University of Mosul
College of Science
Department of Physics
Second stage
Lecture 1

# Modern Physics II

2024-2025

Lecture 1

1- Quantum Mechanics
2- Wave function
3- Normalization
4- Well behaved function

Preparation
Lecturer. Hala I. Jasim

# Modern Physics II

قبل البدء بمادة الفيزياء الحديثة٢ لابد من العودة الى الفصل الثالث من كتاب مفاهيم في الفيزياء الحديثة ( ترجمة د. منعم مشكور ) وخصوصا الفقرات ( ٣-٢ ) و ( ٣-٣ ) كما اننا سنكون بحاجة الى استخدام هذا الكتاب في جميع مادة الكورس الثاني بالاضافة الى المحاضرات باللغة الانكليزية وخصوصا للطلبة ذوي القابلية الضعيفة بهذه اللغة ومن ثم نعود الى مادة الكورس الثاني حيث اننا سنبدأ بمادة الفصل الخامس ( ميكانيك الكم ) من الكتاب المقرر .

## Quantum Mechanics

Classical mechanics is an approximation of quantum mechanics . The fundamental difference between classical ( or Newtonian ) mechanics and quantum mechanics lies in what they describe . In classical mechanics , the future history of a particle is completely determined by its initial position and momentum together with forces that act upon it . In the everyday world these quantities can all be determined well enough for the predictions of Newtonian mechanics to agree with what we find .

Quantum mechanics also arrives at relationships between observable quantities , but the uncertainty principle suggests that the nature of an observable quantity is different in the atomic realm . Cause and effect are still related in quantum mechanics , but what they concern needs careful interpretation . In quantum mechanics the kind of certainty about the future characteristic of classical mechanics is impossible because the initial state of a particle cannot be established with sufficient accuracy , the more we know about the position of a particle now , the less we know about its momentum and hence about its position later .

The quantities whose relationships quantum mechanics explores are probabilities . Instead of asserting , for example , that the radius of the electron's orbit in the a ground state hydrogen atom is always exactly $5.3 \times 10^{-11}$ m , as the Bohr theory does , quantum mechanics states that this is the most probable radius . In a suitable experiment most trials will yield a different value , either larger or smaller , but the value most likely to be found will be $5.3 \times 10^{-11}$ m .

The certainties of classical mechanics are illusory , and their apparent agreement with experiment occurs because ordinary objects consist of so many individual atoms that departures from average behavior are unnoticeable .

### Wave function :

The quantity with which quantum mechanics is concerned is the **wave function $\psi$** of a body . While $\Psi$ itself has no physical interpretation , the square of its absolute magnitude $|\Psi|^2$ evaluated at a particular place at a particular time is proportional to the probability of finding the body there at that time . The linear momentum , angular momentum , and energy of the body are other quantities that can be established from $\Psi$ .

The problem of quantum mechanics is to determine Ψ for a body when its freedom of motion is limited by the action of external forces .

Wave functions are usually complex with both real and imaginary parts . A probability must be a positive real quantity . The probability density $|\Psi|^2$ for a complex Ψ is therefore taken as the product ( $\Psi^*\Psi$ ) of Ψ and its **complex conjugate** $\Psi^*$. The complex conjugate of any function is obtained by replacing i ( $= \sqrt{-1}$ ) by - i whenever it appears in the function . Every complex function Ψ can be written in the form

$\Psi = A + iB$ **wave function**

Where A and B are real functions . The complex conjugate $\Psi^*$ of Ψ is

$\Psi^* = A - iB$ **complex conjugate , and so**

$|\Psi|^2 = \Psi^*\Psi = A^2 - i^2B^2 = A^2 + B^2$ , since $i^2 = -1$

Hence $|\Psi|^2 = \Psi^*\Psi$ is always real quantity ,as required .

## Normalization

Even before we consider the actual calculation of ψ , we can establish requirements it must always fulfill . For one thing , since $|\Psi|^2$ is proportional to the probability density ( **P** ) of finding the body described by Ψ , the integral of $|\Psi|^2$over all space must be finite – the body must be somewhere , after all .If

$\int_{-\infty}^{\infty} |\psi|^2 dV = 0$ the particle does not exist

And the integral obviously cannot be ( ∞ ) and still mean anything . Furthermore ,$|\psi|^2$ cannot be negative or complex because the way it is defined . The only possibility left is that the integral be a finite quantity , if ψ is to describe properly a real body .

It is usually convenient to have $|\psi|^2$ be equal the probability density ( P ) of finding the particle described by ψ , rather than merely be proportional to ( P ) .

If $|\psi|^2$ is to equal P , then it must be true that

$\int_{-\infty}^{\infty} |\psi|^2 \, dV = 1$ ------------------ ( 5.1 ) **Normalization**

Since the particle exists somewhere at all times

$\int_{-\infty}^{\infty} P \, dV = 1$

A wave function that obeys Eq. ( 5.1 ) is said to be normalized . Every acceptable wave function can be normalized by multiplying it by appropriate constant , we shall shortly see how this is done.

## Well behaved functions

The well – behaved functions are admissible as mathematical representations of real bodies , these functions must have the following characteristic .

1- $\psi$ must be continuous and single – valued **everywhere** .

2- $\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}, \frac{\partial\psi}{\partial z}$ , must be continuous and single – valued everywhere .

3- $\psi$ must be normalizable , which means that $\psi$ must go to zero as $x \rightarrow \pm\infty$ , $y \rightarrow \pm\infty$ , $z \rightarrow \pm\infty$ in order that $\int |\Psi|^2\, dV$ over all space be a finite constant .

Given a normalized and otherwise acceptable wave function $\Psi$ , the probability that the particle it describes will be found in a certain region is simply the integral of the probability density $|\Psi|^2$ over that region . Thus for a particle restricted to motion in the x – direction , the probability of finding it between $x_1$ and $x_2$ is given by

$$P_{x1\,x2} = \int_{x1}^{x2} |\Psi|^2\, dx \quad \text{------------------------------} \; (5.2) \;\; \textbf{Probability}$$

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Second stage

Lecture 2

# Modern Physics II

2024-2025

Lecture 2
1- The Wave Equation
2- Partial Derivatives

Preparation
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## The wave Equation :

Schrodinger's equation , which is the fundamental equation of quantum mechanics in the same sense that the second law of motion is the fundamental equation of Newtonian mechanics , is a wave equation in the variable $\Psi$ .

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} \quad \text{------------------} \ (5.3)$$ **Wave equation**

Which governs a wave whose variable is **y** that propagates in the x – direction with the speed **v** .

## Partial Derivatives

Suppose we have a function **f ( x , y )** of two variables , x and y , we want to know how **f** varies with only one of them written $\frac{\partial f}{\partial x}$ .

$$\frac{\partial f}{\partial x} = \left(\frac{df}{dx}\right)_{y = \text{constant}}$$

If , $\mathbf{f = c\,x^2}$

$$\frac{df}{dx} = 2cx$$

And so , if , $\mathbf{f = yx^2}$

$$\frac{\partial f}{\partial x} = \left(\frac{df}{dx}\right)_{y = \text{constant}} = 2y\,x$$

The partial derivative of $\mathbf{f = y\,x^2}$ with respect to the other variable , y , is

$$\frac{\partial f}{\partial y} = \left(\frac{df}{dy}\right)_{x = \text{constant}} = x^2$$

Second order partial derivatives occur often in physics , as in the wave function . To find $\frac{\partial^2 f}{\partial x^2}$ ,we first calculate $\partial f/\partial x$ and then differentiate again , still keeping y constant :

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right)$$

For $f = yx^2$

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}(2yx) = 2y$$

Similarly

$$\frac{\partial^2 f}{\partial y^2} = \frac{\partial}{\partial y}(x^2) = 0$$

Solution of the wave equation may be of many kinds , reflecting the variety of waves that can occur – a single traveling pulse , a train of waves of constant amplitude and wavelength , and so on

All solutions of the wave equation must be of the form

$$Y = F\left(t, \pm \frac{x}{v}\right) \text{ ------------------------------ } (5.4)$$

Where F is any function that can be differentiated . The solutions $F\left(t - \frac{x}{v}\right)$ represent waves travelling in + x direction , and the solutions $F\left(t, + \frac{x}{v}\right)$ represent waves travelling in the - x direction .

Let us consider the wave equivalent of " free particle " which is a particle that is not under the influence of any forces and therefore pursues a straight path at constant speed . this wave is described by the general solution of Eq.

( 5.3 ) for undamped ( that is ,constant amplitude A ) , monochromatic ( constant angular frequency $w$ ) harmonic waves in + x direction namely

$$y = A\, e^{-iw(t - x/v)} \text{ ------------------------------ } (5.5)$$

In this formula y is a complex quantity , with both real and imaginary parts , because

$$e^{-i\theta} = \cos\theta - i\sin\theta$$

Eq. ( 5.5 ) can be written in the form

$$Y = A\cos w\left(t - \frac{x}{v}\right) - iA\sin w\left(t - \frac{x}{v}\right) \text{ ---------------------- } (5.6)$$

Only the real part of Eq. ( 5.6 ) has significance in the case of waves in a stretched string . There y represent the displacement of the string from its normal position ( Fig. 5.1 ) , and the imaginary of Eq. ( 5.6 ) is discarded as irrelevant .

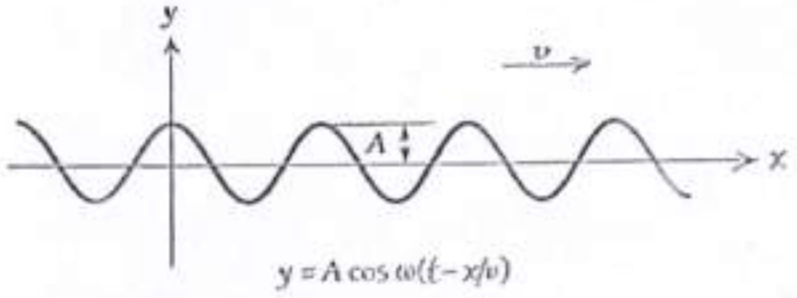

Figure 5.1 Waves in the xy plane traveling in the +x direction along a stretched string lying on the x axis.

Example : Verify that Eq. ( 5.5 ) is a solution of the wave equation .

Solution : the derivative of an exponential function $e^u$ is , $\frac{d}{dx}(e^u) = e^u \frac{du}{dx}$

The partial derivative of y with respect to x ( which means t is a constant ) , from Eq. ( 5.5 ) is therefore

$$\frac{\partial y}{\partial x} = \frac{iw}{v}\, y$$

And the second partial derivative is

$$\frac{\partial^2 y}{\partial x^2} = \frac{i^2 w^2}{v^2} = -\frac{w^2}{v^2} y$$

Since $i^2 = -1$. The partial derivative of y with respect to t ( now holding x constant ) is

$$\frac{\partial y}{\partial t} = -iw\ y$$

and the second partial derivative is

$$\frac{\partial^2 y}{\partial t^2} = i^2 w^2 y = -w^2 y$$

Combining these result gives

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2}$$

Which is Eq. ( 5.3 ) . Hence Eq. ( 5.5 ) is a solution of the wave equation .

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Second stage

Lecture 3

# Modern Physics II

2024-2025

Lecture 3

1- Schrodinger's Equation: Time – dependent Form
2- Expectation Values

Preparation
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# Schrodinger's Equation : Time – dependent Form

In quantum mechanics the wave function $\psi$ corresponds to the wave variable of wave motion in general . However , $\psi$ , unlike y , is not itself a measureable quantity and may therefore be complex . For this reason we shall assume that $\Psi$ is specified in the x- direction by

$$\psi = \mathrm{A}\, e^{-i\omega(t - x/v)} \quad \text{-----------------------------} \quad (5.8)$$

When we replace ω in above formula by $2\pi\nu$ and $\nu$ by $\lambda\mathrm{v}$ , we obtain

$$\psi = \mathrm{A}\, e^{-2\pi i\,(\nu t - x/\lambda)} \quad \text{-----------------------------} \quad (5.9)$$

We already know that $\nu$ and λ are in terms of the total energy and momentum of the particle being described by $\Psi$ .

Since $\mathrm{E} = \mathrm{h}\nu = 2\pi\hbar\nu$ and , $\lambda = \frac{\hbar}{p} = \frac{2\pi \mathrm{h}}{p}$

We have

$$\psi = \mathrm{A}\, e^{-(i/\hbar)\,(Et - px)} \quad \text{--------------------------} \quad (5.10)$$

Equation ( 5.10 ) is a mathematical description of the wave equation of unrestricted ( free particle)of total energy E and momentum P moving in the +x direction , and this expression is correct only for freely moving particles .

In general , we are most interested in situations where the motion of the particle is subject to various restrictions , for example , is an electron bound to an atom by the electric field of its nucleus . What we must now to do is obtain the fundamental differential equation for $\psi$ , which we can then solve in a specific situation .

We begin by the differentiating Eq. ( 5.10 ) twice with respect to x , yielding

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\psi \quad \text{-----------------------------} \quad (5.11)$$

And once with respect to t , yielding

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar}\Psi \qquad \text{-----------------------------} \ (5.12)$$

At speeds small compared with that of light , the total energy E of a particle is the sum of its kinetic energy ( $p^2/2m$ ) and its potential energy V , where V is in general a function of position **x** and time **t** .

$$E = \frac{p^2}{2m} + V \qquad \text{-----------------------------} \ (5.13)$$

Multiplying both sides of this equation by the wave function

$$E\,\Psi = \frac{p^2\,\Psi}{2m} + V\,\Psi \qquad \text{-----------------------------} \ (5.14)$$

From Eqs. ( 5.11 ) and ( 5.12 ) we see that

$$E\,\Psi = -\frac{\hbar}{i}\,\frac{\partial \Psi}{\partial t} \qquad \text{-----------------------------} \ (5.15)$$

And $p^2\Psi = -\,\hbar^2\,\frac{\partial^2 \Psi}{\partial x^2}$ ----------------------------- (5.16)

Substituting these expressions for $E\,\Psi$ and $p^2\Psi$ into Eq. ( 5.14 ) , we obtain

$$i\hbar\frac{\partial \Psi}{\partial t} = -\,\frac{\hbar^2}{2m}\,\frac{\partial^2 \Psi}{\partial x^2} + V\Psi \qquad \text{---------------} \ (5.17)$$

**this equation is the time – dependent Schrodinger's equation in one dimension .**

In three dimensions the time - dependent form of Schrodinger's equation is

$$i\hbar\frac{\partial \Psi}{\partial t} = -\,\frac{\hbar^2}{2m}\left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2}\right) + V\,\Psi \qquad \text{----------} \ (5.18)$$

Where the particle's potential V is some function of x , y , z , and t . For known V , Schrodinger's equation may be solved for the wave function $\Psi$ of the particle , from which its probability density $\Psi^2$ may be determined for a specified x , y , z , t .

ان تعميم معادلة شرودينكر من الحالة التي يكون فيها الجسيم طليقا ( free ) الى الحالة التي يكون فيها الجسيم في مجال قوى خارجية هو معقول تماما ، ولكن ليس هناك وسيلة لبرهنة صحة هذا التعميم . فكل ما نستطيع أن نفعله هو فرض معادلة شرودينكر وحلها لعدد من الحالات الفيزياوية ، ومن ثم مقارنة نتائجها بالنتائج العملية ، فاذا اتفقت النتائج النظرية والعملية ، نستنتج بأن معادلة شرودينكر صحيحة ، اما اذا اختلفت هذه النتائج فعلينا أن نهمل نظرية شرودينكر ونبحث عن حل آخر لتلك الظواهر . بعبارة اخرى لا يمكن اشتقاق معادلة شرودينكر من فرضيات ، بل بحد ذاتها تشكل فرضية اولية .

من الناحية العملية ، ظهر أن معادلة شرودينكر تتفق كليا مع النتائج العملية وعلينا أن نتذكر بأن المعادلة ( 5.18 ) صحيحة فقط للمسائل غير النسبية ( nonrelativistic ) في حين أن هناك صيغا اكثر تعقيدا تعالج مسائل تتضمن جسيمات سرعتها قريبة من سرعة الضوء • وتبقى هذه المعادلة فرضية اسوة بفرضية النسبية الخاصة او الميكانيك الاحصائي ، اذن لا يمكن اشتقاق اي من هذه الفرضيات من فرضيات اخرى اساسية ، ومن المهم ان نلاحظ ان معادلة شرودينكر لا تزيد من عدد الفرضيات الفيزياوية ، ذلك لأن قانون نيوتن الثاني في الحركة يمكن استنباطه من معادلة شرودينكر ، اذا ما فهمنا بأن الكميات المتضمنة في الميكانيك الكلاسيكي هي معدلات بدلا من أن تكون محددة •

In other words , Schrodinger's equation cannot be derived from " first principles " , but represents a first principle itself .

## Expectation Values المعدلات ، القيم المتوقعة ،

نستطيع من حل معادلة شرودينكر لجسيم في حالة فيزياوية معينة ، ان نجد دالة الموجة ( x, y, z ,t ) $\Psi$ ، هذه الدالة تحتوي على جميع المعلومات حول الجسيم ضمن حدود مبدأ التحديد uncertainty principle • وما عدا تلك الكميات فأنها تأخذ قيما مكممة ، وتكون جميع هذه المعلومات على صيغة احتمالات probabilities بدلا من اعداد محددة •

As an example , let us calculate the expectation value ‹ x › of the position of a particle confined to the x – axis , that is described by the wave function $\Psi$ ( x, t ) .

