hat{A} which can operate on any function in \mathcal{E} . Such operators are linear and Hermitian.*

We call quantities that we measure (e.g. momentum, energy, position, velocity, etc.) observables. For each observable, there corresponds a unique operator. The equation satisfied by the wave function (see the Schrödinger equation below) is prescribed in a manner such that the operator for

position $\hat{\mathbf{r}}$ is multiplication by \mathbf{r} and the operator for momentum $\hat{\mathbf{p}}$ is $-i\hbar\nabla$, where $\hbar = h/2\pi$. The operator for energy \hat{E} is set similarly as $i\hbar\partial/\partial t$. The rest of the observable quantities are functions of this basic set, and thus their operators are defined in terms of these three. For example, the operator for angular momentum $\hat{\mathbf{L}}$ is $\hat{\mathbf{r}} \times \hat{\mathbf{p}} = -i\hbar\mathbf{r} \times \nabla$.

In general, an operator acts on a function to yield another function. For example, $\hat{\mathbf{p}}\Psi = -i\hbar\nabla\Psi$ and $\hat{\mathbf{r}}\Psi = \mathbf{r}\Psi$. Linear operators satisfy the following criterion for wave functions Ψ_1 and Ψ_2 with c_1 and c_2 as constants:

$$\hat{A}(c_1\Psi_1 + c_2\Psi_2) = c_1\hat{A}\Psi_1 + c_2\hat{A}\Psi_2 \quad (1)$$

With operators, the order of operation is important. If \hat{A} and \hat{B} are operators, $\hat{A}\hat{B}$ may or may not be equal to $\hat{B}\hat{A}$. You can verify, for instance, that $\hat{\mathbf{r}}\hat{\mathbf{p}} \neq \hat{\mathbf{p}}\hat{\mathbf{r}}$.

Operators representing observables must be Hermitian (we'll define the mathematical condition below). This condition insures that the observable quantities predicted by the theory are purely real numbers.

POSTULATE 3: *The expectation (or average) value of any observable, $\langle A(t) \rangle$, in a physical system at a given time t is given by:*

$$\langle A(t) \rangle = \int \Psi^*(\mathbf{r}, t) \hat{A} \Psi(\mathbf{r}, t) d\mathbf{r} \quad (2)$$

Furthermore, the possible values for an observable A (e.g. A_1, A_2, \dots) in a system with wave function Ψ are the eigenvalues of the operator \hat{A} . That is, the A_i must satisfy $\hat{A}\phi_n = A_n\phi_n$, where the set of ϕ_n form a complete, orthonormal set of functions with respect to all Ψ in \mathcal{E} .

This postulate relates the idea of a wave function to the quantities which we actually measure. It does not tell us what the exact value of a measurement will yield, but it does tell us what the average of a large number of measurements will be. The second part also tells us what the 'allowed' values of measurement are. That is, each measurement that we make must be one of the A_i values. This condition here foreshadows the existence of discrete, rather than continuous, system variables.

We use a shorthand notation (called Dirac notation) to deal with quantities such as those in equation (2). Dirac notation is summarized in the following example:

$$\int \Psi^* \hat{A} \Psi d\mathbf{r} = \langle \Psi | \hat{A} | \Psi \rangle \quad \int \Psi^* \Psi d\mathbf{r} = \langle \Psi | \Psi \rangle \quad (3)$$

To insure that the set of A_i values are all real, we set the *Hermitian condition* on all operators representing observables. This condition is given as:

$$\langle \Psi_1 | \hat{A} | \Psi_2 \rangle = \langle \Psi_1 | \hat{A} | \Psi_2 \rangle^* \quad (4)$$

For $\Psi_1 = \Psi_2$, this condition tells us that the expectation value for an observable is always real since $\langle A \rangle = \langle A \rangle^*$ implies that $\langle A \rangle$ is real. Similarly, this condition also insures that all A_i are real.

The functions ϕ_n which satisfy $\hat{A}\phi_n = A_n\phi_n$ are the eigenfunctions of the operator \hat{A} . Each eigenfunction ϕ_n represents a particular system state called an 'eigenstate.' To each eigenstate, there corresponds an eigenvalue A_n which would be the observed value of the measurement of A if the system were found in the eigenstate ϕ_n .

Requiring that the eigenfunctions form a complete set with respect to members of \mathcal{E} means that the set of eigenfunctions forms a basis in \mathcal{E} . As such, each ϕ_n is a member of \mathcal{E} , and thus the condition $\langle\phi_n|\phi_n\rangle = 1$ must hold for eigenfunctions as well. In addition, any function in \mathcal{E} (i.e. any wave function) can be expressed as a linear combination of the functions ϕ_n . That is

$$\Psi = \sum_{i=1}^{\infty} C_i\phi_i, \quad (5)$$

where C_i are complex constants. These eigenfunctions additionally must form an orthonormal set, which requires that $\langle\phi_i|\phi_j\rangle = \delta_{ij}$. Combining the orthonormality condition with equation (5), we can show that $C_i = \langle\phi_i|\Psi\rangle$.

As a direct result of equation (2) and equation (5), the probability P_n of finding a system characterized by a wave function Ψ in an eigenstate ϕ_n corresponding to an eigenvalue A_n is given by:

$$P_n = |C_n|^2 = |\langle\phi_n|\Psi\rangle|^2. \quad (6)$$

Thus, when expressed as linear combination of the eigenstates ϕ_n , **the wave function Ψ contains both the possible states that the system can be in, as well as the respective probabilities that a measurement will find the system in a given state.**

POSTULATE 4: *The wave function $\Psi(\mathbf{r}, t)$ obeys the Schrödinger equation:*

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar\frac{\partial\Psi(\mathbf{r}, t)}{\partial t} \quad (7)$$

where \hat{H} is the operator for the total system energy (kinetic plus potential) called the Hamiltonian.