To make the procedure clear , we shall first answer a slightly different question : what is the average position x of a number of particles distributed along the x – axis in such a way that there are $N_1$ particles at $x_1$ , $N_2$ particles at $x_2$ , and so on ?

The average position x in this case is the same as the center of mass of the distribution , and so

$$\bar{X} = \frac{N_1X_1 + N_2X_2 + N_3X_3 + ---}{N_1 + N_2 + N_3 + ----}$$

$$= \frac{\sum N_iX_i}{\sum N_i}$$

عندما نتعامل مع جسيم واحد ، علينا ان نعوض عدد الجسيمات $N_i$ عند الموقع $x_i$ بالاحتمالية $P_i$ لوجود الجسيم داخل مسافة dx حول النقطة $x_i$ ، هذه الاحتمالية

$$P_i = |\psi_i|^2 \, dx$$

وحيث أن $\Psi_i$ هي دالة موجة الجسيم عند النقطة $x = x_i$ ، فبتعويض هذه الكمية وتحويل عملية الجمع الى تكامل ، نجد أن معدل موقع الجسيم هو

$$< x > = \frac{\int_{-\infty}^{\infty} x\,|\psi|^2\,dx}{\int_{-\infty}^{\infty}|\psi|^2\,dx} \quad \text{------------------------} \; (5.19)$$

واذا كانت دالة الموجة $\Psi_i$ مقومة normalized فأن مقام المعادلة ( 5.19 ) يساوي احتمالية وجود الجسيم ما بين $x = -\infty$ و $x = \infty$ عليه فأن المقام يساوي واحد لأن الجسيم موجود على محور x ، وبذلك فأن

$$\langle x \rangle = \int_{-\infty}^{\infty} x\,|\psi|^2 dx \quad \text{------------------------} \; (5.20)$$

هذه النتيجة توضح أن ‹ x › تكون عند مركز توزيع $|\psi|^2$

The same procedure as that followed above can be used to obtain the expectation value $\langle G(x)\rangle$ of any quantity ( for example , potential energy V(x ) ) that is a function of the position x of a particle described by a wave function $\Psi$ . The result is

$$\langle G(x)\rangle = \int_{-\infty}^{\infty} G(x)\,|\psi|^2\,dx \quad \text{----------------} \; (5.21) \text{ Expectation value}$$

وهذه المعادلة تكون صحيحة حتى لو تغيرت G(x) مع الزمن ، اذ بأي حال من الأحوال علينا أن نحسب $\langle G(x)\rangle$ عند لحظة معينة t ، ذلك لأن دالة الموجة $\Psi$ نفسها تتغير مع الزمن .

$$< G(r) > = \int_{-\infty}^{\infty} G(r)\,|\psi_r|^2\,dr \quad \text{......*}$$ Expectation value in three dimension.

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Second stage
Lecture 4

# Modern Physics II

2024-2025

Lecture 4
1- Schrodinger's Equation : Steady - State Form
2- Energy Quantized

Preparation
Lecturer. Hala I. Jasim

# Schrodinger's Equation : Steady – State Form

**معادلة شرودينكر غير المعتمدة على الزمن**

في كثير من الأحيان نجد أن الطاقة الكامنة للجسيم لا تتغير مع الزمن ، وعليه فأن القوة المؤثرة على الجسيم ، وبالتالي $V$ ، تعتمد على موقع الجسيم فقط ، في هذه الحالة يمكن تبسيط معادلة شرودينكر بأزالة متغير الزمن t ، نلاحظ أولا أن دالة الموجة ($\Psi$) في حيز ذي بعد واحد one dimensional wave function لجسيم طليق ( free) تأخذ الصيغة

$$\Psi = A\, e^{-(i/\hbar)(Et-px)}$$

$$= A\, e^{-(iE/\hbar)t} \,.\, e^{+(ip/\hbar)x}$$

$$= \psi\, e^{-(iE/\hbar)t} \qquad \text{------------------------------} \quad (5.22)$$

أي أن $\Psi$ هي حاصل ضرب دالة الزمن $e^{-(iE/\hbar)t}$ ودالة الموقع $\psi = Ae^{+(ip/\hbar)x}$ ، وبصفة عامة تأخذ دالة موجة جسيم تحت تأثيرقوة ثابتة بالنسبة للزمن ، نفس الصيغة اعلاه لحالة جسيم طليق

حيث أن المعادلة ( 5.17 ) تمثل معادلة شرودينكر المعتمدة على الزمن في بعد واحد

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\,\Psi$$

نعوض المعادلة (5.22 ) في المعادلة ( 5.17 )

ولكي نقوم بالتعويض وكما نلاحظ من المعادلة (5.17 ) فعلينا أن نجد ( $\frac{\partial \Psi}{\partial t}$ ) و ( $\frac{\partial^2 \Psi}{\partial x^2}$ )

$$\frac{\partial \Psi}{\partial t} = \psi\, e^{-(iE/\hbar)t} \,.\, \left( -\frac{iE}{\hbar} \right)$$

$$= \left( -\frac{iE}{\hbar} \right) \psi\; e^{-(iE/\hbar)t}$$

ومن ثم نجد ( $\frac{\partial^2 \Psi}{\partial x^2}$ ) حيث نجد أولا ( $\frac{\partial \Psi}{\partial x}$ ) ثم نجد ( $\frac{\partial^2 \Psi}{\partial x^2}$ )

$$\frac{\partial \Psi}{\partial x} = \frac{\partial}{\partial x}\left( \psi \; e^{-(iE/\hbar)t} \right) = e^{-(iE/\hbar)t} \; \frac{\partial \psi}{\partial x}$$

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{\partial}{\partial x}\left( \frac{\partial \Psi}{\partial x} \right)$$

$$= \frac{\partial}{\partial x}\left( e^{-(iE/\hbar)t} \; \frac{\partial \psi}{\partial x} \right)$$

$$= e^{-(iE/\hbar)t} \; \frac{\partial^2 \psi}{\partial x^2}$$

وبعد أن وجدنا ( $\frac{\partial \Psi}{\partial t}$ ) ، ( $\frac{\partial^2 \Psi}{\partial x^2}$ ) نعوض كل منهما في معادلة ( 5.17 ) فنحصل على

$$i\hbar \left(-\frac{iE}{\hbar}\right) \psi \; e^{-(iE/\hbar)t} = -\frac{\hbar^2}{2m} \left( e^{-(iE/\hbar)t} \; \frac{\partial^2 \psi}{\partial x^2} \right) + V \psi \; e^{-(iE/\hbar)t}$$

$$E \psi \; e^{-(iE/\hbar)t} = \frac{\hbar^2}{2m} \; e^{-(iE/\hbar)t} \; \frac{\partial^2 \psi}{\partial x^2} + V \psi \; e^{-(iE/\hbar)t}$$

وبعد أن عوضنا نقسم المعادلة الاخيرة على العامل المشترك في هذه المعادلة وهو ( $e^{-(iE/\hbar)t}$ ) فنحصل على

$$E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V \psi$$

وبترتيب المعادلة نحصل على

$$(E - V)\psi + \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = 0$$

والان نضرب طرفي المعادلة ب ( $\frac{2m}{\hbar^2}$ ) فنحصل على المعادلة ( 5.23 )

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V)\psi = 0 \qquad \text{-----------------------} \; (5.23)$$

وهذه المعادلة تسمى ب (Steady – state Schrodinger's equation in one dimension )

( أي معادلة شرودينكر غير المعتمدة على الزمن في بعد واحد )

In three dimension

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - V)\psi = 0 \qquad \text{------------------} \; (5.24)$$

وهذه المعادلة ( 5.24 ) هي معادلة شرودينكر غير المعتمدة على الزمن في ثلاثة ابعاد

Steady – State Schrodinger's equation in three – dimension .

In general , Schrodinger's steady – state equation can be solved only for certain values of the energy

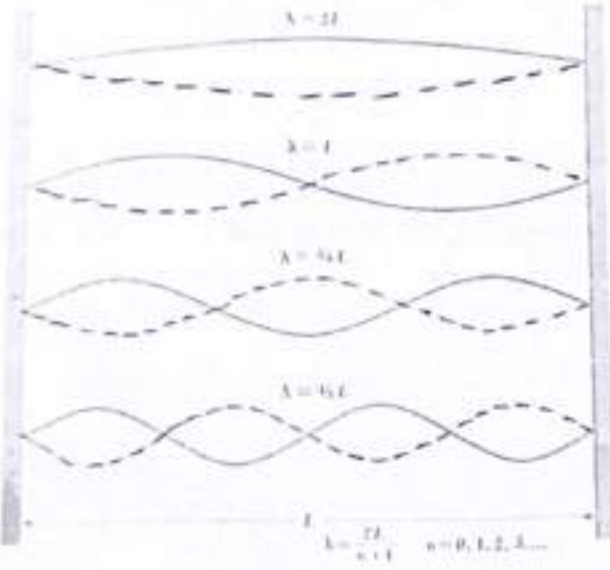
وبصورة عامة ليس هناك حل فيزياوي لمعادلة شرودينكر غير المعتمدة على الزمن ، الا لقيم معينة للطاقة $E$ وعلى وجه التحديد ،الموجة ومشتقاتها الجزئية الثلاثة يجب أن تكون مستمرة continuous ، ومحدودة finite واحادية القيمة single – valued ، واذا لم يكون هناك مثل هذه الدالة الموجية ، فالنظام لا يمكن أن يوجد

في حالة مستقرة . وعليه فأن تكمم الطاقة energy quantized ( أي أن الطاقة تأخذ قيما محددة تسمى بالقيم المسموحة ) يظهر بصورة طبيعية في ميكانيك الكم . وأن هذا التكمم صفة عامة لجميع النظم المستقرة . وهناك مثال قريب لتكمم الطاقة ، وهو ما يحدث لحالة موجة مستقرة في سلك مشدود طوله L ومثبت عند طرفيه فهنا نجد بدلا من أن تكون هناك موجة واحدة تنتشر بصورة مستمرة باتجاه واحد ، نجد موجتين تنتشران انيا بالاتجاهين x + و x - بحيث أن الازاحة عند نهايتي السلك تساوي صفرا دائما ( كما

هو موضح في الشكل ادناه ) ان دالة موجية مقبولة للازاحة y (x ,t ) يجب أن تحقق مع مشتقاتها نفس المواصفات السابقة وهي أن تكون مستمرة ومحدودة واحادية القيمة . وكذلك يجب أن تكون هذه الدالة حقيقية لأنها تمثل كمية يمكن قياسها في هذه الحالة . والحل الوحيد للمعادلة الموجية

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2}$$

هو الحل الذي يحقق الصفات المطلوبة وفي نفس الوقت يحقق y = 0 عند طرفي السلك .



الشكل ٥ - ٢ موجة مستقرة في سلك مشدود مثبت عند طرفيه

وهذا الحل يمتلك اطوال موجية تتحدد بالعلاقة

$\lambda_n = \frac{2L}{n+1}$ n = 0 , 1, 2 ,3

ان وجود هذه القيم المحددة للطول الموجي ( $\lambda_n$ ) انما هو نتيجة تقييد الحلول الرياضية للمعادلة الموجية بالشروط الفيزياوية الموضوعة ٠ ان قيم الطاقة $E_n$ التي تأخذ عندها معادلة شرودينكر حلولا مقبولة فيزياويا تدعى بالقيم المسموحة ( eigen values ) في حين تدعى دالات الموجة التابعة لهذه الطاقات بالدالات المسموحة ( eigen functions ) ٠

ان مستويات الطاقة المنفصلة في ذرة الهيدروجين هي مثال للطاقات المسموحة حيث

$$E_n = \frac{-me^4}{32\pi^2\varepsilon_0^2 h^2}\left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3$$

ومثال اخر على تكمم كمية ديناميكية هو تكمم الزخم الزاوي angular momentum ، وسوف نجد لحالة ذرة الهيدروجين بأن القيم المسموحة للزخم الزاوي الكلي تتحدد بالعلاقة

$$L_l = \sqrt{l(l+1)}\hbar \qquad l = 0, 1, 2, \text{----------}, (n-1)$$

وبصورة عامة ، يمكن ان تكون كمية ديناميكية ( G ) غير مكممة ٠ وفي هذه الحالة لا تؤدي قياسات G على عدد كبير من الجسيمات الى قيمة معينة ثابتة ، بل الى قيم منتشرة متوسطها هو المعدل لهذه الكمية ‹ G ›

$$\langle G \rangle = \int_{-\infty}^{\infty} G\,|\psi|^2\,dx$$

وعلى سبيل المثال ، فأن موقع الالكترون في ذرة الهيدروجين ليس مكمما ٠ لذا علينا أن نتصور بأن الالكترون موجود بجوار النواة باحتمالية معينة $|\psi|^2$ لوحدة الحجوم من دون أن يكون هناك مكان متوقع أو مدار كلاسيكي ٠

والاحتمالية المقصودة في هذه الحالة هي ايجاد الكترون كامل في حيز معين ، وعلى الرغم من أن هذه الاحتمالية تنتشر في الفضاء ، فأن الالكترون نفسه غير منتشر ٠

## 5.7 SCHRÖDINGER'S EQUATION: STEADY-STATE FORM

### *Eigenvalues and eigenfunctions*

In a great many situations the potential energy of a particle does not depend on time explicitly; the forces that act on it, and hence $U$, vary with the position of the particle only. When this is true, Schrödinger's equation may be simplified by removing all reference to $t$.

We begin by noting that the one-dimensional wave function $\Psi$ of an unrestricted particle may be written

$$\Psi = Ae^{-(i/\hbar)(Et-px)} = Ae^{-(iE/\hbar)t}e^{+(ip/\hbar)x} = \psi e^{-(iE/\hbar)t} \tag{5.31}$$

Evidently $\Psi$ is the product of a time-dependent function $e^{-(iE/\hbar)t}$ and a position-dependent function $\psi$. As it happens, the time variations of *all* wave functions of particles acted on by forces independent of time have the same form as that of an unrestricted particle. Substituting the $\Psi$ of Eq. (5.31) into the time-dependent form of Schrödinger's equation, we find that

$$E\psi e^{-(iE/\hbar)t} = -\frac{\hbar^2}{2m}e^{-(iE/\hbar)t}\frac{\partial^2\psi}{\partial x^2} + U\psi e^{-(iE/\hbar)t}$$

Dividing through by the common exponential factor gives

**Steady-state Schrödinger equation in one dimension**

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E-U)\psi = 0 \tag{5.32}$$

Equation (5.32) is the steady-state form of Schrödinger's equation. In three dimensions it is

**Steady-state Schrödinger equation in three dimensions**

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E-U)\psi = 0 \tag{5.33}$$

An important property of Schrödinger's steady-state equation is that, if it has one or more solutions for a given system, each of these wave functions corresponds to a specific value of the energy $E$. Thus energy quantization appears in wave mechanics as a natural element of the theory, and energy quantization in the physical world is revealed as a universal phenomenon characteristic of *all* stable systems.

A familiar and quite close analogy to the manner in which energy quantization occurs in solutions of Schrödinger's equation is with standing waves in a stretched string of length L that is fixed at both ends. Here, instead of a single wave propagating indefinitely in one direction, waves are traveling in both the $+x$ and $-x$ directions simultaneously. These waves are subject to the condition (called a **boundary condition**) that the displacement $y$ always be zero at both ends of the string. An acceptable function $y(x, t)$ for the displacement must, with its derivatives (except at the ends), be as well-behaved as $\psi$ and its derivatives—that is, be continuous, finite, and single-valued. In this case $y$ must be real, not complex, as it represents a directly measurable quantity. The only solutions of the wave equation, Eq. (5.3), that are in accord with these various limitations are those in which the wavelengths are given by

$$\lambda_n = \frac{2L}{n+1} \qquad n = 0, 1, 2, 3, \ldots$$

as shown in Fig. 5.3. It is the *combination* of the wave equation and the restrictions placed on the nature of its solution that leads us to conclude that $y(x, t)$ can exist only for certain wavelengths $\lambda_n$.

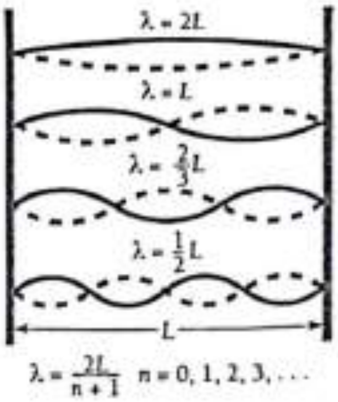


Figure 5.3 Standing waves in a stretched string fastened at both ends.

## Eigenvalues and Eigenfunctions

The values of energy $E_n$ for which Schrödinger's steady-state equation can be solved are called **eigenvalues** and the corresponding wave functions $\psi_n$ are called **eigenfunctions**. (These terms come from the German *Eigenwert*, meaning "proper or characteristic value," and *Eigenfunktion*, "proper or characteristic function.") The discrete energy levels of the hydrogen atom

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3, \ldots$$

are an example of a set of eigenvalues. We shall see in Chap. 6 why these particular values of $E$ are the only ones that yield acceptable wave functions for the electron in the hydrogen atom.