Equation (7) above is called the time-dependent Schrödinger equation (TDSE). We have established that the wave function gives the most complete description of a system. The TDSE then governs the dynamics of the wave function (e.g. how it changes in response to external stimuli). If we specify the initial state of a system (i.e. the initial conditions), then we know the wave function $\Psi(t_0)$ at the initial time t_0 . If we want to know the wave function at a later time t_1 , then we solve the TDSE using $\Psi(t_0)$ as the initial condition.

The Hamiltonian for a system is typically the kinetic energy of the objects in it plus the potential energy. For example, for a single particle system, the kinetic energy T is $p^2/2m$ and the potential energy is often some function of position $V(x, y, z)$. In this case, $\hat{V} = V$, while $\hat{T} = (-\hbar^2/2m)\nabla^2$. Thus, $\hat{H} = (-\hbar^2/2m)\nabla^2 + V$.

For situations in which the Hamiltonian is independent of time, we can factor $\Psi(\mathbf{r}, t)$ into $\psi(\mathbf{r})f(t)$. Inserting this into the TDSE and using the standard separation of variables procedure, we end up with two equations, one which is a function of coordinates only, and one which is a function of time only. Both equations must be equal to a constant α . The spatial equation is $\hat{H}\psi(\mathbf{r}) = \alpha\psi(\mathbf{r})$. If \hat{H} is the operator for total energy, then α must be the total time independent system energy E . Thus, we replace α with E and get the time independent Schrödinger equation $\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$. The time equation is solved for $f(t)$ yielding $f(t) = e^{-iEt/\hbar}$. Then the overall wave function can be expressed as $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-iEt/\hbar}$.

POSTULATE 5: *There exists an intrinsic angular momentum in some particles which is designated the spin. Spin is a characteristic of a given particle. As such, the spin of a particle is an additional independent variable in the wave function.*

POSTULATE 6: *No two fermions can occupy the same state (i.e. have the same wave function).*

These two postulates are included for completeness, though we'll only touch briefly on them. For many problems, these postulates have no influence on the form of the equations involved. Postulate 6 is often called the Pauli exclusion principle. By fermions, we refer to particles with a spin of $\pm\frac{1}{2}$ such as electrons, protons, and neutrons.

Applying the postulates to a sample problem

To illustrate the postulates, we'll consider a simple system of a particle confined to move in one dimension between two points, say $x = 0$ and $x = a$. This is often called the "Particle in a 1-D Box" problem since we can envision the particle confined by walls to a region on the x -axis. This problem can be easily extended to three dimensions to produce a more physically useful result which we show in the last section of this handout.

To confine a particle of mass m to the specified region, we apply a potential V which is zero for $0 < x < a$ and infinity for $x \leq 0$ and $x \geq a$.

Our goal now is to solve for the wave function of our particle. This will then give us the most complete set of information about our system.

First we find the Hamiltonian for our system. For a general 3-D, one-particle system,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z). \quad (8)$$

For our 1-D system, the y and z terms drop, and $V = V(x)$. In the region of $0 < x < a$, $V = 0$, and then our Hamiltonian is simply $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. Since there is no explicit time dependence in

our Hamiltonian, we can solve the time independent Schrödinger equation to get the spatial part of our wave function. The form of the equation is:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi. \quad (9)$$

which has the general solution:

$$\psi = Ae^{i\sqrt{2mEx}/\hbar} + Be^{-i\sqrt{2mEx}/\hbar}. \quad (10)$$

We solve for the two constants A and B by applying the two boundary conditions which say that the wave function must vanish at $x = 0$ and $x = a$. That is, the probability of finding the particle where the potential is infinite must be zero.

Applying $\psi(0) = 0$ tells us that $A = -B$, so our wave function becomes

$$\psi(x) = A(e^{i\sqrt{2mEx}/\hbar} - e^{-i\sqrt{2mEx}/\hbar}) = C \sin\left(\frac{\sqrt{2mEx}}{\hbar}\right) \quad (11)$$

where $C = 2iA$. When we apply $\psi(a) = 0$, we get that the sine term must be zero for $x = a$, implying that the argument of sine must be some multiple of π . This gives us the condition that

$$\frac{\sqrt{2mE_n}a}{\hbar} = \pm n\pi \quad n = 1, 2, 3, \dots \quad (12)$$

or $E_n = (n\pi\hbar)^2/2ma^2$ where n is an integer. This condition tells us that our particle can only exist in one of a series of discrete energy levels. Other energies are not allowed. We say that the energy of the system is *quantized*. This result is directly analogous to the standing wave problem in a vibrating string fixed at $x = 0$ and $x = a$. The string can only vibrate at frequencies where the length a is an integral number of half-wavelengths. Similarly, the 'wavelike' particle can only exist in such a cavity if an integral number of its half-wavelengths is equal to a .

In addition, since there is no potential energy for the particle, the total energy E_n must also be equal to $p_x^2/2m$ so that the allowed values of momentum are $p_x = \pm(n\pi\hbar)/a$.