An important example of a dynamical variable other than total energy that is found to be quantized in stable systems is angular momentum **L**. In the case of the hydrogen atom, we shall find that the eigenvalues of the magnitude of the total angular momentum are specified by

$$L = \sqrt{l(l+1)}\,\hbar \qquad l = 0, 1, 2, \ldots, (n-1)$$

Of course, a dynamical variable $G$ may not be quantized. In this case measurements of $G$ made on a number of identical systems will not yield a unique result but instead a spread of values whose average is the expectation value

$$\langle G \rangle = \int_{-\infty}^{\infty} G|\psi|^2\, dx$$

In the hydrogen atom, the electron's position is not quantized, for instance, so that we must think of the electron as being present in the vicinity of the nucleus with a certain probability $|\psi|^2$ per unit volume but with no predictable position or even orbit in the classical sense. This probabilistic statement does not conflict with the fact that experiments performed on hydrogen atoms always show that each one contains a whole electron, not 27 percent of an electron in a certain region and 73 percent elsewhere. The probability is one of *finding* the electron, and although this probability is smeared out in space, the electron itself is not.

## Operators and Eigenvalues

University of Mosul
College of Science
Department of Physics
Second stage
Lecture 5

# Modern Physics II

2024-2025

Lecture 5
1- The Particle in a box : Energy Quantization
2- Uncertainty Principle

Preparation
Lecturer. Hala I. Jasim

# The particle in a box : Energy Quantization

## جسيم في صندوق : تكمم الطاقة

ان أول مثال لاستخدام معادلة شرودينكر ، هو دراسة جسيم يتحرك ذهابا وايابا بين جدران صندوق (الشكل 5.3 ) واهتمامنا بهذه المسألة يعود الى ثلاثة اسباب

1- to see how Schrodinger's equation is solved when the motion of a particle is subject to restrictions .

2- To learn the characteristic properties of solutions of this equation , such as the limitation of particle energy to certain specific values only .

3- To compare the prediction of quantum mechanics with those of Newtonian mechanics .

نستطيع وصف حركة الجسيم بأنها محصورة على طول محور x بين x = 0 و x = L ، نتيجة وجود جدران صلبة جدا عند النهايتين ، وعند اصطدام الجسيم بهذه الجدران ، فأنه لا يفقد طاقة ولذلك تبقى طاقته الكلية محفوظة ( constant ) ان هذه المسألة ، وفق المضمون الدقيق في ميكانيك الكم تمثل طاقة كامنة V تساوي ما لانهاية عند جدران الصندوق ، وأن V تساوي كمية ثابتة ( وللسهولة نعتبرها تساوي صفرا ) داخل الصندوق ٠

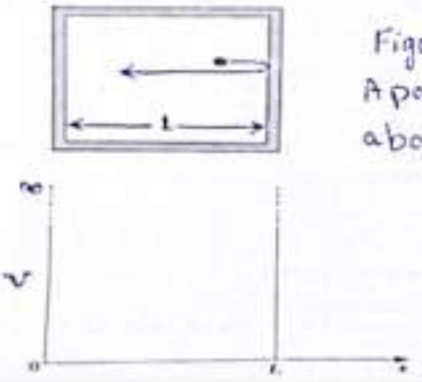


Figure (5-3)
A particle confined to
a box of width L

ولما كان الجسيم لا يمكن أن يمتلك مالا نهاية من الطاقة لذلك فهو لا يستطيع أن يخترق جدران الصندوق ويهرب الى الخارج ٠ وعليه فأن دالة الموجة ψ تساوي صفرا عند x ≤ 0 و x ≥ L فتكون المسألة هنا هي حساب قيمة $\psi$ داخل الصندوق وعلى وجه التحديد بين x = 0 و x = L ٠

بالعودة الى المعادلة ( 5.23 ) معادلة شرودينكر غير المعتمدة على الزمن في بعد واحد وبالتعويض عن V = 0 نحصل على معادلة شرودينكر داخل الصندوق وهي

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\,\psi = 0 \quad \text{--------------------} \; (5.25)$$

حيث V = 0 داخل الصندوق ، ويكون التفاضل الكلي $d^2\psi/dx^2$ هو نفس التفاضل الجزئي وذلك لأن $\psi$ تعتمد على x فقط ٠

Equation ( 5.25 ) has the two possible solutions

$$\psi = A \sin \sqrt{\frac{2mE}{\hbar^2}}\ x \quad \text{------------------------} \quad (5.26)$$

$$\psi = B \cos \sqrt{\frac{2mE}{\hbar^2}}\ x \quad \text{--------------------} \quad (5.27)$$

ويمكن التحقق من هذين الحلين بالتعويض المباشر في المعادلة ( 5.25 ) ، ان مجموع الحلين هو أيضا حل للمعادلة المذكورة ، على حين أن المعاملات A و B ثابتان ويجب حسابهما لكل مسألة ، أن هذه الحلول يجب أن تحقق الشرط الفيزياوي boundary condition ، $\psi = 0$ عند x = 0 و x = L ، ولما كان $\cos 0 = 1$ ، لذلك فأن الحل الثاني

للمعادلة ( 5.27 ) لا يمكن أن يصف حالة الجسيم داخل الصندوق لأن $\psi \neq 0$ عند x = 0 ، من هذا نستنتج أن B يجب أن يساوي صفرا ، ولما كان $\sin 0 = 0$ ، فأن الحل الأول معادلة ( 5.26 ) يعطينا دائما $\psi = 0$ عند x = 0 ونحصل على $\psi = 0$ عند x = L اذا كان

$$\sqrt{\frac{2mE}{\hbar^2}}\ L = \pi, 2\pi, 3\pi, \text{-----}$$

$$= n\pi \qquad n = 1, 2, 3, \text{---}, \qquad \text{---------------} \quad (5.28)$$

This result comes about because the sines of the angles π ,2π , 3π , ----- , are all ( zero )

وذلك لأن جيب الزوايا ---- , $\pi, 2\pi, 3\pi$ يساوي صفرا .

From Eq. ( 5.28 ) it is clear that the energy of the particle can have only certain values .

وهذه القيم تمثل القيم المسموحة eigenvalues التي بدورها تشكل مستويات طاقة النظام ، وهذه الطاقات المسموحة يمكن الحصول عليها من المعادلة ( 5.28 ) وذلك بتربيع طرفي المعادلة حيث

$$\frac{2mE}{\hbar^2} L^2 = n^2\pi^2$$

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

ولأن قيم E تعتمد على n لذلك يمكن الرمز لها ب ( $E_n$ ) حيث

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad n = 1, 2, 3, \text{---}, \qquad \text{-------------} \quad (5.29)$$

وهذه المعادلة تمثل الطاقات المسموحة لجسيم في صندوق particle in a box وأن العدد n يدعى بالعدد الكمي ( quantum number ) .

وجسيم محصور في صندوق لا يستطيع أن يمتلك طاقة عدا الطاقات المبينة في المعادلة ( 5.29 ) ٠ هذه الصفة ( تكمم الطاقة ) هي نتيجة حصر الجسيم داخل الصندوق وبالتالي تحديد دالته الموجية ٠

It is significant that the particle cannot have zero energy , if it did , the wave function $\psi$ would have to be zero everywhere in the box and this means that the particle cannot be present there .

ان عدم السماح ل E = 0 بالاضافة الى تحديد E بقيم محددة كما في المعادلة ( 5.29 ) هي صفات كمية بحتة وليس لها مرادف في الميكانيك الكلاسيكي ، ذلك انه في الميكانيك الكلاسيكي تكون جميع قيم الطاقة – ومن ضمنها الصفر – مسموحة ٠

ان مبدأ عدم التحديد ( uncertainty principle ) يعطى بالعلاقة

$$\Delta x \, \Delta p \geq \hbar$$

ان هذا المبدأ يبين لنا لماذا تكون E = 0 لجسيم محصور داخل الصندوق غير مسموح بها ٠

لما كان الجسيم محصور داخل الصندوق فأن عدم التحديد في موقعه يساوي عرض الصندوق Δx = L وعليه فأن عدم التحديد في زخم الجسيم هو

$$\Delta p \geq \frac{\hbar}{L}$$

الذي لا يتفق مع كون E = 0 ( يعني ان p = 0 ) ٠ ونلاحظ أن زخم الجسيم التابع للطاقة $E = E_1$ ( التي تكون كليا على شكل طاقة حركية )

$$E = \frac{1}{2} m v^2 \rightarrow 2E = mv^2 \rightarrow 2mE = m^2 v^2$$

$$2mE = p^2 \rightarrow p = \pm\sqrt{2mE}$$

$$p_1 = \pm\sqrt{2mE_1}$$

وبالتعويض عن $E_1$ من المعادلة ( 5.29 )

$$p_1 = \pm\sqrt{2mE_1} = \pm\frac{\pi\hbar}{L}$$

وهذا المقدار من الزخم يتفق مع مبدأ عدم التحديد كما نلاحظ ٠ ولكي نقتنع بأن المعادلة ( 5.29 ) لا تتعارض مع مشاهداتنا اليومية في حين أنها تعطينا نتائج متميزة للعالم الدقيق ، دعنا نحسب مستويات الطاقة

١- لالكترون في صندوق عرضه ( $1 A^0$ )

٢- لكرة صلبة كتلتها ( 10 gm ) داخل صندوق عرضه ( 10 cm ) ٠

في الحالة الاولى لدينا $L = 1 A^0 = 10^{-10}\, m$ , $m = 9.1 \times 10^{-31}$ Kg ولذلك تكون مستويات الطاقة المسموحة ٠

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad , \qquad \hbar = \frac{h}{2\pi} = \frac{6.62 \times 10^{-34}}{2 \times 3.14} = 1.054 \times 10^{-34}\, J.s$$

$$E_n = \frac{n^2 \times (3.14)^2 \times (1.054 \times 10^{-34}\, J.s)^2}{2 \times 9.1 \times 10^{-31}\, Kg \times (10^{-10}\, m)^2}$$

$$= 6.0 \times 10^{-18}\, n^2\, Joule = 38\, n^2\, eV$$

فأقل طاقة يمتلكها الالكترون داخل الصندوق في هذه الحالة هي ( $E_1$ ) عندما ( n = 1 ) ، حيث

$$E_1 = 38\ eV$$

ومستويات الطاقة الأخرى تتدرج كالآتي $E_2$=152 $eV$ ، $E_3$ = 342 $eV$ ، $E_4$ = 608 $eV$ وهكذا كما في الشكل ( 5.4 ) وهذه المستويات متباعدة بصورة كافية بحيث يمكن تمييزها .

وفي الحالة الثانية لدينا

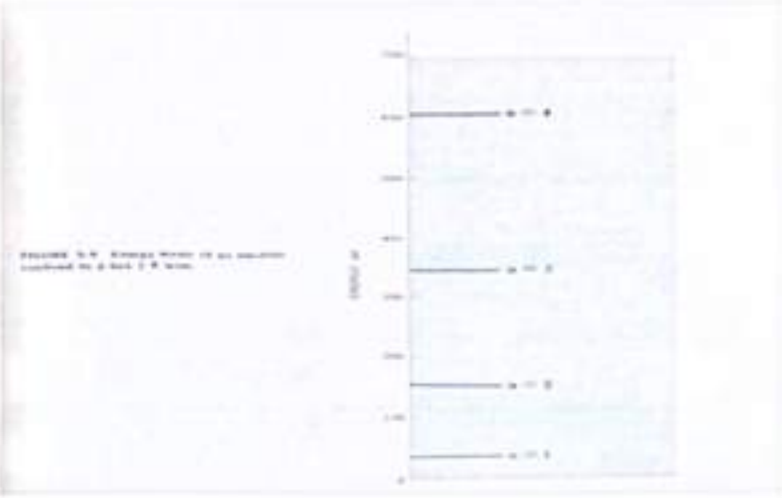
$$L = 10\, cm \ , \ m = 10\ gm = 10^{-2}\, Kg$$

وعليه فأن مستويات الطاقة المسموحة للكرة تكون

$$E_n = \frac{n^2\pi^2\, (1.054 \times 10^{-34}\ J.s)^2}{2 \times 10^{-2}\ Kg \times (10^{-1} m)^2}$$

$$= 5.5 \times 10^{-64}\ n^2\, Joule$$

في هذه الحالة تكون الطاقة الدنيا للكرة والتي تنتج من n = 1 هي فقط ( $5.5 \times 10^{-64}\, Joule$ ) ، ان كرة بهذه الطاقة الحركية لها سرعة تساوي ( $3.3 \times 10^{-31} m/s$ ) فقط ، وكرة بهذه السرعة لا يمكن تمييزها عن كرة ساكنة. والسرعة الاعتيادية لكرة بهذه المواصفات هي ( $\frac{1}{3}\, m/s$ ) وهذه السرعة تمثل عددا كميا كبيرا جدا ( n = $10^{30}$ ) ، ان مستويات الطاقة للكرة في هذه الحالة تكون متقاربة جدا بحيث لا يمكن تمييز هذه المستويات عن بعضها البعض ، وبالتالي فأنها تظهر على شكل مستمر . ولذا لا يمكن تمييز الظواهر الكمية من خلال تجاربنا اليومية وهذه الصفة تشير الى سبب نجاح ميكانيك نيوتن في تفسير الظواهر الفيزياوية في المشاهدات اليومية .



# The particle in a box : Energy Quantization

To solve Schrodinger's equation, even in its simpler steady-state form, usually requires sophisticated mathematical techniques. For this reason the study of quantum mechanics has traditionally been reserved for advanced students who have the required proficiency in mathematics. However, since quantum mechanics is the theoretical structure whose results are closest to experimental reality, we must explore its methods and applications if we are to achieve any understanding of modern physics. As we shall see, even a relatively limited mathematical background is sufficient for us to follow the trains of thought that have led quantum mechanics to its greatest achievements.

One first problem using Schrodinger's equation is that of a particle bounding back and forth between the walls of a box (Fig. 5-3).

Our interest in this problem is three-fold: to see how schrodinger's equation is solved when the motion of a particle is subject to restrictions ; to learn the characteristic properties of solutions of this equation, such as the limitation of particle energy to certain specific values only ; and to compare the predictions of quantum mechanics with those of Newtonian mechanics.

Ne may specify the particle's motion by saying that t is restricted to traveling along the $x$ axis between $x=0$ and $x=L$ by infinitely hard walls. A particle does not lose energy when it collides with such walls, so that its total energy stays constant.

From the formal point of view of quantum mechanics, the potential energy $V$ of the particle is infinite on both sides of the box, while $V$ is a constant—say 0 for convenience—on the inside. Since the particle cannot have an infinite amount of energy, it cannot exist outside the box, and so its wave function $\psi$ is 0 for $x \leqslant 0$ and $x \geqslant L$. Our task is to find what $\psi$ is within the box, namely, between $x=0$ and $x=L$.

Within the box Schrodinger's equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad \text{———} (5.25)$$

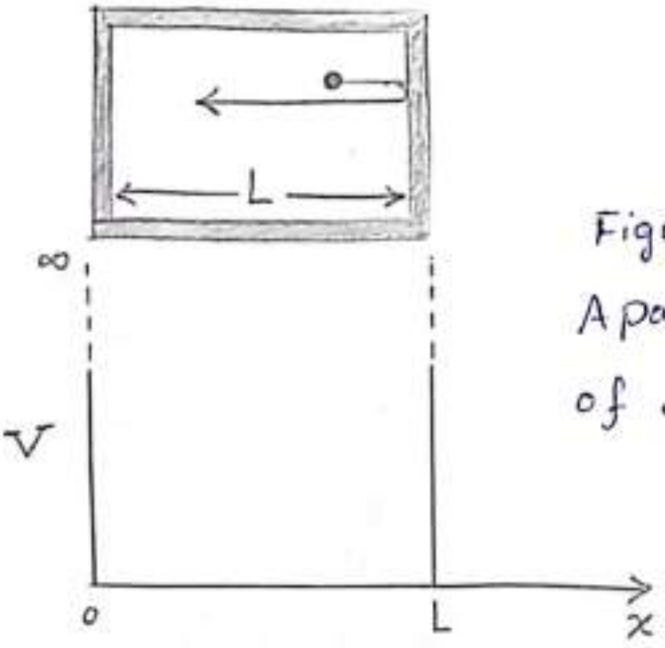


Figure (5-3):
A particle confined to a box of width L.

since $V=0$ there. (The total derivative $d^2\psi/dx^2$ is the same as the partial derivative $\partial^2\psi/\partial x^2$ because $\psi$ is a function of $x$ only in this problem). Equation (5-25) has the two possible solutions

$$\psi = A \sin \sqrt{\frac{2mE}{\hbar^2}}\, x \quad ------ \quad (5\cdot26)$$

$$\psi = B \cos \sqrt{\frac{2mE}{\hbar^2}}\, x \quad ------ \quad (5\cdot27)$$

which we can verify by substitution back into Eq. 5-25; their sum is also a solution. A and B are constants to be evaluated.