To solve for the final constant C , we invoke the normalization condition

$$\langle \psi | \psi \rangle = 1 = C^*C \int_0^a \sin^2 \frac{n\pi x}{a} dx \quad (13)$$

Since the integral term is $a/2$ we get $|C|^2 = 2/a$. We have some choice here in our value for C , but the choice has no consequence on our measurements so it is truly arbitrary. As such, we choose C to be real, and thus $C = \sqrt{2/a}$. This gives us the spatial part of the wave function for the particle in a 1-D box as:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \quad (14)$$

The full form of the wave function is then $\Psi_n(x, t) = \psi_n(x)f(t)$ where $f(t) = e^{-iE_nt/\hbar}$. The $f(t)$ term is referred to as the 'global phase factor,' and has a constant modulus of one. Rarely

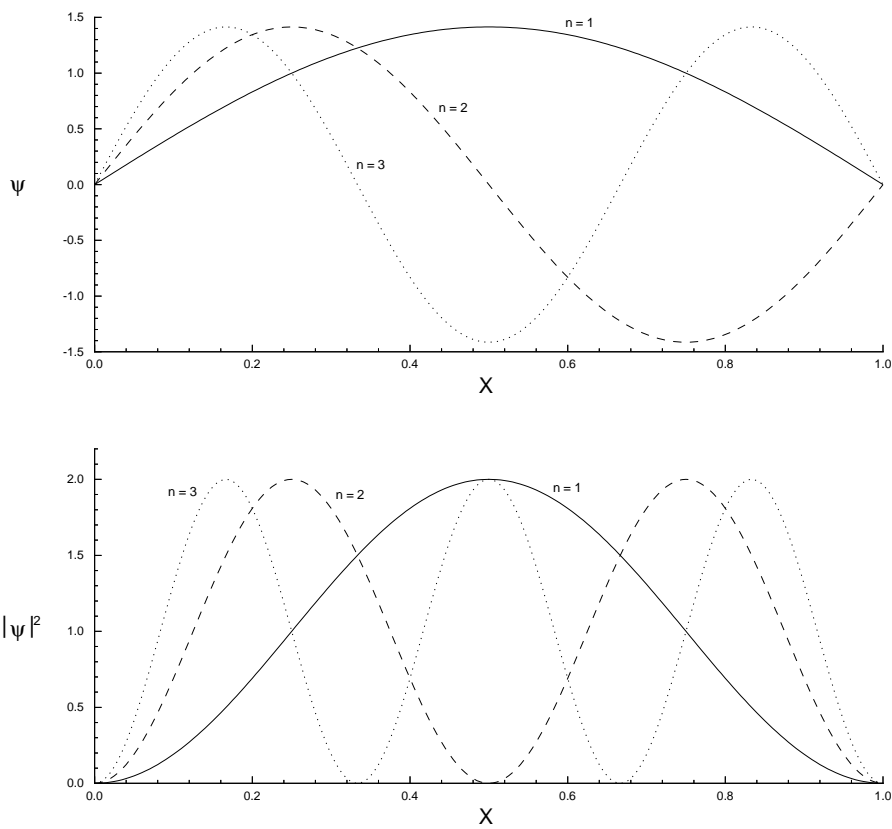


Figure 1: Wave function and probability density curves for a particle in a one-dimensional box of unit length.

does the global phase factor play a role in a quantum mechanics problem, but it does reflect the fact that there is a temporal dependence in a wave function, even when the Hamiltonian is time-independent. For any given time t , the global phase factor is just a constant. We can choose to do our measurements at any time, and the results would be the same. For simplicity, we choose $t = 0$, and then $\Psi(x, t = 0) = \psi(x)$.

The wave functions and probability densities for the first three energy levels are shown in Figure 1. Perhaps the most notable feature of this result is that for $n > 1$, there are points between $x = 0$ and $x = a$ where the probability of finding the particle is zero. One way of perceiving this is that the particle can move from, say $x = a/4$ to $x = 3a/4$ in the $n = 2$ case without passing through $x = a/2$. Another way of perceiving this result, the more commonly accepted viewpoint, is that the particle does not exist in a defined state until observed. The particle is effectively smeared out over the $0 < x < a$ region and only collapses to a particular point upon being measured.

Now that we have the wave function for our system, we should be able to get information such as the expectation values for the position and momentum of the particle as well as the allowed values for position and momentum of the particle.

For position, the expectation value $\langle x \rangle = \langle \psi | \hat{x} | \psi \rangle$. We can integrate to get this by writing:

$$\langle x \rangle = \frac{2}{a} \int_0^a x \sin^2 \frac{n\pi x}{a} dx = \frac{2}{a} \left(\frac{a^2}{4} \right) = \frac{a}{2} \quad (15)$$

Not surprisingly, the expectation or average position value is in the center of the region irrespective of E_n . To obtain the allowed position values, we must solve $\hat{x}\phi_n = x\phi_n$ which holds for all ϕ_n , so any value of x within $0 < x < a$ is allowed. Thus, position is a continuous variable.

For momentum, we obtain the expectation value in the same fashion. Remembering that the operator for p_x is $-i\hbar(\partial/\partial x)$ we get:

$$\langle \hat{p}_x \rangle = \langle \psi | \hat{p}_x | \psi \rangle = \frac{-4i\hbar}{a} \int_0^a \frac{n\pi}{a} \sin \frac{n\pi x}{a} \cos \frac{n\pi x}{a} dx = 0 \quad (16)$$

The average value of momentum is zero, which is again expected because of the symmetry of the problem. For any state in which the particle is traveling to the left, there must be an equally probable state with the particle traveling to the right with opposite momentum.

We already have the allowed values of momentum from the energy quantization, and now we'd like to find the relative probabilities of measuring each of the two possible momenta for a given particle. To do so, we must expand ψ in terms of the eigenfunctions of \hat{p}_x . We find the eigenfunctions of \hat{p}_x by solving $\hat{p}_x\phi_n = p_x\phi_n$, or

$$-i\hbar \frac{\partial \phi_n}{\partial x} = \pm \frac{n\pi\hbar}{a} \phi_n \quad (17)$$

The two eigenfunctions are thus $\phi_{n,1} = B_1 e^{in\pi x/a}$ and $\phi_{n,2} = B_2 e^{-in\pi x/a}$. The constants B_1 and B_2 are determined by the normalization condition to be $1/\sqrt{a}$. Next, noting that $2i \sin z = e^{iz} - e^{-iz}$, we observe that:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} = \sqrt{\frac{2}{a}} \frac{1}{2i} (e^{in\pi x/a} - e^{-in\pi x/a}) \quad (18)$$

$$= -\frac{i}{\sqrt{2}} \left(\frac{1}{\sqrt{a}} e^{in\pi x/a} - \frac{1}{\sqrt{a}} e^{-in\pi x/a} \right) = -\frac{i}{\sqrt{2}} (\phi_{n,1} - \phi_{n,2}). \quad (19)$$

The final expression then lists the wave function as a linear combination of the momentum eigenfunctions. The coefficients of each eigenfunction differ only in sign, and thus their squares both yield a value of one-half. Therefore, both the forward and backward momentum states are equally probable, as expected.

This example indicates the general procedure for solving problems in quantum mechanics. Several points are deserving of mention. First, setting the boundary conditions on a problem typically results in quantization of some form, as we saw here. Second, we can never predict exactly which state a system will be found in, only the relative probabilities of the system being found in any one of its possible states. That is the best we can do, and all that information is in the wave function. Third, the predictions of quantum theory are often at odds with our classical picture of particles traveling along a trajectory. That line of reasoning is inappropriate for quantum phenomena. Finally, while we have solved for the wave function for this simple problem in closed form, very few problems of practical interest are similarly soluble. Rather, to obtain working solutions, we resort to perturbation and variational methods and (typically involved) numerical computations.

Some other important results

Of the problems that are soluble in closed form, four are most useful for understanding molecular structure and interactions. Molecules interact with light and with each other by exchanging energy and momentum. Thus, in order to understand these interactions, we must first determine nature's rules for molecular energy and momentum storage. In general, we find that molecules can store energy in translational, rotational, vibrational, and electronic modes. We will find that each of these energy modes is quantized, and the set of specific allowable energy levels can be determined by quantum mechanics.

Translational Energy

To obtain the allowed translational energy levels for a particle, we consider a single particle in a three-dimensional box. This problem is completely analogous to the one-dimensional problem. However, instead of dropping the y and z terms in equation (8), we include them and then use separation variables to obtain three differential equations identical to equation (9). For each axis, the motion is quantized with a quantum number n_i . For a 'box' with dimensions $a \times b \times c$, we get the following energy levels:

$$E_{n_1, n_2, n_3} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) \quad (20)$$

where $n_i = 1, 2, 3, \dots$. This equation also dictates that the energy storage in each axis is independent of the storage in the other axes. If the dimensions of the box are equal, then the volume $V = a^3$, and the allowable energy levels can be expressed as:

$$E_{n_1, n_2, n_3} = \frac{\pi^2 \hbar^2}{2mV^{2/3}} (n_1^2 + n_2^2 + n_3^2). \quad (21)$$

This problem also illustrates the issue of *degeneracy*. Note that the states $(n_1, n_2, n_3) = (1, 1, 2), (1, 2, 1),$ and $(2, 1, 1)$ all have the same energy. Thus, we say this energy level ($E = \frac{3\pi^2 \hbar^2}{mV^{2/3}}$) is three-fold degenerate because three system states have the same value of energy. In general, if m eigenfunctions have the same eigenvalue A_k , then we say that the k th eigenvalue is m -fold degenerate.

Rotational Energy

A molecule can also store internal energy in rotation. We consider a diatomic molecule with two atoms of mass m_1 and m_2 which maintain a fixed distance r_o as they rotate. This is the so-called rigid rotor problem. This problem is mathematically equivalent to that of a single particle of mass $\mu = m_1 m_2 / (m_1 + m_2)$ confined to rotate at a distance of r_o about the origin, as shown in Figure 2.

We can thus use the single particle approach for our wave function, but spherical coordinates are more appropriate. Setting the $\partial/\partial r$ terms to zero since we're only considering a single fixed

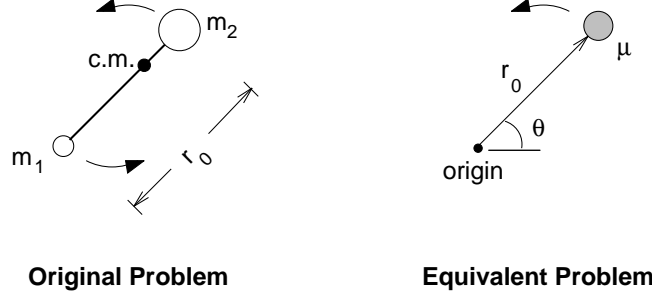


Figure 2: The rigid rotor problem and its equivalent one-particle formulation

value of r , we get for the Hamiltonian $\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2$ in spherical coordinates:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \left[\frac{1}{r_0^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r_0^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (22)$$

We then use this value for \hat{H} in the time independent Schrödinger equation to obtain a relation for the energy levels in a rigid rotor. Noting that $I = \mu r_0^2$ and denoting our rotational wavefunction as $Y(\theta, \phi)$, the Schrödinger equation can be rearranged to yields:

$$\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] + \frac{2IE}{\hbar^2} Y = 0 \quad (23)$$

We can separate variables as $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$. In doing so, we obtain two expressions, one in θ and one in ϕ which must then be equal to a constant we'll call $-m^2$, again choosing the form based on knowledge of what is to come. The equation in Φ is:

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2 \quad (24)$$

which has the solution $\Phi = Ae^{im\phi} + Be^{-im\phi}$. For the function to be single-valued, $\Phi(\phi) = \Phi(\phi + 2\pi)$, which then requires that m be zero or a positive or negative integer.