These solutions are subject to the important boundary condition that $\psi = 0$ for $x=0$ and for $x=L$. Since $(\cos 0 = 1)$, the second solution cannot describe the particle because it does not vanish at $x=0$. Hence we onclude that $B=0$. Since ($\sin 0=0$), the first soution always yields $\psi=0$ at $x=0$, as required, ut $\psi$ will be 0 at $x=L$ only when

$$\sqrt{\frac{2mE}{\hbar^2}}\,L = \pi, 2\pi, 3\pi, \ldots \qquad (5\text{-}28)$$

$$= n\pi \qquad ; \; n = 1, 2, 3, \ldots$$

This result comes about because the sines of the angles $\pi, 2\pi, 3\pi, \ldots$ are all (0). From Eq. (5·28) it is clear that the energy of the particle can have only certain values, which are the eigenvalues mentioned in the previous section. These eigen values, constituting the energy levels of the system, are

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \qquad ; \; n = 1, 2, 3, \ldots \qquad (5\cdot 29)$$

The integer $n$ corresponding to the energy level $E_n$ is called its quantum number. A particle confined to a box cannot have an arbitrary energy: the fact of its confinement leads to restrictions on its wave function that permit it to have only those energies specified by Eq. (5-29).

It is significant that the particle cannot have zero energy; if it did, the wave function $\psi$ would have to be zero everywhere in the box, and this means that the particle cannot be present there.

The exclusion of $E=0$ as a possible value for the energy of a trapped particle, like the limitation of $E$ to a discrete set of definite values, is a quantum-mechanical result that has no counterpart in classical mechanics, where all energies, including zero, are presumed possible.

The uncertainty principle provides confirmation that $E=0$ is not admissible. Because the particle is trapped in the box, the uncertainty in its position is $\Delta x = L$, the width of the box. The uncertainty in its momentum must therefore be $\Delta p \geqslant \frac{\hbar}{L}$

which is not compatible with $E=0$. We note that the momentum corresponding to $E_1$ is, since the particle energy here is entirely kinetic,

$$p_1 = \pm\sqrt{2m E_1} = \pm \frac{\pi\hbar}{L}$$

which it in accord with the uncertainty principle.

Why are we not aware of energy quantization in our own experience? Surely a marble rolling back and forth between the sides of a level box with a smooth floor can have any speed, and therefore any energy, we choose to give it, including zero. In order to assure ourselves that Eq. (5-29) does not conflict with our direct observations while providing unique insights on a microscopic scale, we shall compute the permitted energy levels of (1) an electron in a box 1A° wide and (2) a 10-g marble in a box 10 cm wide.

In case (1) we have $m = 9.1 \times 10^{-31}$ kg and $L = 1 A° = 10^{-10}$ m, so that the permitted electron energies are

$$E_n = \frac{n^2 \times \pi^2 \times (1.054 \times 10^{-34} \text{ J.s})^2}{2 \times 9.1 \times 10^{-31} \text{ kg} \times (10^{-10} \text{ m})^2}$$

$$= 6.0 \times 10^{-18} \; n^2 \text{ J} \quad = 38 \; n^2 \text{ eV}$$

The minimum energy the electron can have is 38 eV, corresponding to $n=1$. The sequence of energy levels continues with $E_2 = 152$ eV, $E_3 = 342$ eV, $E_4 = 608$ eV, and so on (Fig.(5-4)). These energy levels are sufficiently far apart to make the quantization of electron energy in such a box conspicuous if such a box actually did exist.

In case 2 we have $m = 10\,g = 10^{-2}\,kg$ and $L = 10\,cm = 10^{-1}\,m$, so that the permitted marble energies are

$$E_n = \frac{n^2 \times \pi^2 \times (1.054 \times 10^{-34}\,J\cdot s)^2}{2 \times 10^{-2}\,kg \times (10^{-1}\,m)^2}$$

$$= 5.5 \times 10^{-64}\, n^2\, J$$

The minimum energy the marble can have is $5.5 \times 10^{-64}\,J$, corresponding to $n=1$. A marble with this kinetic energy has a speed of only $3.3 \times 10^{-31}\,(m/s)$ and is therefore experimentally indistinguishable from a stationary marble. A reasonable speed a marble might have is, say, $1/3\,(m/s)$ — which corresponds to the energy level of quantum number $n = 10^{30}$! The permissible energy levels are so very close together, then, that there is no way to determine whether the marble can take on only those energies predicted by Eq. (5-29) or any energy whatever.

Hence in the domain of everyday experience quantum effects are imperceptible; this accounts for the success in this domain of Newtonian mechanics.

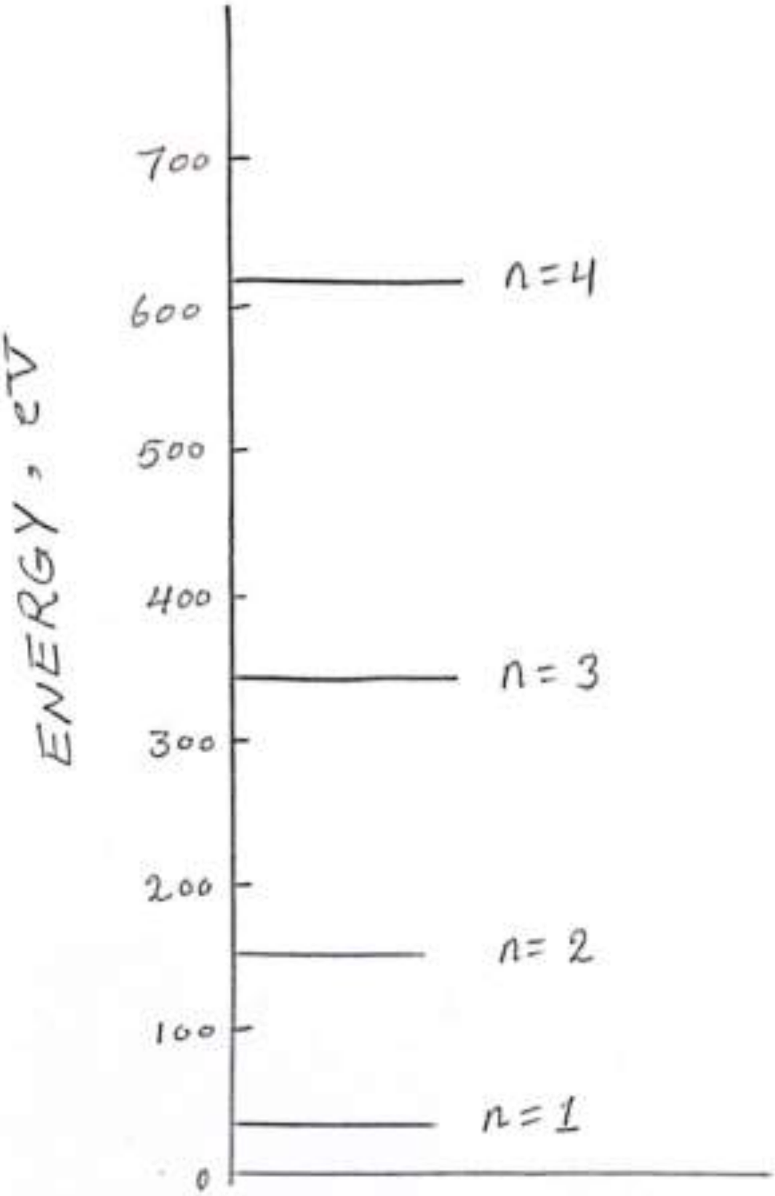


Figure (5-4) : Energy levels of an electron confined to abox 1A wide.

University of Mosul
College of Science
Department of Physics
Second stage
Lecture 6

# Modern Physics II

2024-2025

## Lecture 6

1- The Particle in a box : Wave Functions
2- Application of the uncertainty principle

Preparation
Lecturer. Hala I. Jasim

# The particle in a box : wave functions

جسيم في صندوق : دالات الموجة

In the previous section we found that the wave function of a particle in a box whose energy is $E$ is given by

$$\psi = A \sin\sqrt{\frac{2mE}{\hbar^2}}\ x$$

وان القيم المسموحة للطاقة ( $E$ ) هي

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

وبالتعويض عن $E$ ب $E_n$ في معادلة دالة الموجة للجسيم اعلاه نحصل

$$\psi_n = A\sin\frac{n\pi x}{L} \quad \text{-------------} \ (5.30)$$

This equation ( 5.30 ) represent the eigenfunctions corresponding to the eigenvalues $E_n$

ومن السهل أن نبرهن بأن الدالات الموجية ( 5.30 ) تحقق جميع الصفات المطلوبة والتي ناقشناها سابقا : حيث $\psi_n$ ، لكل قيم $n$ هي احادية القيمة ل ( $x$ ) وأن كلا من $\psi_n$ ، $\partial\psi_n/\partial x$ مستمرة ، وبالإضافة لذلك فإن تكامل $|\psi_n|^2$على جميع الفضاء محدود ( finite ) ونستطيع البرهان على هذا بتكامل $|\psi_n|^2 dx$ من x = 0 الى x = L حيث أن الجسيم محصور ضمن هذه الحدود

$$\int_{-\infty}^{\infty} |\psi_n|^2\, dx = \int_0^L |\psi_n|^2 dx$$

$$= A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$$

$$\int_0^L |\psi_n|^2\, dx = \frac{A^2}{2}\left[\int_0^L dx - \int_0^L \cos\left(\frac{2n\pi x}{L}\right) dx\right]$$

$$= \frac{A^2}{2}\left[x - \left(\frac{L}{2n\pi}\right)\sin\frac{2n\pi x}{L}\right]_0^L$$

$$= A^2\,\frac{L}{2} \quad \text{-----------------} \ (5.31)$$

وللحصول على دالات موجية مقومة ل( $\psi_n$ ) علينا أن نختار قيمة مناسبة ل( $A$ ) بحيث أن $|\psi_n|^2 dx$ تساوي الاحتمالية ( $pdx$ ) لايجاد الجسيم بين x و x + dx فإذا كانت $|\psi_n|^2$ تساوي ( p ) فإن

$$\int_{-\infty}^{\infty} |\psi_n|^2 dx = 1 \qquad \text{------------------} \; (5.32)$$

$$\int_{-\infty}^{\infty} p dx = 1$$

هي الصيغة الرياضية للقول أن هناك احتمالا 100% لوجود الجسيم في مكان ما في الفضاء ، وبمقارنة المعادلتين (5.31) و (5.32) نحصل على

$$1 = A^2 \frac{L}{2}$$

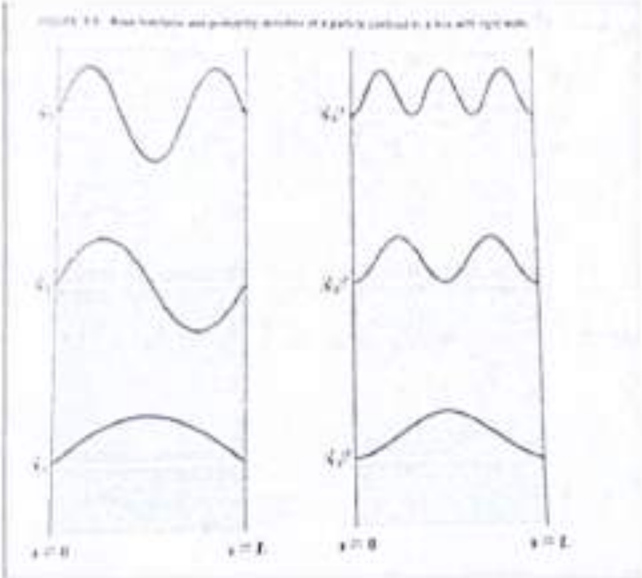
وبذلك نجد أن دالة الموجة لجسيم داخل الصندوق تكون مقومة إذا كان

$$A = \sqrt{\frac{2}{L}} \qquad \text{---------} \; (5 \cdot 33)$$

وبالتعويض عن قيمة A في معادلة دالات الموجة نجد أن دالات الموجة المقومة تأخذ الصيغة

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \qquad \text{----------------------} \; (5.34)$$

والشكل ( 5.5 ) يوضح الدالات الموجية المقومة $\psi_1$ ، $\psi_2$ ، $\psi_3$ والكثافات الاحتمالية probability densities $|\psi_1|^2$ ، $|\psi_2|^2$ ، $|\psi_3|^2$ ، ونلاحظ من الشكل ،في حين أن $\psi_n$ ( n = 1, 2,3 ) تأخذ قيما موجبة وسالبة ، نجد أن $|\psi_n|^2$ لها قيما موجبة فقط



ولما كانت $\psi_n$ دالة مقومة ينتج أن $|\psi_n|^2$ تساوي كثافة الاحتمالية ( p ) لايجاد الجسيم عند كل موقع x ، ولكل من الدالات الموجية لدينا ( $\psi_1$ ، $\psi_2$ ، $\psi_3$ ) فإن $|\psi_n|^2 = 0$ عند x = 0 و x = L ، التي تمثل حدود الصندوق ، واحتمالية وجود الجسيم عند موقع معين داخل الصندوق تختلف تبعا للعدد الكمي n ، فعلى سبيل المثال ، $|\psi_1|^2$ لها قيمة عظمى عند ( $\frac{1}{2} L$ ) ، على حين $|\psi_2|^2$ تساوي صفر عند ذلك الموقع ، وهذا يعني أنه في حالة n =1 ، هناك احتمالية كبيرة جدا لايجاد الجسيم عند منتصف الصندوق ، في حين أن هذه الاحتمالية تساوي صفرا في حالة n = 2 ،

*من جهة أخرى فإن الفيزياء الكلاسيكية تشير الى أن هناك نفس الاحتمالية لوجود الجسيم في جميع المواقع داخل* الصندوق .

**Example:** An electron is in a box ( 0.1 nm ) across , which is the order of magnitude of atomic dimensions . Find its permitted energies .

<u>Solution :</u> here m = $9.1 \times 10^{-31}$ Kg and L = 0.1 nm = $1 \times 10^{-10}$ m

So that the permitted energies are

$$E_n = \frac{n^2\pi^2(\,1.054 \times 10^{-34}\ J.s)^2}{2 \times 9.1 \times 10^{-31} Kg \times (\,10^{-10}\,)^2}$$

$$= 6.0 \times 10^{-18}\ n^2\,J = 38\,n^2\,eV$$

The minimum energy the electron can have is 38 $eV$ , corresponding to n = 1 , the sequence of energy levels continues with $E_2 = 152\ eV$ , $E_3 = 342\ eV$ , $E_4 = 608\ eV$

*وهكذا وكما في الشكل* ( 5.4 ) نلاحظ أن هذه المستويات متباعدة بصورة كافية بحيث يمكن تمييز ها .

## Applications of the uncertainty principle :

### تطبيقات على مبدأ عدم التحديد :

إن ثابت بلانك ( $h$ ) صغير جدا ( $6.63 \times 10^{-34} J.s$ ) حيث أن تأثير مبدأ عدم التحديد يكون مهم فقط في عالم الذرات والجسيمات الأولية ز وفي هذا العالم الدقيق هناك عدة ظواهر يمكن تفسير ها على أساس هذا المبدأ .

أحد الأسئلة المهمة هو معرفة فيما اذا يمكن للإلكترون أن يوجد داخل النواة ز كما سنلاحظ لاحقا .

One interesting question is whether electrons are present in atomic nuclei .