The equation for $\Theta(\theta)$ can be written:

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left[\frac{2IE}{\hbar^2} \sin^2 \theta - m^2 \right] \Theta = 0. \quad (25)$$

This equation can be manipulated into the Legendre equation by making the substitution $\xi = \cos \theta$. This substitution converts our equation for $\Theta(\theta)$ to a new equation for $P(\xi)$ in the following form:

$$(1 - \xi^2) \frac{d^2 P}{d\xi^2} - 2\xi \frac{dP}{d\xi} + \left[\frac{2IE}{\hbar^2} - \frac{m^2}{(1 - \xi^2)} \right] P = 0. \quad (26)$$

The only solutions for this equation in the range of $0 \leq \theta \leq \pi$ which are continuous, single-valued, and finite are for values $2IE/\hbar^2 = J(J + 1)$, where J are zero or positive integers. These solutions are the associated Legendre functions. This result then quantizes the energy of the rigid rotor to:

$$E_J = J(J + 1) \frac{\hbar^2}{2I} \quad J = 0, 1, 2, 3, \dots \quad (27)$$

If we look at the operator for the z-component of the angular momentum, we find that its eigenvalues are $m\hbar$. Thus, from energy conservation conditions, we obtain the condition that $|m| \leq J$. For example, if $J = 2$ then m could be -2, -1, 0, 1, or 2. In general, this gives us $2J + 1$ possible states with the same total energy E_J . Thus, we say that each energy level E_J is $(2J + 1)$ -fold degenerate.

Vibrational Energy

The bond between two atoms acts much like a spring separating two masses. The bond keeps the atoms average separation distance at some value b_0 by exerting an attractive force for $b > b_0$ and a repulsive force for $b < b_0$. For such a potential, the two-atom system can store energy in vibration as the system oscillates back and forth from $b < b_0$ to $b > b_0$. A common assumption is to estimate the potential between two atoms of masses m_1 and m_2 is quadratic, that is $V = \frac{1}{2}k(b - b_0)^2$. Then, as shown in Figure 3, we can reduce the two particle problem to an equivalent one particle problem of a mass $\mu = m_1 m_2 / (m_1 + m_2)$ moving along the x-axis and in a potential well given by $V = \frac{1}{2}kx^2$.

Then $x = 0$ corresponds to $b = b_0$, and the appropriate one-dimensional single particle Hamiltonian is: $\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$. Substituting this into the time independent Schrödinger equation yields:

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \phi}{\partial x^2} + \frac{1}{2}kx^2 \phi = E\phi \quad (28)$$

which has the solutions $\phi = H(\gamma x)e^{-\gamma x^2/2}$, where $\gamma = \sqrt{\mu k}/\hbar$. The functions $H(\gamma x)$ are only finite if γ satisfies the following condition:

$$\frac{2\mu E}{\hbar^2 \gamma} - 1 - 2v = 0, \quad (29)$$

where v is zero or a positive integer. In this case, the $H(\gamma x)$ are the Hermite polynomials of order v , written $H_v(\gamma x)$. The restriction on γ then limits the possible values of the energy to $E_v = (v + \frac{1}{2})\hbar\omega$ for $v = 0, 1, 2, \dots$ and $\omega = \sqrt{k/\mu}$. The energy levels are non-degenerate.

Another important observation from this result is that the zero-point energy E_0 is not zero but is rather a finite $\frac{1}{2}\hbar\omega$. Thus, we can never remove all the energy from a harmonic oscillator.

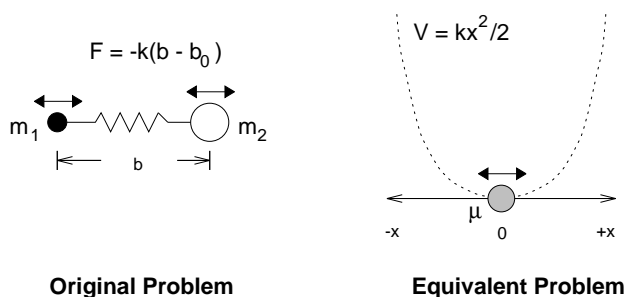


Figure 3: The harmonic oscillator problem and its equivalent one-particle formulation

Internuclear potentials for real molecules can often be well approximated by the harmonic potential for low values of v , that is, when there is little vibrational energy being stored. However, for many molecules, the harmonic approximation is poor, even for $v = 1$. Corrections to this formula to account for 'anharmonicity' are available in the spectroscopy literature.

Electronic Energy

The final form of energy storage that we consider is electronic energy. This is effectively the potential energy of the system of charges in an atom or molecule. Recall that the nuclei of a molecule are positively charged, and the electrons negatively charged. From classical electrostatics we recall Coulomb's Law which tells us that the potential energy of two charges is inversely proportional to the distance between them. Thus, we can imagine that a molecular state with electrons in close proximity to the nuclei would have a *lower* electronic energy than a molecular state in which the electrons were further away. Indeed, we will see this is the case; however, as before, the allowed molecular states will be quantized, that is only certain energies will be allowed.