إن نصف قطر نواة الذرة هو حوالي ( $10^{-14}\ m$ ) . ولكي يكون الإلكترون موجودا داخل النواة ، فإن الخطأ في موقعه ( $\Delta x$ ) يجب أن لا يزيد عن ( $10^{-14}\ m$ ) ، وبذلك يمكن ايجاد الخطأ في زخم الإلكترون ( $\Delta p$ ) حيث أن

$$\Delta x\,\Delta p \geq \frac{\hbar}{2} \qquad \text{( uncertainty principle )}$$

$$\Delta p \geq \frac{\hbar}{2\,\Delta x} \geq \frac{1.054 \times 10^{-34}\ Js}{2 \times 10^{-14}\ m}$$

$$\Delta p \geq 0.5 \times 10^{-20}\ Kg.m/s$$

إن زخم الإلكترون ( p ) يجب أن يساوي على الأقل هذا المقدار ،وعندما يكون زخم الإلكترون يساوي $0.5 \times 10^{-20}\ Kg.m/s$ فإن طاقته الحركية ( T ) تكون أكبر بعدة مرات من طاقة الإلكترون السكونية $m_0c^2$ . ولذا يمكننا استخدام الصيغة القصوى للعلاقة النسبية حيث

T = pc

$$= 0.5\times 10^{-20}\ Kg.m/s \times 3\times 10^{8}\ \text{m/s}$$

$$= 1.5\times 10^{-12}\ \text{J} = 9.4\ \text{MeV}$$

وعليه فيجب أن تكون الطاقة الحركية للإلكترون داخل النواة بحدود ( 10 MeV ) ٠ مع أن القياسات التجريبية تظهر أن الإلكترونات المنبعثة من النوى غير المستقرة تحمل طاقة أقل بكثير من هذه القيمة ٠ من هذا نستنتج أن الإلكترون لا يمكن أن يوجد داخل النواة ٠ والآن علينا أن نبحث عن الطاقة اللازمة للإلكترون لكي يتحدد في الذرة ٠ إن نصف قطر ذرة الهيدروجين حوالي ( $5\times 10^{-11}$m ) ولذلك فإن الخطأ في تحديد موقع الإلكترون بحدود هذا المقدار فيكون الخطأ في تحديد زخم الإلكترون هو

$$\Delta p \cong 1.1\times 10^{-24}\ Kg.m/s$$

إن الكترون زخمه بهذا المقدار يكون في حالة غير نسبية ولذا فإن طاقة الإلكترون الحركية تساوي

$$T = \frac{p^2}{2m} = \frac{(1.1\times 10^{-24}\ Kg.m/s)^2}{2\times 9.1\times 10^{-31}\ Kg}$$

$$= 6.6\times 10^{-19}\ J$$

$$= 4.1\ eV$$

وهذه الطاقة تكون معقولة تماما ٠

وهناك علاقة أخرى لمبدأ عدم التحديد تكون مفيدة أيضا ٠ فربما نرغب في قياس الطاقة E المنبعثة خلال الفترة الزمنية ( $\Delta t$ ) نتيجة لعملية ذرية معينة ، فلو كانت هذه الطاقة تنبعث على شكل موجات كهرومغناطيسية فإن تحديد الفترة الزمنية سيؤثر على دقة قياس تردد الموجة ( v ) ٠

لنفترض أن الخطأ في تحديد العدد الموجي لمجموعة الموجات هو (1 ) ، ولما كان تردد الموجات يساوي عدد الموجات التي نحسبها مقسومة على طول الفترة الزمنية ، فإن الخطأ ( $\Delta v$ ) في قياس التردد يكون

$$\Delta v = \frac{1}{\Delta t}$$

وقيمة الخطأ في الطاقة التابعة للخطأ ( $\Delta v$ ) هي

$$\Delta E = h\,\Delta v = \frac{\hbar}{\Delta t} \qquad ; \qquad \hbar = \frac{h}{2\pi} \rightarrow h = \hbar\, 2\pi$$

$$\Delta E\,\Delta t \geq \hbar$$

والحقيقة أننا نستخدم تحليلات أكثر دقة فنحصل على

$$\Delta E\,\Delta t \geq \frac{\hbar}{2}$$

وتنص هذه المعادلة على أن حاصل ضرب الخطأ في قياس الطاقة $\Delta E$ والخطأ في تحديد الزمن $\Delta t$ للعملية الذرية ، أكبر أو يساوي $\frac{\hbar}{2}$ ٠

# The particle in abox : wave functions

In the previous section we found that the wave function of a particle in abox whose energy is $E$ is

$$\psi = A \sin \sqrt{\frac{2mE}{\hbar^2}}\, x$$

Since the possible energies are

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

subsituting $E_n$ for $E$ yields

$$\psi_n = A \sin \frac{n\pi x}{L} \quad \text{-------} (5\text{-}30)$$

for the eigenfunctions corresponding to the energy eigenvalues $E_n$.

It is easy to verify that these eigenfunctions meet all the requirements we have discussed: for each quantum number $n$, $\psi_n$ is a single-valued function of $x$, and $\psi_n$ and $(\partial \psi_n / \partial x)$ are continuous. Furthermore, the integral of $|\psi_n|^2$ over all space is finite, as we can see by integrating $|\psi_n|^2 dx$ from $x=0$ to $x=L$ (since the particle, by hypothesis, is confined within these limits):

$\Longrightarrow$

$$\int_{-\infty}^{\infty} |\psi_n|^2 \, dx = \int_0^L |\psi_n|^2 \, dx$$

$$= A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$\int_{-\infty}^{\infty} |\psi_n|^2 \, dx = A^2 \frac{L}{2} \quad \text{-------} (5.31)$$

To normalize $\psi$ we must assign a value to A such that $|\psi_n|^2$ is equal to the probability $p\,dx$ of finding the particle between $x$ and $x+dx$, rather than merely proportional to $p$. If $|\psi_n|^2$ is to equal $p$, then it must be true that

$$\int_{-\infty}^{\infty} |\psi_n|^2 \, dx = 1 \quad \text{-------} (5.32)$$

since

$$\int_{-\infty}^{\infty} p \, dx = 1$$

is the mathematical way of stating that the particle exists somewhere at all times. Comparing Eq. (5.31) and (5.32), we see that the wave functions of a particle in a box are normalized if

$$A = \sqrt{\frac{2}{L}} \quad \text{-------} 5.33$$

The normalized wave functions of the particle are therefore

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad \text{------} (5.34)$$

The normalized wave functions $\psi_1$, $\psi_2$ and $\psi_3$ together with the probability densities $|\psi_1|^2$, $|\psi_2|^2$, and $|\psi_3|^2$ are plotted in Fig.(5.5).

While $\psi_n$ may be negative as well as positive, $|\psi_n|^2$ is always positive and, since $\psi_n$ is normalized, its valu at a given $x$ is equal to the probability $P$ of finding the particle there.

In every case $|\psi_n|^2 = 0$ at $x = 0$ and $x = L$, the boundaries of the box. At a particular point in the box the probability of the particle being present may be very different for different quantum numbers.

For instance, $|\psi_1|^2$ has its maximum value of ($\frac{1}{2}$ L) in the middle of the box, while $|\psi_2|^2 = 0$ there: a particle in the lowest energy level of $n=1$ is most likely to be in the middle of the box, while a particle in the next higher state of $n=2$ is never there! Classical physics, of course, predicts the same probability for the particle being anywhere in the box.

The wave functions shown in Fig. (5.5) resemble the possible vibrations of a string fixed at both ends, such as those of the stretched string of fig. (5.2). This is a consequence of the fact that waves in a stretched string and the wave representing a moving particle are described by equations of the same form, so that, when identical restrictions are placed upon each kind of wave, the formal results are identical.

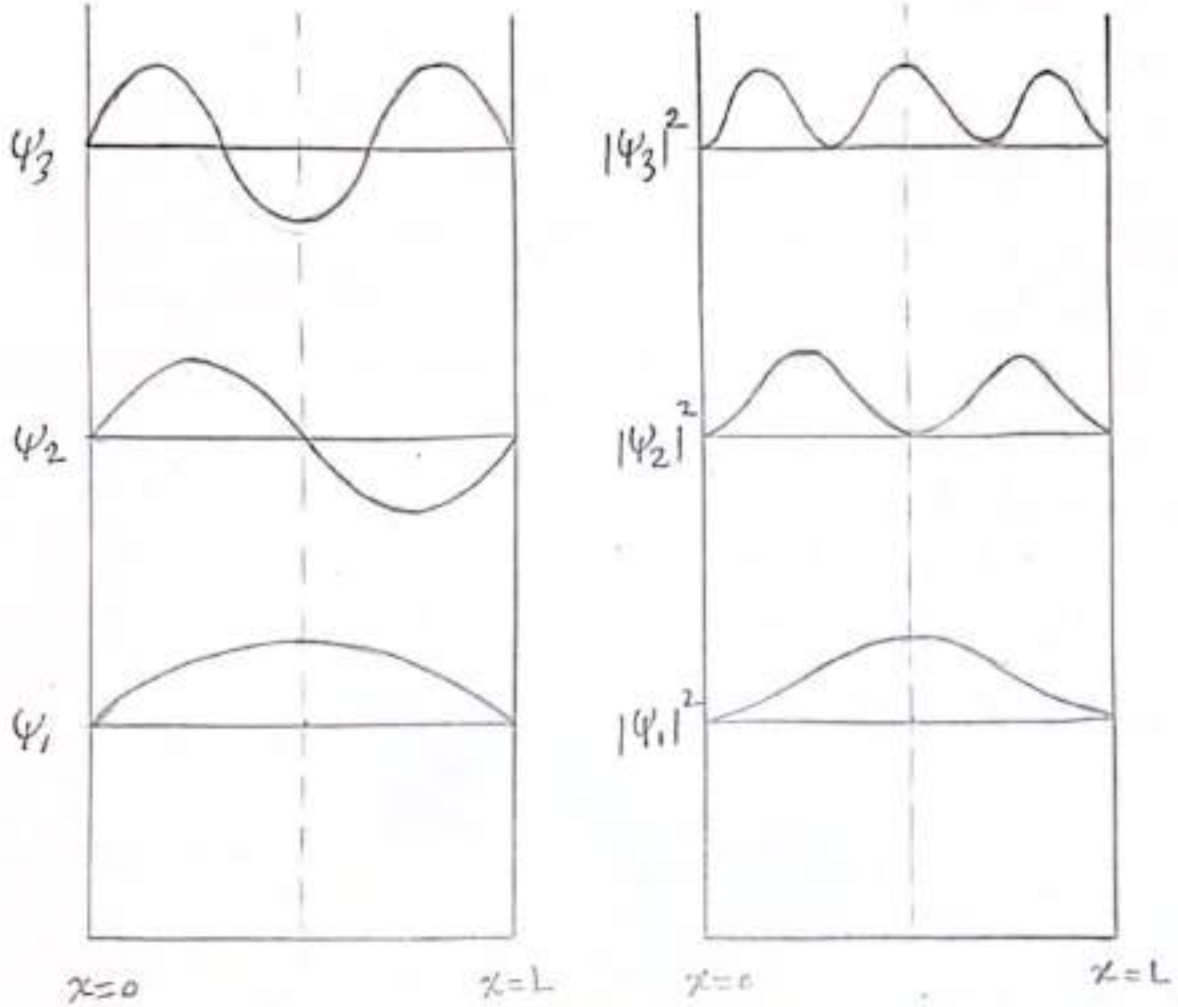


Figure (5.5) Wave functions and probability of a particle confined to a box with rigid walls.

# Applications of the uncertainty principle:

plank's constant h is so small that the limitations imposed by the uncertainty principle are significant only in the relam of the atom. On such scale, however, this principle is of great help in understanding many phenomenea. It is worth keeping in mind that the lower limit of $\hbar/2$ for $\Delta x \Delta p$ is rarely attained.

$\therefore$ $\Delta x \Delta p \geqslant \frac{\hbar}{2}$ (uncertainty principle)

- Another form of the uncertainty principle concerns energy and time. We might wish to measure the energy E emitted during the time interval $\Delta t$ in an atomic process. If the energy is in the form of em waves, the limited time available restricts the accuracy with which we can determine the frequency $\nu$ of the waves. Let us assume that the minimum uncertainty in the number of waves we count in a wave group is one wave. Since the frequency of the waves under study is equal to the number of them we count divided by the time interval, the uncertainty $\Delta\nu$ in our frequency measurement is

$\Delta\nu \geqslant \frac{1}{\Delta t}$ , the corresponding energy uncertainty is:

$$\Delta E = h\,\Delta\nu = \frac{h}{\Delta t} \quad \text{or} \quad \Delta E\,\Delta t \geqslant h$$

A more precise calculation based on the nature of wave groups changes this result to

$\Delta E \Delta t \geqslant \frac{\hbar}{2}$ (uncertainty in energy and time), and this equation states that the product of the uncertainty

$\Delta E$ in an energy measurment and the uncertainty $\Delta t$ in the time at which the measurement is made is equal to or greater than $\hbar/2$.

University of Mosul

College of Science

Department of Physics

Second stage

Lecture 7

# Modern Physics II

2024-2025

## Lecture 7

Quantum Theory of the hydrogen atom

1- Schrodinger's equation for the hydrogen atom

2- Separation of variables

Preparation
Lecturer. Hala I. Jasim

# Chapter 6 / Quantum Theory of the Hydrogen Atom

النظرية الكمية لذرة الهيدروجين / تساعدنا النظرية الذرية الحديثة على فهم التفاعلات الذرية ، وتكوين الجزيئات المستقرة ، وترتيب العناصر في الجدول الدوري ، وكذلك فهم الصفات الكهربائية والمغناطيسية والميكانيكية للمواد الصلبة .

## 6.1 Schrodinger's equation for the hydrogen atom :-

A hydrogen atom consists of a proton, a particle of electric charge +e, and an electron, a particle of charge −e which is 1836 times lighter than the proton. For the sake of convenience we shall consider the proton to be stationary, with the electron moving about in its vicinity but prevented from escaping by the proton's electric field. As in the Bohr theory, the correction for proton motion is simply a matter of replacing the electron mass m by the reduced mass m'.

تتكون ذرة الهيدروجين من بروتون ذي شحنة (+e) والكترون ذي شحنة (-e) ، والذي هو اخف من البروتون بـ (1836) مرة. للسهولة نفترض ان البروتون ثابت وان الالكترون يدور حوله متأثراً بالقوة الكهربائية بين الجسيمين . والحقيقة هي انه - كما في حالة نظرية بور يمكننا ان نأخذ بنظر الاعتبار حركة البروتون ، وذلك بتعويض كتلة الالكترون m بالكتلة المصغرة m' .

Schrodinger's equation for the electron in three dimensions, which is what we must use for the hydrogen atom, is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad \text{-----} (6\text{-}1)$$

The potential energy (V) here is the electric potential energy

$$V = -\frac{e^2}{4\pi\varepsilon_0 r} \qquad \text{-----} (6.2)$$

Electric potential energy of a charge (-e) when it is the distance r from another charge(+e

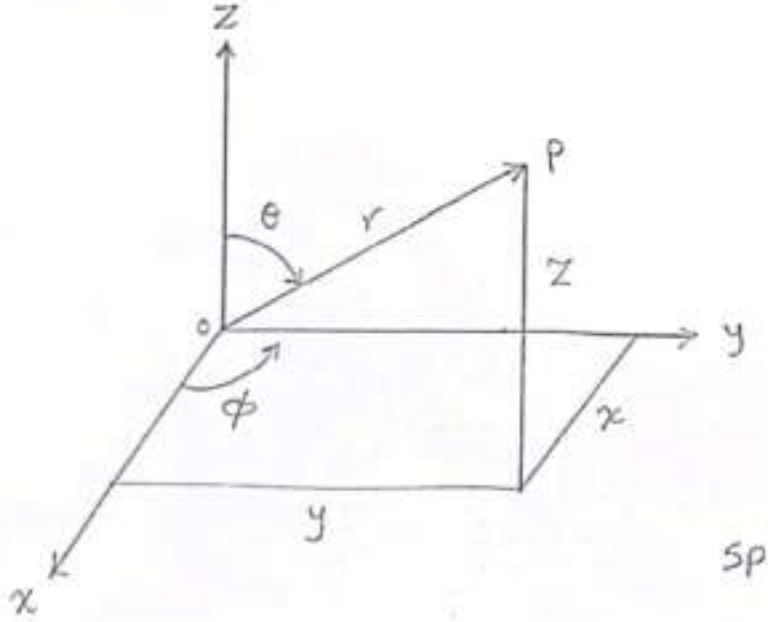
حيث $V$ تمثل الطاقة الكامنة الالكتروستاتيكية ولنظام متكون من شحنة $(-e)$ وشحنة $(+e)$ على مسافة $r$ بينهما.

Since $V$ is a function of $(r)$ rather than of $x, y, z$ we cannot substitute Eq. (6-2) directly into Eq. (6-1).

ولما كانت $V$ هي دالة لـ $r$ وليست لـ $(x, y, z)$ ، لذا لا يمكن تعويض المعادلة (6-2) مباشرة في المعادلة (6-1) .

There are two alternatives. One is to express $V$ in terms of the cartesian coordinates $(x, y, z)$ by replacing $r$ by $\sqrt{x^2+y^2+z^2}$. The other is to express Schrodinger's equation in terms of the spherical polar coordinates $(r, \theta, \phi)$ defined in Fig. (6-1). Owing to the symmetry of the physical situation, doing the latte is appropriate here,

هناك طريقتان لتوحيد المتغيرات ، اما ان نكتب $V$ بدلالة الاحداثيات الديكارتية cartesian coordinate $(x, y, z)$ وذلك بتعويض $(r)$ بالمقدار $\sqrt{x^2+y^2+z^2}$. أو كتابة معادلة شرودنكر بدلالة الاحداثيات القطبية (spherical polar coordinate) $(r, \theta, \phi)$ المبينة بالشكل (6-1) . والطريقة الثانية اكثر ملائمة للمسألة وذلك لتناظر الكروي الموجود.



$x = r \sin\theta \cos\phi$

$y = r \sin\theta \sin\phi$

$z = r \cos\theta$

Figure (6-1)
spherical polar coordinates

The sphereical polar coordinates $r, \theta, \phi$ of the point p shown in fig. (6-1) have the following interpretations:

يمكن توضيح الاحداثيات القطبية $(r, \theta, \phi)$ للنقطة p على النحو التالي :

$r$ = length of radius vector from origin o to point p

$$r = \sqrt{x^2 + y^2 + z^2}$$

r = طول الموجه الشعاعي من نقطة الاصل (صفر) الى النقطة p .

$\theta$ = angle between radius vector and +z axis

= zenith angle

$$= \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$\theta = \cos^{-1} \frac{z}{r}$$

$\theta$ = الزاوية بين الموجه الشعاعي والاتجاه +Z وتدعى بزاوية السمت .