The simplest system to look at for electronic structure of atoms is the hydrogen atom, consisting of a single positively charged proton, and a less massive, negatively charged electron. For this case, we have a system of two particles of charge $+e$ and $-e$, of masses m_p and m_e with a Coulomb force of $F = -e^2/4\pi\epsilon_0 b^2$ between the particles. Here b is the distance between the particles, and ϵ_0 is the permittivity of free space which is the appropriate constant which gives us consistent units. The force generates a potential according to $F = -dV/db$ and thus, $V = -e^2/4\pi\epsilon_0 b$. As we did for rotation, we consider the system fixed in space (we can treat the translational energy independently), and we reduce the two particle problem to that of a single particle of mass $\mu = m_p m_e / (m_p + m_e)$. In this case, the equivalent problem is that of a single particle of mass μ in a potential centered at the origin of the form $V(r) = -e^2/4\pi\epsilon_0 r$, where r is the radial coordinate in the (r, θ, ϕ) spherical coordinate system. The appropriate setup is shown in Figure 4.

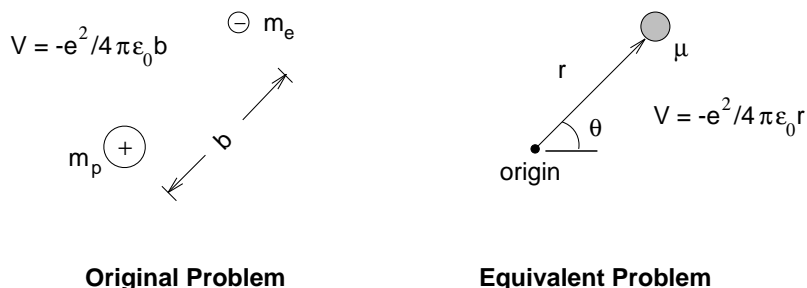


Figure 4: The hydrogen atom problem and its equivalent one-particle formulation

Our Hamiltonian then takes on the simple form:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}. \quad (30)$$

Again we use spherical coordinates to solve the problem, and separate variables into $\Phi(r, \theta, \phi) = R(r)Y(\theta, \phi)$. The equation for $Y(\theta, \phi)$ is the same equation as solved for the rigid rotor problem if we replace I with μ . Thus, this solution is known, and it introduces two quantum numbers l and m describing the angular momentum of the electron and the orientation of the angular momentum of the electron. These are the analogs of the J and m for the rigid rotor problem. If we introduce this notation into the problem and then isolate the $R(r)$ equation, we get:

$$-\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] R = ER \quad (31)$$

Introducing the variable $x = 2r/na_0$ and the constant $a_0 = 4\pi\epsilon_0\hbar^2/\mu e^2$ called the Bohr radius, we find solutions to be:

$$R_{nl}(r) = -\frac{2}{n^2 a_0^{3/2}} \left[\frac{(n-l-1)!}{[(n+l)!]^3} \right]^{1/2} e^{-x/2} x^l L_{n+l}^{2l+1}(x) \quad (32)$$

where n is a new quantum number that can take on integer values of 1,2,3,..., and the $L_{n+l}^{2l+1}(x)$ are the associated Laguerre polynomials given by:

$$L_s^t(x) = -\sum_{k=0}^{s-t} (-1)^k \frac{(s!)^2 x^k}{(s-t-k)!(t+k)!k!}. \quad (33)$$

For example, for $n = 2$ and $l = 0$, $L_2^1(x) = 2x - 4$.

Thus, for electronic states of the H atom, there are 3 quantum numbers n , l , and m called the principal, azimuthal, and magnetic quantum numbers. The principal quantum number n correlates to the mean distance of the electron from the nucleus. Thus, as we could expect, a higher n value gives a larger electronic energy. Indeed, this is the only quantum number that figures into the energy, and we can derive the allowed quantized energy levels of the hydrogen atom:

$$E_n = -\frac{1}{2n^2} \left(\frac{e^2}{4\pi\epsilon_0 a_0} \right) \quad (34)$$

As with the rigid rotor, the azimuthal quantum number l determines the angular momentum of a state. It can take on integer values of 0 to $n-1$. The magnetic quantum number m determines the orientation of the angular momentum, and it can take on integer values from $-l$ to l . Specification of each of the quantum numbers specifies the electronic state of the atom, though only n is required to specify the energy.

For larger atoms and molecules, the same basic theory applies, though the problems cannot be solved in closed form. Nevertheless, for each electron in an atom or molecule, typically the same three quantum numbers are used to categorize its state. The state of the system of many electrons then involves summing over the contributions of all the system's electrons. Of course, the same idea of quantization applies to complex as well as simple molecules, and thus only discrete electronic energy levels are observed.

Summary of key results

Quantum mechanics gives us, among other things, the set of energy levels in which a molecule can be found for each of the basic types of energy: translational, vibrational, rotational, and electronic. The following table summarizes the key information:

Mode of Energy Storage	Allowed energy levels	Degeneracy
Translation	$\frac{\pi^2 \hbar^2}{2mV^{2/3}}(n_1^2 + n_2^2 + n_3^2)$	Varied
Rotation	$J(J+1)\frac{\hbar^2}{2I}$	$2J+1$
Vibration	$(v + \frac{1}{2})\hbar\omega$	1
Electronic (H atom)	$-\frac{1}{2n^2} \left(\frac{e^2}{4\pi\epsilon_0 a_0} \right)$	$2n^2$

The assumptions made in obtaining these results are important to note. For rotational energy, we've assumed the internuclear distance is constant, while for vibration, we've assumed a harmonic potential. In addition, we implicitly assume that the energy stored in vibration and rotation are independent of each other; that is, $E_J \neq \text{fcn}(v)$ and $E_v \neq \text{fcn}(J)$. To first order, these approximations are good. When high accuracy is required, a small correction term will be required for each of the listed assumptions.