$\phi$ = angle between the projection of the radius vector in the xy plane and the +x axis, measured in the direction shown

= azimuth angle

$$\phi = \tan^{-1} \frac{y}{x}$$

$\phi$ = الزاوية المحصورة بين مسقط الموجه الشعاعي على المستوي xy والاتجاه $(+x)$ وتدعى بزاوية الزوال azimuth angle

In spherical polar coordinates schrodinger's equation is written:

باستخدام الاحداثيات القطبية تأخذ معادلة شرودنكر الصيغة التالية :

$$\frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \psi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad \text{----(6-3)}$$

Subsituting Eq. (6-2) for the potential energy $V$ and multiplying the entire equation by $(r^2 \sin^2\theta)$, we obtain:

$$\sin^2\theta \frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) + \sin\theta \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \psi}{\partial \theta}\right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2 m r^2 \sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)\psi = 0 \quad \text{--(6-4)}$$

Hydrogen atom

Equation (6-4) is the partial differential equation for the wav function $\psi$ of the electron in a hydrogen atom. Together wi the various conditions $\psi$ must obey, namely that $\psi$ be normalizable and that $\psi$ and its derivatives be continuous and single-valued at each point $r, \theta, \phi$, this equation completely specifies the behavior of the electron.

المعادلة (6-4) هي معادلة تفاضلية جزئية لدالة الموجة ψ للالكترون في ذرة الهيدروجين بعد تطبيق الشروط المبينة سابقاً في الفصل الخامس على الدالة ψ (يجب ان تكون احادية القيمة في كل نقطة من $(r,\theta,\phi)$) نجد ان المعادلة (6-4) تحدد سلوك الالكترون في ذرة الهيدروجين .

We must Solve Eq. (6-4) for $\psi$, which can be solved by separating variables. And describes the space in which the electron moves.

والمعادلة (6-4) التي يمكن حلها بطريقة فصل المتغيرات ووصف الفضاء الذي يتحرك فيه الالكترون .

When Eq. (6-4) is solved, it turns out that three quantum numbers are required to describe the electron in a hydrogen atom, in place of the single quantum number of the Bohr theory.

بحل المعادلة (6-4) تنتج ثلاثة اعداد كمية لوصف حالة الالكترون في ذرة الهيدروجين بدلا من عدد كمي واحد كما في نظرية بور .

In the Bohr model, the electron's motion is basically one-dimensional, since the only quantity that varies as it moves is its position in a definite orbit. One quantum numb is enough to specify the state of such an electron, just as one quantum number is enough to specify the state o a particle in a one dimensional box.

في حالة نظرية بور تكون حركة الالكترون بصورة اساسية من بعد واحد، اذ ان زاوية الزوال $\phi$ هي المتغير الوحيد في حركة الالكترون، وهذه الحركة تتطلب عدداً كمياً واحداً لوصف حالة الالكترون كما هي الحال لجسيم محصور في صندوق ذي بعد واحد.

In a hydrogen atom the electron's motion is restricted b the inverse square electric field of the nucleus instead of b the walls of a box, but nevertheless the electron is free to move in three dimensions, and it is accordingly not surprisin that three quantum numbers govern its wave function also.

تتحدد حركة الالكترون في ذرة الهيدروجين بالمجال الكهربائي للنواة، والذي يتبع قانون التربيع العكسي بدلاً من الجدران في حالة الصندوق، ومع هذا تبقى حركة الالكترون في ذرة الهيدروجين في ثلاثة ابعاد وعليه نتوقع ايضاً ان تكون هناك ثلاثة اعداد كمية تصف حالة الالكترون.

The three quantum numbers revealed by the solution of Eq.(6-4 together with their possible values, are as follows:

الاعداد الكمية الثلاثة مع قيمها المسموحة التي تنتج من حل المعادلة (6-4):

principal quantum number = $n = 1, 2, 3, \ldots$ العدد الكمي الاساسي

Orbital quantum number = $l = 0, 1, 2, \ldots, n-1$

العدد الكمي المداري

Magnetic quantum number = $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

العدد الكمي المغناطيسي

The principal quantum number $n$ governs the total energy of the electron, and corresponds to the quantum number $n$ of the Bohr theory. The orbital quantum number $l$ governs the magnitude of the electron's angular momentum about the nucleus, and the magnetic quantum number $m_l$ governs the direction of the angular momentum.

والعدد الكمي الاساسي $n$ يحدد الطاقة الكلية للالكترون ، وهو يمثل العدد الكمي $n$ في نظرية بور . والعدد الكمي المداري $l$ يحدد كمية الزخم الزاوي للالكترون حول النواة ، في حين يحدد العدد الكمي المغناطيسي $m_l$ مركبة الزخم الزاوي بالاتجاه z .

## (6-2) Separation of variables فصل المتغيرات

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* ذكرنا في الفقرة السابقة ان المعادلة (6-4) والتي تمثل معادلة تفاضلية جزئية لدالة الموجة $\psi$ للالكترون في ذرة الهيدروجين يمكن حلها بطريقة فصل المتغيرات .

The advantage of writing Schrodinger's equation in spherical polar coordinates for the problem of the hydrogen atom is that in this form it may be separated into three independent equatio. each involving only a single coordinate. Such a separation is possible here because the wave function $\psi(r, \theta, \phi)$ has the form of a product of three different functions: $R(r)$, which depends on $r$ alone; $\Theta(\theta)$ which depends on $\theta$ alone; and $\Phi(\phi)$, which depends on $\phi$ alone.

إن كتابة معادلة شرودنكر لذرة الهيدروجين بدلالة الاحداثيات القطبية تساعدنا على فصل

تنفصل المعادلة التفاضلية الجزئية (6-4) إلى ثلاثة معادلات ، كل منها بمتغير واحد. والطريقة هي ان نكتب دالة الموجة $\psi(r,\theta,\phi)$ على شكل حاصل ضرب ثلاثة دوال : $R(r)$ تعتمد على $r$ فقط ، و $\Theta(\theta)$ التي تعتمد على $\theta$ فقط ، و $\Phi(\phi)$ التي تعتمد على $\phi$ فقط .

we can proceed by assuming that :

$$\psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi) \quad ----(6-5)$$

دالة موجة ذرة الهيدروجين
Hydrogen atom wave function

The function $R(r)$ describes how the wave function $\psi$ of th electron varies along a radius vector from the nucleus, with $\theta$ and $\phi$ constant. The function $\Theta(\theta)$ describes how $\psi$ varies with zenith angle $\theta$ along a meridian on a sphere centere at the nucleus, with $r$ and $\phi$ constant. The function $\Phi(\phi$ describes how $\psi$ varies with azimuth angle $\phi$ along a parallel on a sphere centered at the nucleus, with $r$ and $\theta$ constant

ان الدالة $R(r)$ توضح تغير دالة الموجة $\psi$ للالكترون بتغير الاحداثي النصف قطري مع ثبات $\theta$ و $\phi$ ثابتة ، والدالة $\Theta(\theta)$ توضح تغير $\psi$ مع زاوية السمت $\theta$ مع ثبات $r$ و $\phi$ ثابتة ، والدالة $\Phi(\phi)$ توضح تغير $\psi$ مع زاوية الزوال $\phi$ مع ثبات $r$ و $\theta$ ثابتة .

From Eq. (6-5), which we may write more simply as:

$$\psi = R\Theta\Phi$$

and we see that

$$\frac{\partial\psi}{\partial r} = \Theta\Phi\frac{\partial R}{\partial r} = \Theta\Phi\frac{dR}{dr}$$

$$\frac{\partial\psi}{\partial\theta} = R\Phi\frac{\partial\Theta}{\partial\theta} = R\Phi\frac{d\Theta}{d\theta}$$

$$\frac{\partial^2\psi}{\partial\phi^2} = R\Theta\frac{\partial^2\Phi}{\partial\phi^2} = R\Theta\frac{d^2\Phi}{d\phi^2}$$

The change from partial derivatives to ordinary derivatives can be made because we are assuming that each of the functior $R$, $\Theta$ and $\Phi$ depends only on the respective variables $r$, $\theta$ and $\phi$

when we substitute $R\Theta\Phi$ for $\psi$ in Schrodinger's equation for the hydrogen atom (6-4) and divide the entire equation b. $R\Theta\Phi$, we find that

عليه بتعويض $R\Theta\Phi$ محل $\psi$ في معادلة شرودنكر لذرة الهيدروجين (6-4) وتقسيم المعادلة على $R\Theta\Phi$ ، نجد :

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}$$
$$+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon r}+E\right)=0 \quad \cdots\text{(6-6}$$

The third term of Eq. (6-6) is a function of azimuth angle $\phi$ only, while the other terms are functions of $r$ and $\theta$ only. Let us rearrange Eq. (6-6) to read:

ان الحد الثالث في المعادلة (6-6) هو دالة للزاوية $\phi$ فقط ، في حين الحدود الاخرى هي دالة لـ $r$ و $\theta$ فقط . يمكننا اعادة كتابة المعادلة (6-6) بالشكل :

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$
$$+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r}+E\right)=-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} \quad \cdots(6\text{-}7)$$

This equation can be correct only if both sides of it are equ to the same constant, since they are functions of different variabl As we shall see, it is convenient to call this constant $(m_l^2)$. The differential equation for the function $\phi$ is therefore

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m_l^2 \quad \text{-----}(6-8)$$

المعادلة (6-7) يمكن ان تكون صحيحة فقط عندما تساوي طرفاها كمية ثابتة ، وذلك لأنه الطرفين هما دالتان لمتغيرات مختلفة ، ومن المناسب ان نكتب الثابت المساوي لطرفي المعادلة (6-7) بالشكل (6-8) .

Next we substitute $m_l^2$ for the right-hand side of Eq. (6-7), divide the entire equation by $\sin^2\theta$, and rearrange the vari terms, which yields:

بتعويضه $m_l^2$ بدلاً عن الطرف الايمن من المعادلة (6-7) وتقسيم حدود المعادلة الناتجة على $\sin^2\theta$ وتم اعادة ترتيب الحدود وفق ما يلي :

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) =$$

$$\frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) \quad \text{----}(6-9)$$

Again we have an equation in which different variables apper on each side, requiring that both sides be equal to the same constant. This constant is called $l(l+1)$, once more for reasons that will be apparent later. The equations for the functions $\Theta$ and $R$ are therefore :

نلاحظ هنا ايضاً ان طرفي المعادلة هما دالتان لمتغيرين مختلفين ، وعليه فان الطرفين يجب ان يساويا كمية ثابتة نرمز لها والثابت ب $l(l+1)$ :

$$\frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = l(l+1) \quad \text{-----}(6-10)$$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) = l(l+1) \quad \text{----}(6-11)$$

من المناسب اعادة كتابة المعادلات (6-8) ، (6-10) و (6-11) بالصيغ التالية:

Equations (6-8), (6-10) and (6-11) are usually written:

$$\frac{d^2\Phi}{d\phi^2} + m_l^2 \Phi = 0 \qquad \text{------ (6-12) Equation for } \Phi$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta = 0 \qquad \text{---- (6-13)}$$

Equation for $\Theta$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2m}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) - \frac{l(l+1)}{r^2}\right]R = 0 \qquad \text{---- (6-14}$$

Equation for R

Each of these is an ordinary differential equation for a single function of a single variable. Only the equation for R depends on the potential energy $V(r)$

وكل من هذه المعادلات هو معادلة تفاضلية اعتيادية في متغير واحد .

We have therefore accomplished our task of simplifying Schrodinger equation for the hydrogen atom, which began as a partial differential equation for a function $\psi$ of three variables. The assumption embodied in Eq. (6-5) is evidently valid.

University of Mosul

College of Science

Department of Physics

Second stage

Lecture 8

Modern Physics II

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Lecture 8

# Quantum Theory of the hydrogen atom

## Electron probability density

Preparation

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# Chapter 6

## (6-3) Electron Probability Density (6-3) كثافة الاحتمالية للالكترون

In Bohr's model of the hydrogen atom the electron is visualized as revolving around the nucleus in a circular path. This mode is pictured in a spherical polar coordinate system in Fig. (6-7) It implies that if a suitable experiment were performed; the electron would always be found a distance of ($r = n^2 a_0$) (where n is the quantum number of the orbit and $a_0$ is the radius of the innermost orbit) from the nucles and in the equatorial plane $\theta = 90^\circ$, while its azimuth angle $\phi$ changes with time.

حسب انموذج بور لذرة الهيدروجين ، يتحرك الالكترون بمدار دائري حول النواة . ان الشكل (6-7) يوضح هذا الانموذج بدلالة الاحداثيات القطبية . ونلاحظ من هذا الشكل انه لو اجرينا تجربة مناسبة لوجدنا ان الالكترون دائماً موجود على مسافة ($r = n^2 a_0$) من النواة ($n$ هو العدد الكمي الاساسي و $a_0 = 0.53A$ يمثل نصف قطر اول مدار) وان حركة الالكترون محددة في المستوى الاستوائي $\theta = 90^\circ$ بينما زاوية الزوال $\phi$ وحدها تتغير مع الزمن .

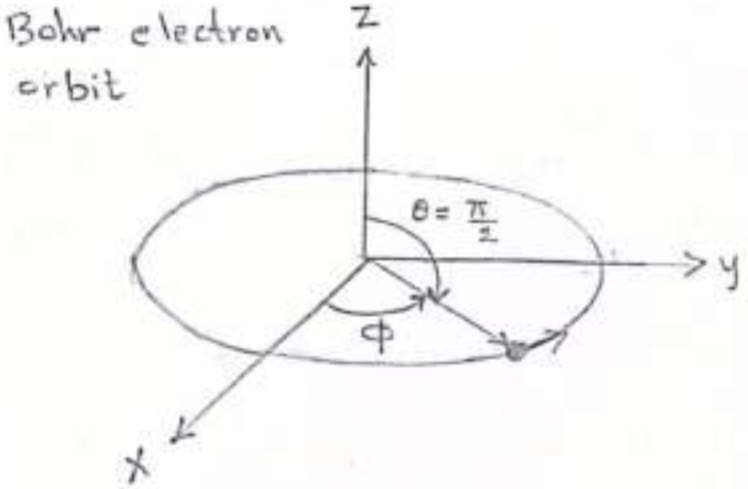

Figure (6-7) The Bohr model of the hydrogen atom in a spherical polar coordinate system.

The quantum theory of the hydrogen atom modifies the Bohr model in two ways:

1- No definite values for $r, \theta$ or $\phi$ can be given, but only the relative probabilities for finding the electron at various locations. This imprecision is, of course, a consequence of the wave nature of the electron.

ان النظرية الكمية لذرة الهيدروجين تصحح نظرية بور من جانبين : اولاً ، لايمكن تحديد احداثيات الالكترون $r$ ، $\theta$ او $\phi$ : حيث ان النظرية الكمية تحدد فقط توزيع احتمال وجود الالكترون في المناطق المختلفة ، وعدم التحديد هذا ناتج من الصفة الموجية للالكترون .

2- We cannot even think of the electron as moving around the nucleus in any conventional sense since the probability density $|\psi|^2$ is independent of time and varies from place to place.

وثانياً : لانستطيع ان نتصور الالكترون يتحرك حول النواة بمدارات تقليدية ، وذلك لان كثافة الاحتمالية $|\psi|^2$ لاتعتمد على الزمن ، وهي تتغير بصورة كبيرة من موقع الى آخر .

The probability density $|\psi|^2$ that corresponds to the electron wave function $\psi = R\Theta\Phi$ in the hydrogen atom is:

$$|\psi|^2 = |R|^2 |\Theta|^2 |\Phi|^2 \qquad \text{------} \quad (6.23)$$

As usual the square of any function that is complex is to be replaced by the product of the function and its complex conjugate.

حيث نفهم من هذه الصيغة ان في حالة الدالة المعقدة ، مربع القيمة المطلقة للدالة يعني حاصل ضرب الدالة مع مرافقها المعقد .

(we recall that the complex conjugate of a function is formed by changing $i$ to $-i$ whenever it appears).

From Eq. (6-15) we see that the azimuthal wave function is given by:

$$\Phi(\phi) = A e^{im_l \phi}$$

The azimuthal probability density $|\Phi|^2$ is therefore

$$|\Phi|^2 = \Phi^* \Phi = A^2 e^{-im_l \phi} e^{im_l \phi} = A^2 e^0 = A^2$$

The likelihood of finding the electron at a particular azimuth angle $\phi$ is a constant that does not depend upon $\phi$ at all. The electron's probability density is symmetrical about the z axis regardless of the quantum state it is in, and the electron has the same chance of being found at one angle $\phi$ as at another.

كثافة الاحتمالية الزوالية $|\Phi|^2$ والتي تصف توزيع احتمالية وجود الالكترون كدالة لزاوية الزوال $\phi$ هي كمية ثابتة لا تعتمد على الزاوية $\phi$ ، وعليه فإن كثافة احتمالية وجود الالكترون تكون متوزعة بصورة متناظرة حول محور z بصرف النظر عن الحالة الكمية التي تصف حالة الالكترون؛ هناك نفس الاحتمال لتواجد الالكترون عند كل زاوية $\phi$ من زوايا الزوال

The radial part $R$ of the wave function, in contrast to $\Phi$, not only varies with $r$ but does so in different way for each combination of quantum numbers $n$ and $l$. Evidently $R$ is a maximum at $r=0$ that is, at the nucleus itself for all s states, which correspond to $L=0$ since $l=0$ for such states. The value of $R$ is zero at $r=0$ for state that possess angular momentum.

على نقيض $\Phi$ ، فأن الدالة الدخيلة القطرية R لدالة الموجة $\psi$ لاتتغير مع الموقع
r ، بل تأخذ اشكالاً مختلفة لاعداد كمية n و l مختلفة . ان R لجميع حالات
s تأخذ قيمة عظمى عندما $r=0$ (اي عند موقع النواة) . في حين للحالة ذات الزخم
الزاوي الذي يساوي صفراً ، تكون قيمة R صفراً عندما $r=0$ .

The probability density of the electron at the point $r, \theta, \phi$ is proportional to $|\psi|^2$, but the actual probability of finding it in the infinitesimal volume element $dv$ there is $|\psi|^2 dv$. In spherical polar coordinates Fig. (6-9),

$$dv = (dr)(r\,d\theta)(r \sin\theta\, d\phi)$$

$$= r^2 \sin\theta\, dr\, d\theta\, d\phi \qquad \text{------ (6.24)}$$

(Volume element)

ان كثافة الاحتمالية للالكترون عند النقطة $(r,\theta,\phi)$ تتناسب مع $|\psi|^2$ ، على
حين الاحتمالية لوجود الالكترون في حجم صغير $dv$ هي $|\psi|^2 dv$ . وصيغة
$dv$ بدلالة الاحداثيات القطبية ↑

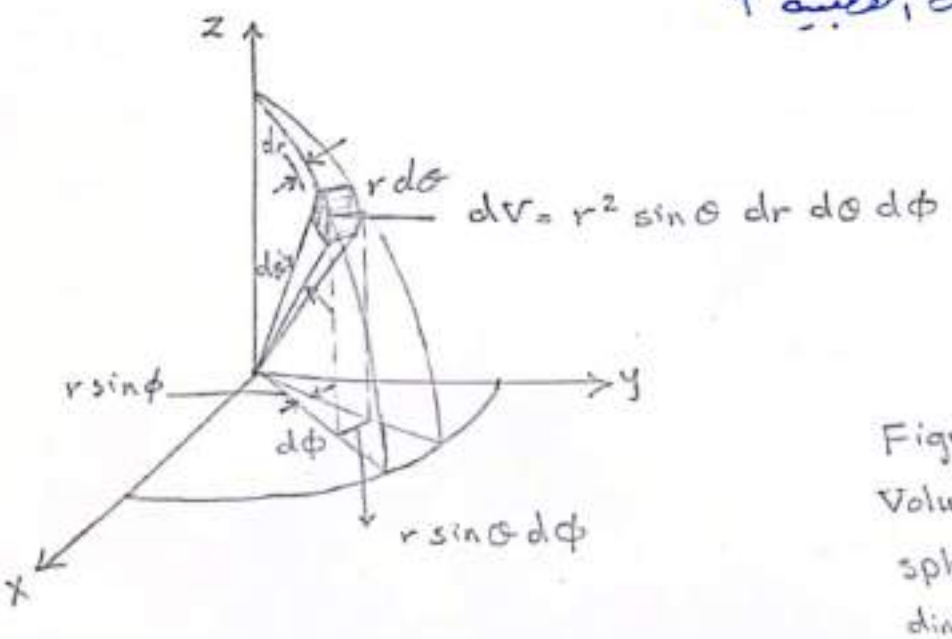

Figure (6-9)
Volume element $dv$ in spherical polar coordinates.

As $\Theta$ and $\Phi$ are normalized functions, the actual probability $p(r)dr$ of finding the electron in a hydrogen atom somewhere in the spherical shell between $r$ and $r+dr$ from the nucleus is :

ولما كانت كل من $\Theta$ و $\Phi$ و $R$ دالات معيّرة ، فإن الاحتمالية $P(r)dr$ لايجاد الإلكترون في ذرة الهيدروجين على مسافة $r$ و $r+dr$ من النواة هي :

$$p(r)dr = r^2|R|^2 dr \int_0^{\pi} |\Theta|^2 \sin\theta \, d\theta \int_0^{2\pi} |\Phi|^2 d\phi$$

$$= r^2|R|^2 dr \qquad \text{-------} \; (6\text{-}25)$$

The most probable value of $r$ for a 1s electron turns out to be exactly $a_0$, the orbital radius of a ground state electro in the Bohr model. However, the average value of $r$ for a 1 electron is $1.5a_0$, which is puzzling at first sight because th energy levels are the same in both the quantum mechanical and Bohr atomic models. This apparent discrepancy is removed when we recall that the electron energy depends upon $(1/r)$ rather than upon $(r)$ directly, and the average value of $(1/r$ for a 1s electron is exactly $(1/a_0)$ .

ان معدل r للالكترون للحالة 1s هو $(1.5\,a_0)$ ، وهذه النتيجة تبدو لأول وهلة غريبة لأن مستويات الطاقة تأخذ نفس القيم في كل من انموذج بور والنظرية الكمية لذرة الهيدروجين . والحقيقة هي انه لا اختلاف في قيمة r ليس مهماً، إذ ان طاقة الالكترون تتغير مع $(1/r)$ وليس طردياً مع r .

**Example** : verify that the average value of $(1/r)$ for a 1S electron in the hydrogen atom is $(1/a_0)$.

**Solution**:

The wave function of a 1s electron is

$$\psi = \frac{e^{-r/a_0}}{\sqrt{\pi}\, a_0^{3/2}}$$

since $dV = r^2 \sin\theta \, dr \, d\theta \, d\phi$ , we have the expectation value of $(1/r)$ :

$$< \frac{1}{r} > = \int_0^\infty \left(\frac{1}{r}\right) |\psi|^2 dV$$

$$= \frac{1}{\pi a_0^3} \int_0^\infty r e^{-2r/a_0} dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

The integral have the respective values

$$\int_0^\infty r e^{-2r/a_0} dr = \left[\frac{a_0^2}{4} e^{-2r/a_0} - \frac{a_0 r}{2} e^{-2r/a_0}\right]_0^\infty = \frac{a_0^2}{4}$$

$$\int_0^\pi \sin\theta \, d\theta = \left[-\cos\theta\right]_0^\pi = 2$$

$$\int_0^{2\pi} d\phi = \left[\phi\right]_0^{2\pi} = 2\pi$$

$$\therefore < \frac{1}{r} > = \left(\frac{1}{\pi a_0^3}\right)\left(\frac{a_0^2}{4}\right)(2)(2\pi) = \frac{1}{a_0}$$

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Second stage

Lecture 9

# Modern Physics II

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Lecture 9

Many Electron Atoms

1- Electron spin

2- Conclusion principle

Preparation

Lecturer. Hala I. Jasim

## 7.1 ELECTRON SPIN

***Round and round it goes forever***

The theory of the atom developed in the previous chapter cannot account for a number of well-known experimental observations. One is the fact that many spectral lines actually consist of two separate lines that are very close together. An example of this **fine structure** is the first line of the Balmer series of hydrogen, which arises from transitions between the $n = 3$ and $n = 2$ levels in hydrogen atoms. Here the theoretical prediction is for a single line of wavelength 656.3 nm while in reality there are two lines 0.14 nm apart—a small effect, but a conspicuous failure for the theory.

Another failure of the simple quantum-mechanical theory of the atom occurs in the Zeeman effect, which was discussed in Sec. 6.10. There we saw that the spectral lines of an atom in a magnetic field should each be split into the three components specified by Eq. (6.43). While the normal Zeeman effect is indeed observed in the spectra of a few elements under certain circumstances, more often it is not. Four, six, or even more components may appear, and even when three components are present their spacing may not agree with Eq. (6.43). Several anomalous Zeeman patterns are shown in Fig. 7.1 together with the predictions of Eq. (6.43). (When reproached in 1923 for looking sad, the physicist Wolfgang Pauli replied, "How can one look happy when he is thinking about the anomalous Zeeman effect?")

In order to account for both fine structure in spectral lines and the anomalous Zeeman effect, two Dutch graduate students, Samuel Goudsmit and George Uhlenbeck, proposed in 1925 that

> Every electron has an intrinsic angular momentum, called spin, whose magnitude is the same for all electrons. Associated with this angular momentum is a magnetic moment.

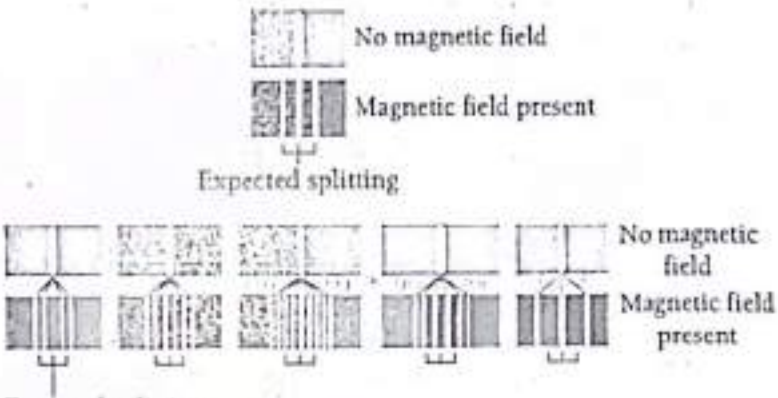

Figure 7.1 The normal and anomalous Zeeman effects in various spectral lines.

**Table 7.1** Quantum Numbers of an Atomic Electron

| Name | Symbol | Possible Values | Quantity Determined |
|---|---|---|---|
| Principal | $n$ | $1, 2, 3, \ldots$ | Electron energy |
| Orbital | $l$ | $0, 1, 2, \ldots, n-1$ | Orbital angular-momentum magnitude |
| Magnetic | $m_l$ | $-l, \ldots, 0, \ldots, +l$ | Orbital angular-momentum direction |
| Spin magnetic | $m_s$ | $-\frac{1}{2}, +\frac{1}{2}$ | Electron spin direction |

The space quantization of electron spin is described by the spin magnetic quantum number $m_s$. We recall that the orbital angular-momentum vector can have the $2l + 1$ orientations in a magnetic field from $+l$ to $-l$. Similarly the spin angular-momentum vector can have the $2s + 1 = 2$ orientations specified by $m_s = +\frac{1}{2}$ ("spin up") and $m_s = -\frac{1}{2}$ ("spin down"), as in Fig. 7.2. The component $S_z$ of the spin angular momentum of an electron along a magnetic field in the $z$ direction is determined by the spin magnetic quantum number, so that

**z component of spin angular momentum**

$$S_z = m_s\hbar = \pm\frac{1}{2}\hbar \tag{7.2}$$

Figure 7.2 The two possible orientations of the spin angular-momentum vector are "spin up" ($m_s = +\frac{1}{2}$) and "spin down" ($m_s = -\frac{1}{2}$).

We recall from Sec. 6.10 that gyromagnetic ratio is the ratio between magnetic moment and angular momentum. The gyromagnetic ratio for electron orbital motion is $-e/2m$. The gyromagnetic ratio characteristic of electron spin is almost exactly twice that characteristic of electron orbital motion. Taking this ratio as equal to 2, the spin magnetic moment $\boldsymbol{\mu}_s$ of an electron is related to its spin angular momentum $\mathbf{S}$ by

**Spin magnetic moment**

$$\boldsymbol{\mu}_s = -\frac{e}{m}\mathbf{S} \tag{7.3}$$

The possible components of $\boldsymbol{\mu}_s$ along any axis, say the $z$ axis, are therefore limited to

**z component of spin magnetic moment**

$$\mu_{sz} = \pm\frac{e\hbar}{2m} = \pm\mu_B \tag{7.4}$$

where $\mu_B$ is the Bohr magneton ($= 9.274 \times 10^{-24}$ J/T $= 5.788 \times 10^{-5}$ eV/T).

The introduction of electron spin into the theory of the atom means that a total of four quantum numbers, $n$, $l$, $m_l$, and $m_s$, is needed to describe each possible state of an atomic electron. These are listed in Table 7.1.

## 7.2 EXCLUSION PRINCIPLE

*A different set of quantum numbers for each electron in an atom*

In a normal hydrogen atom, the electron is in its quantum state of lowest energy. What about more complex atoms? Are all 92 electrons of a uranium atom in the same quantum state, jammed into a single probability cloud? Many lines of evidence make this idea unlikely.

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Second stage

Lecture 10

# Modern Physics II

2024-2025

Lecture 10

Many Electron Atoms

1- X-ray spectrum

2- Sodium atom spectra

Preparation

Lecturer. Hala I. Jasim

${}^3P_1 \rightarrow {}^1S_0$ is an example, and is responsible for the strong 2,537-Å line in the ultraviolet. To be sure, this does not mean that the transition probability is necessarily very high, since the three ${}^3P_1$ states are the lowest of the triplet set and therefore tend to be highly populated in excited mercury vapor. The ${}^3P_0 \rightarrow {}^1S_0$ and ${}^3P_2 \rightarrow {}^1S_0$ transitions, respectively, violate the rules that forbid transitions from $J = 0$ to $J = 0$ and that limit $\Delta J$ to 0 or $\pm 1$, as well as violating $\Delta S = 0$, and hence are considerably less likely to occur than the ${}^3P_1 \rightarrow {}^1S_0$ transition. The ${}^3P_0$ and ${}^3P_2$ states are therefore metastable and, in the absence of collisions, an atom can persist in either of them for a relatively long time. The strong spin-orbit interaction in mercury that leads to the partial failure of $LS$ coupling is also responsible for the wide spacing of the elements of the ${}^3P$ triplets.

## 7.12 X-RAY SPECTRA

In Chap. 2 we learned that the X-ray spectra of targets bombarded by fast electrons exhibit narrow spikes at wavelengths characteristic of the target material in addition to a continuous distribution of wavelengths down to a minimum wavelength inversely proportional to the electron energy. The continuous X-ray spectrum is the result of the inverse photoelectric effect, with electron kinetic energy being transformed into photon energy $h\nu$. The discrete spectrum, on the other hand, has its origin in electronic transitions within atoms that have been disturbed by the incident electrons.

Transitions involving the outer electrons of an atom usually involve only a few electron volts of energy, and even removing an outer electron requires at most 24.6 eV (for helium). These transitions accordingly are associated with photons whose wavelengths lie in or near the visible part of the electromagnetic spectrum, as is evident from the diagram in the back endpapers of this book. The inner electrons of heavier elements are a quite different matter, because these electrons experience all or much of the full nuclear charge without nearly complete shielding by intervening electron shells and in consequence are very tightly bound. In sodium, for example, only 5.13 eV is needed to remove the outermost $3s$ electron, while the corresponding figures for the inner ones are 31 eV for each $2p$ electron, 63 eV for each $2s$ electron, and 1,041 eV for each $1s$ electron. Transitions that involve the inner electrons in an atom are what give rise to discrete X-ray spectra because of the high photon energies involved.