Application: The Interaction of Light with Atoms

The area in which quantum effects are macroscopically most observable is in spectroscopy where the discrete nature of atomic and molecular energy levels is seen directly. Spectroscopy is the study of light interaction with matter, and thus the results of a spectroscopic study are governed by the quantum rules of atoms and light. We've presented above the rules governing atoms and molecules, and in this section, we'll give a brief overview of the quantum nature of light before discussing the rudiments of spectroscopy.

Light can be considered to consist of individual packets of energy called photons. Each photon carries a discrete amount of energy associated with its wavelength according to $E = h\nu$, where ν is the frequency of the light, and frequency varies with wavelength λ as $\nu = c/\lambda$. Thus, short wavelength photons are more energetic than long wavelength ones. In addition, the photon carries linear momentum in the direction of propagation in an amount equal to $\mathbf{p} = \hbar\mathbf{k}$ where \mathbf{k} is the wavevector which has a magnitude equal to $1/\lambda$ and points in the direction of propagation. Again, short wavelength photons carry more momentum than long wavelength ones.

In addition, a photon carries at least one unit of angular momentum as spin. Dipole radiation, the most common type of light which is observed, carries only this one unit of angular momentum per photon, and it points in either the direction of propagation or opposite the direction of propagation (circularly polarized light), or it may be a statistical mixture of these two states (elliptically and linearly polarized light).

Photons can interact with atoms in a variety of ways, but the three most fundamental processes are absorption, spontaneous emission, and stimulated emission. These are shown schematically in Figure 5. In absorption, the atom absorbs the energy and momentum of the photon, leaving the atom in an excited (higher energy) state. In spontaneous emission, the reverse of emission, the excited atom emits a photon, leaving the atom with less energy. In stimulated emission, an excited atom interacts with a photon to 'stimulate' the excited atom to emit an identical photon, leaving an atom with a reduced energy and adding a photon to the light field.

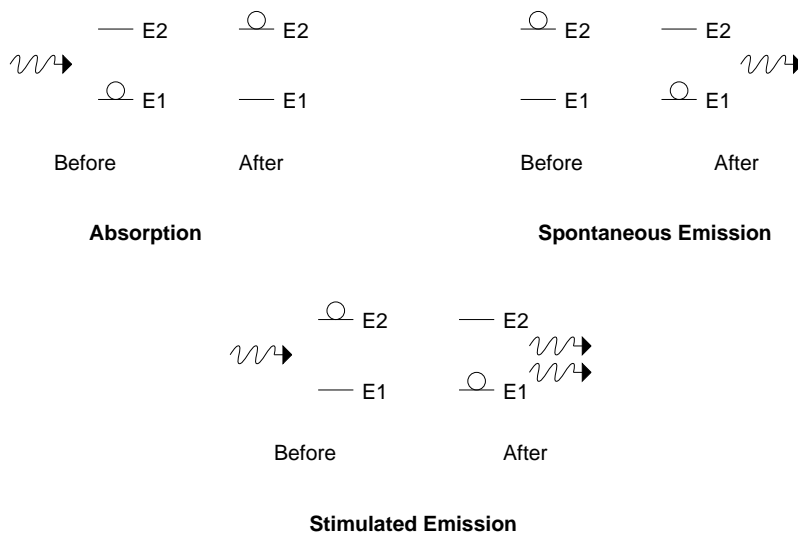


Figure 5: The three fundamental atom/light interaction processes. E2 represents the excited (higher energy) state of the atom, and E1 represents the ground (lower energy) state.

Each of these three processes is governed by a simple rate law. Let's focus on an isolated system of atoms in a radiation field and call the number of atoms in the ground state per unit volume N_1 and the number per unit volume in the excited state N_2 . For this case, the number of photons absorbed per unit time per unit volume is equal to $N_1\rho B_{12}$ where ρ is the field intensity and B_{12} is the Einstein absorption coefficient. The number of photons spontaneously emitted per unit time per unit volume is equal to N_2A where A is the Einstein A coefficient. Similarly, the number of photons created by stimulated emission per unit volume per unit time is $N_2\rho B_{21}$ where B_{21} is the Einstein coefficient for stimulated emission. The Einstein coefficients are all constant for a particular transition, and they can be calculated to a high degree of accuracy using quantum mechanical formulae. These three simple processes can be used to describe the operation of most optical devices including lasers.

If we consider a 2-level atom where we only consider the ground state and excited state, then we can write the equations for the change in ground state population and excited state population as these optical processes shift atoms from one state to the other. Specifically:

$$\frac{dN_2}{dt} = N_1\rho B_{12} - N_2A - N_2\rho B_{21} \quad (35)$$

$$\frac{dN_1}{dt} = N_2A + N_2\rho B_{21} - N_1\rho B_{12} \quad (36)$$

where the positive terms on the right hand side are the rates for processes which shift atoms into the specific level, and the negative terms are rates of processes which take atoms out of that level. We will return to these equations later when we discuss laser operation.

Photon/atom interactions must obey several rules, and these severely limit the types of processes that are seen in nature. First, energy must be conserved in the process. This means that, for example in the case of absorption, the atom can only jump to a state that has exactly $h\nu$ more energy than the ground state. If there is no state allowed where $E_2 - E_1 = h\nu$, then *no absorption can occur*. Similarly for emission, the atom will only emit light with frequencies corresponding to the allowed energy separations in the atom. If we pass light through a pure sample of some chemical species that we're interested in, then only certain wavelengths of the incident light will be absorbed, as shown in Figure 6. From the wavelengths of these 'absorption lines' we can infer the allowed energy levels of the molecules in our sample.

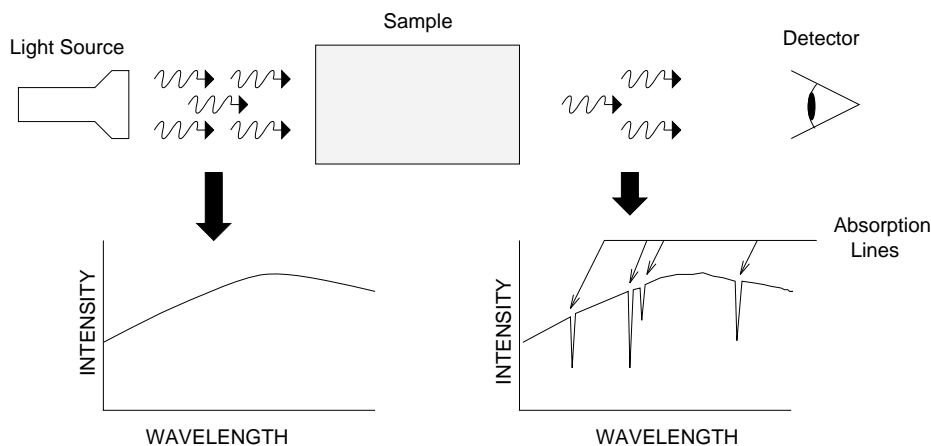


Figure 6: A schematic of an absorption experiment including the spectral makeup of the incident and transmitted light.

For example, consider a sample of atomic hydrogen. Our energy level analysis from equation (34) predicts that we should have allowed energy states like those shown in Figure 7, where each line represents a state or set of states corresponding to specified values of n and l . In Figure 7, we only consider the lowest 3 values of n . The arrowed lines represent possible transitions that we might see in absorption. Thus, we would expect that a sample of atomic hydrogen would show absorption lines at the wavelengths of 103, 121, and 486 nm.

Note however, that there are not lines drawn between all the levels. This suggests that some transitions are not allowed. In an atom/photon interaction, four things must be conserved: energy, angular momentum, linear momentum, and symmetry. We've already shown how energy conservation determines which photons an atom is allowed to absorb. Similarly, the photon has a vector angular momentum of $\pm\hbar$ in the propagation direction (call it the z -axis), and the atom has some integer multiple of \hbar (e.g. $0, \pm 1, \pm 2, \dots$) angular momentum z -direction. After the collision, conservation of angular momentum dictates that the atom must have one more or less unit of z -axis angular momentum. In general this restricts the types of transitions to those obeying $l_{\text{final}} - l_{\text{initial}} = \pm 1$. For example, note that there is not an allowed transition between $(n = 1, l = 0)$ and $(n = 2, l = 0)$ which would have a $\Delta l = 0$. In a similar way, conservation of symmetry further disallows some other transitions which would satisfy angular momentum and energy conservation.

Armed with this knowledge, we can use spectroscopy to test our quantum mechanical calculations of energy levels. The predicted absorption lines and the observed ones should match if the theory is correct (they always do for calculable systems). In addition, the absorption or emission lines of a substance are its fingerprint. For example, if we see an absorption line at 486 nm, we know H atoms are present. Thus, we can use spectroscopy to examine the chemical makeup of systems near and far. Scientists analyze the spectra of stars to determine what they are made of and how hot they are. We do absorption studies of the atmosphere to determine pollutant levels and ozone concentration. We look at the emission and absorption from furnace gases to monitor combustion efficiency and NO_x production, and many similar spectroscopic tools are used in a variety of scientific, industrial, and commercial applications.

Spectroscopy is just one example of a field in which quantum mechanics plays an essential role. Though most of these areas require some advanced knowledge and are fairly new, it is becoming quite common now for modern experimental instrumentation to involve or exploit quantum effects for increasingly precise measurement. Thus, a basic working knowledge, such as that provided in this handout, of quantum mechanics is becoming more and more necessary in the technical community.

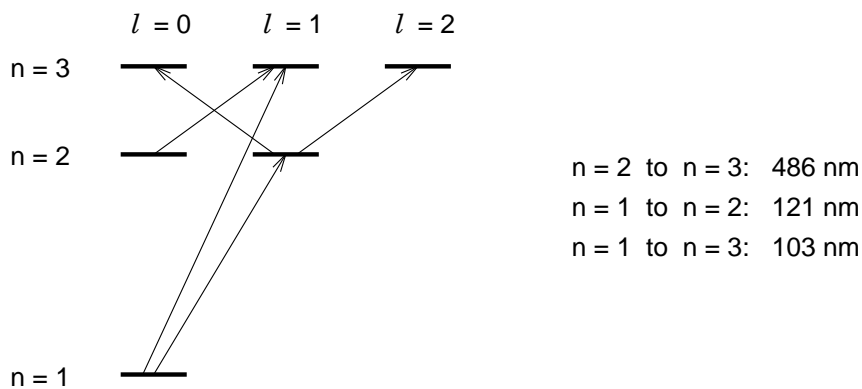


Figure 7: The allowed transitions in absorption between the first three levels of the H atom.