Figure 7-16 shows the energy levels (not to scale) of a heavy atom classed by total quantum number $n$; energy differences between angular-momentum states within a shell are minor compared with the energy differences between shells. Let us consider what happens when an energetic electron strikes the atom

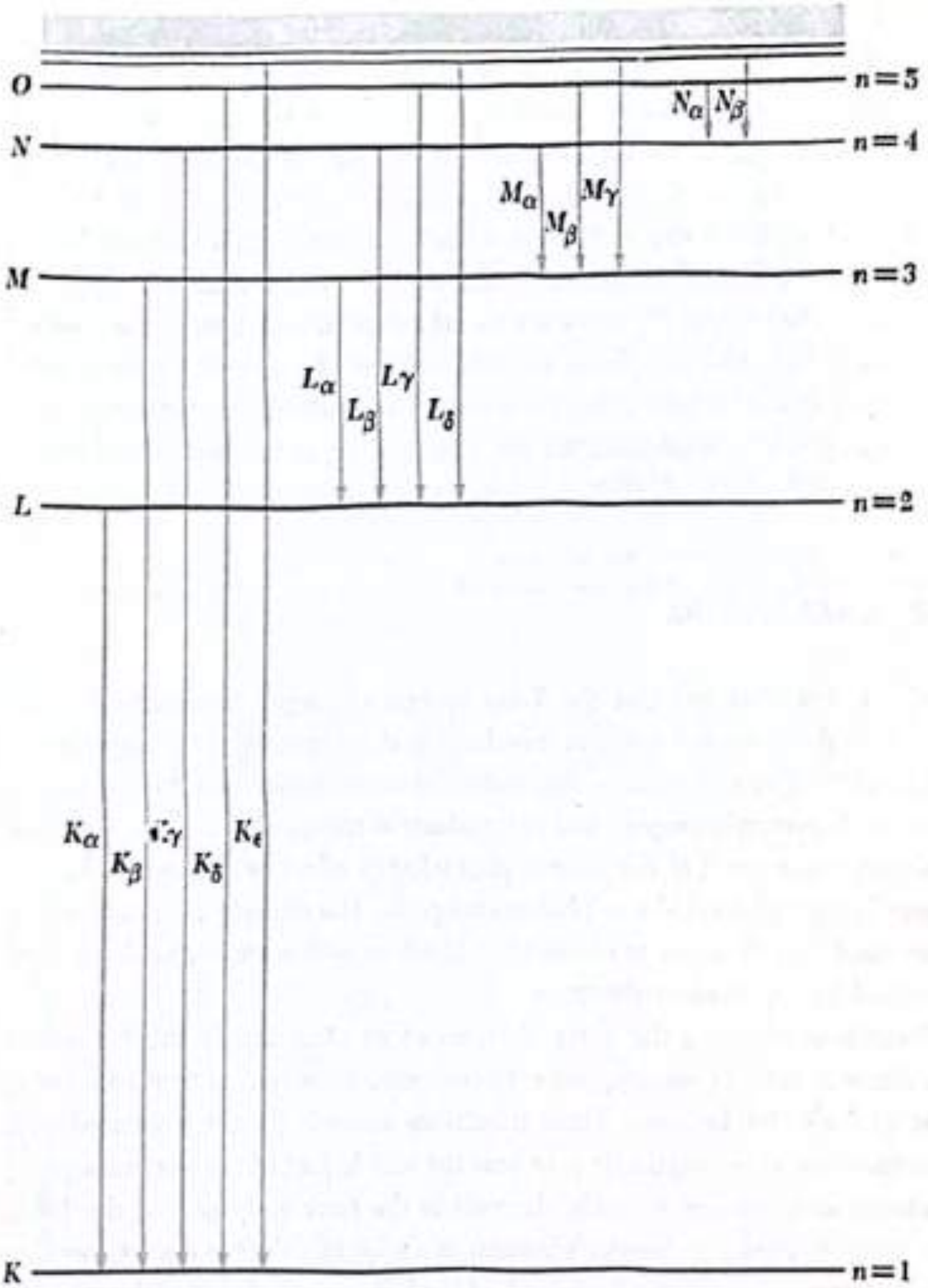


FIGURE 7-16 The origin of X-ray spectra.

and knocks out one of the *K*-shell electrons. (The *K* electron could also be elevated to one of the unfilled upper quantum states of the atom, but the difference between the energy needed to do this and that needed to remove the electron completely is insignificant, only 0.2 percent in sodium and still less in heavier atoms.) An atom with a missing *K* electron gives up most of its considerable excitation energy in the form of an X-ray photon when an electron from an outer shell drops into the "hole" in the *K* shell. As indicated in Fig. 7-16, the *K series* of lines in the X-ray spectrum of an element consists of wavelengths arising in transitions from the $L$, $M$, $N$, . . . levels to the $K$ level. Similarly the longer-wavelength $L$ series originates when an $L$ electron is knocked out of the atom, the $M$ series when an $M$ electron is knocked out, and so on. The two spikes in the X-ray spectrum of molybdenum in Fig. 2-8 are the $K_\alpha$ and $K_\beta$ lines of its $K$ series.

An atom with a missing inner electron can also lose excitation energy by the *Auger effect* without emitting an X-ray photon. In the Auger effect an outer-shell electron is ejected from the atom at the same time that another outer-shell electron drops to the incomplete inner shell; the ejected electron carries off the atom's excitation energy instead of a photon doing this. In a sense the Auger effect represents an internal photoelectric effect, although the photon never actually comes into being within the atom. The Auger process is competitive with X-ray emission in most atoms, but the resulting electrons are usually absorbed in the target material while the X rays readily emerge to be detected.

In Sec. 6.4 we saw that individual orbital angular-momentum states are customarily described by a lowercase letter, with $s$ corresponding to $l = 0$, $p$ to $l = 1$, $d$ to $l = 2$, and so on. A similar scheme using capital letters is used to designate the entire electronic state of an atom according to its total orbital angular-momentum quantum number $\mathsf{L}$ as follows:

| | | | | | | |
|---|---|---|---|---|---|---|
| $\mathsf{L} = 0$ | 1 | 2 | 3 | 4 | 5 | 6... |
| $S$ | $P$ | $D$ | $F$ | $G$ | $H$ | $I$... |

A superscript number before the letter ($^2P$ for instance) is used to indicate the *multiplicity* of the state, which is the number of different possible orientations of **L** and **S** and hence the number of different possible values of $J$. The multiplicity is equal to $2\mathsf{S} + 1$ in the usual situation where $\mathsf{L} > \mathsf{S}$, since $\mathsf{J}$ ranges from $\mathsf{L} + \mathsf{S}$ through 0 to $\mathsf{L} - \mathsf{S}$. Thus when $\mathsf{S} = 0$, the multiplicity is 1 (a *singlet* state) and $\mathsf{J} = \mathsf{L}$; when $\mathsf{S} = \frac{1}{2}$, the multiplicity is 2 (a *doublet* state) and $\mathsf{J} = \mathsf{L} \pm \frac{1}{2}$; when $\mathsf{S} = 1$, the multiplicity is 3 (a *triplet* state) and $\mathsf{J} = \mathsf{L} + 1$, $\mathsf{L}$, or $\mathsf{L} - 1$; and so on. (In a configuration in which $\mathsf{S} > \mathsf{L}$, the multiplicity is given by $2\mathsf{L} + 1$.) The total angular-momentum quantum number $\mathsf{J}$ is used as a subscript after the letter, so that a $^2P_{3/2}$ state (read as "doublet $P$ three-halves") refers to an electronic configuration in which $\mathsf{S} = \frac{1}{2}$, $\mathsf{L} = 1$, and $\mathsf{J} = \frac{3}{2}$. For historical reasons, these designations are called *term symbols*.

In the event that the angular momentum of the atom arises from a single outer electron, the principal quantum number $n$ of this electron is used as a prefix: thus the ground state of the sodium atom is described by $3^2S_{1/2}$, since its electronic configuration has an electron with $n = 3$, $l = 0$, and $s = \frac{1}{2}$ (and hence $j = \frac{1}{2}$) outside closed $n = 1$ and $n = 2$ shells. For consistency it is conventional to denote the above state by $3^2S_{1/2}$ with the superscript 2 indicating a doublet, even though there is only a single possibility for $\mathsf{J}$ since $\mathsf{L} = 0$.

## •7.10 ONE-ELECTRON SPECTRA

We are now in a position to understand the chief features of the spectra of the various elements. Before we examine some representative examples, it should be mentioned that further complications exist which have not been considered here, for instance those that originate in relativistic effects and in the coupling between electrons and vacuum fluctuations in the electromagnetic field (see Sec. 6.10). These additional factors split certain energy states into closely spaced substates and therefore represent other sources of fine structure in spectral lines.

Figure 7-12 shows the various states of the hydrogen atom classified by their total quantum number $n$ and orbital angular-momentum quantum number $l$. The selection rule for allowed transitions here is $\Delta l = \pm 1$, which is illustrated by

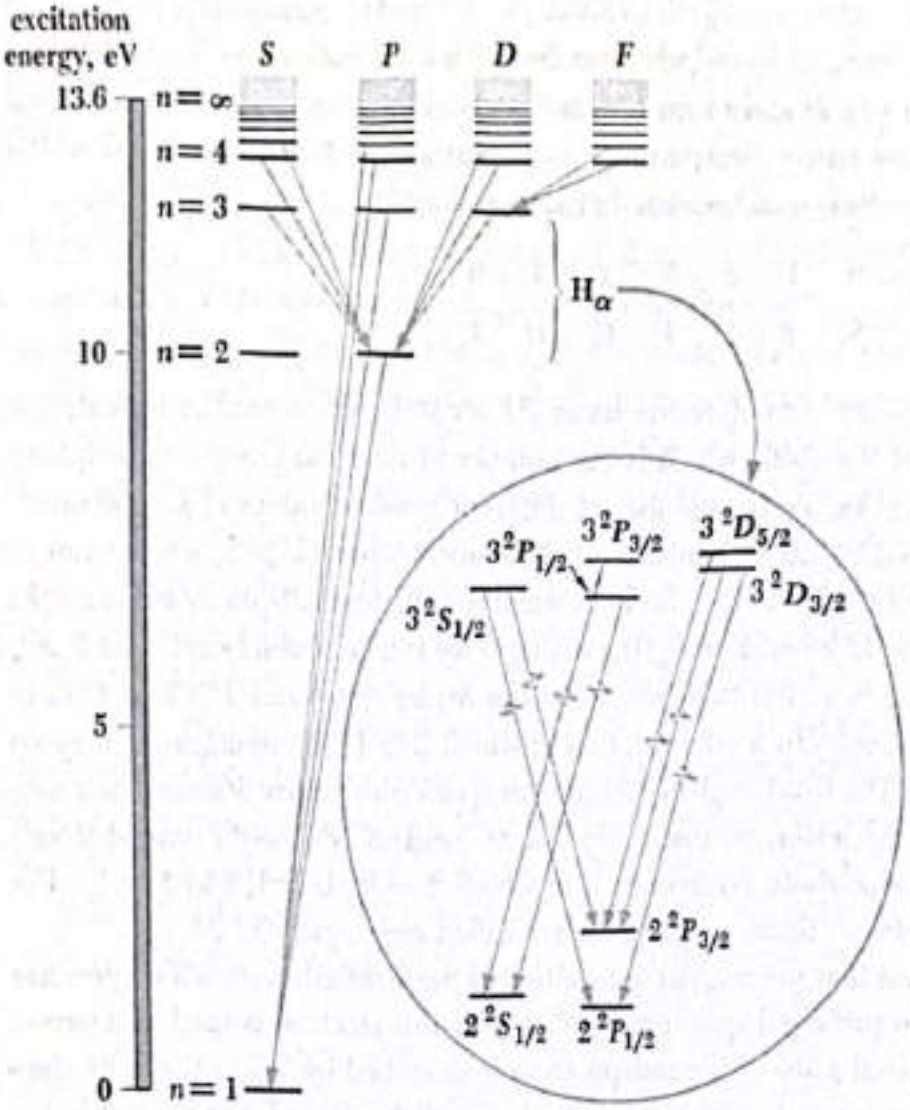


**FIGURE 7-12** Energy-level diagram for hydrogen showing the origins of some of the more prominent spectral lines. The detailed structures of the $n = 2$ and $n = 3$ levels and the transitions that lead to the various components of the H$_\alpha$ line are pictured in the inset.

the transitions shown. To indicate some of the detail that is omitted in a simple diagram of this kind, the detailed structures of the $n = 2$ and $n = 3$ levels are pictured; not only are all substates of the same $n$ and different $j$ separated in energy, but the same is true of states of the same $n$ and $j$ but with different $l$. The latter effect is most marked for states of small $n$ and $l$, and was first established in 1947 in the "Lamb shift" of the $2^2S_{1/2}$ state relative to the $2^2P_{1/2}$ state. The various separations conspire to split the $H_\alpha$ spectral line ($n = 3 \rightarrow n = 2$) into seven closely spaced components.

The sodium atom has a single $3s$ electron outside closed inner shells, and so, if we assume that the 10 electrons in its inner core completely shield $+10e$ of nuclear charge, the outer electron is acted upon by an effective nuclear charge of $+e$ just as in the hydrogen atom. Hence we expect, as a first approximation, that the energy levels of sodium will be the same as those of hydrogen except that the lowest one will correspond to $n = 3$ instead of $n = 1$ because of the exclusion principle. Figure 7-13 is the energy-level diagram for sodium and, by comparison with the hydrogen levels also shown, there is indeed agreement for the states of highest $l$, that is, for the states of highest angular momentum.

To understand the reason for the discrepancies at lower values of $l$, we need only refer to Fig. 6-11 to see how the probability for finding the electron in a hydrogen atom varies with distance from the nucleus. The smaller the value of $l$ for a given $n$, the closer the electron gets to the nucleus on occasion. Although the sodium wave functions are not identical with those of hydrogen, their general behavior is similar, and accordingly we expect the outer electron

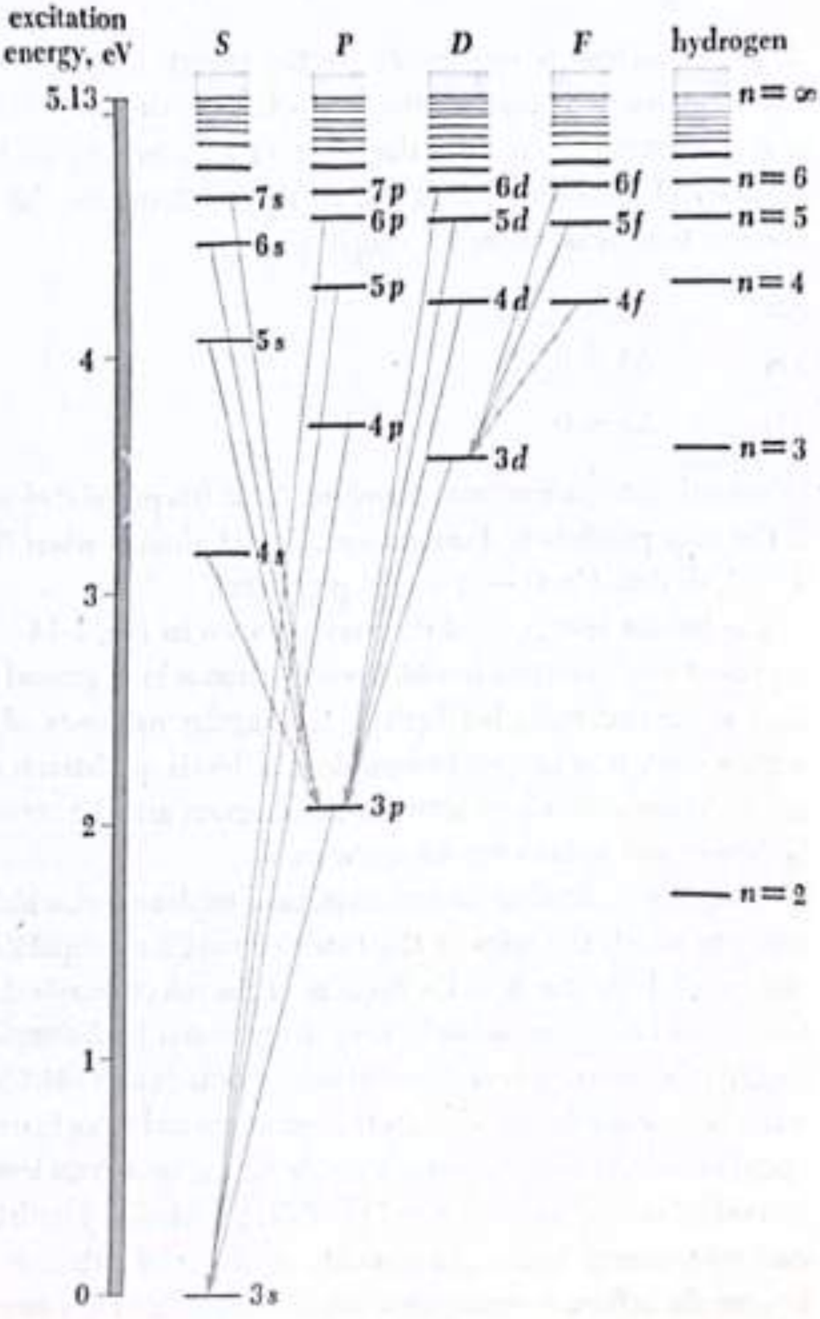


FIGURE 7-13 Energy-level diagram for sodium. The energy levels of hydrogen are included for comparison.

in a sodium atom to penetrate the core of inner electrons most often when it is in an *s* state, less often when it is in a *p* state, still less often when it is in a *d* state, and so on. The less shielded an outer electron is from the full nuclear charge, the greater the average force acting on it, and the smaller (that is, the more negative) its total energy. For this reason the states of small *l* in sodium are displaced downward from their equivalents in hydrogen, as in Fig. 7-13, and there are pronounced differences in energy between states of the same *n* but different *l*.

# THE PHYSICS OF MOLECULES 8

What is the nature of the forces that bond atoms together to form molecules? This question, of fundamental importance to the chemist, is hardly less important to the physicist, whose theory of the atom cannot be correct unless it provides a satisfactory answer. The ability of the quantum theory of the atom not only to explain chemical bonding but to do so partly in terms of an effect that has no classical analog is further testimony to the power of this approach.

## 8.1 MOLECULAR FORMATION

A molecule is a stable arrangement of two or more atoms. By "stable" is meant that a molecule must be given energy from an outside source in order to break up into its constituent atoms. In other words, a molecule exists because the energy of the joint system is less than that of the system of separate noninteracting atoms. If the interactions among a certain group of atoms reduce their total energy, a molecule can be formed; if the interactions increase their total energy, the atoms repel one another.

Let us consider what happens when two atoms are brought closer and closer together. Three extreme situations may occur:

1. A *covalent bond* is formed. One or more pairs of electrons are shared by the two atoms. As these electrons circulate between the atoms, they spend more time between the atoms than elsewhere, which produces an attractive force. An example is $H_2$, the hydrogen molecule, whose electrons belong jointly to the two protons (Fig. 8-1*a*).

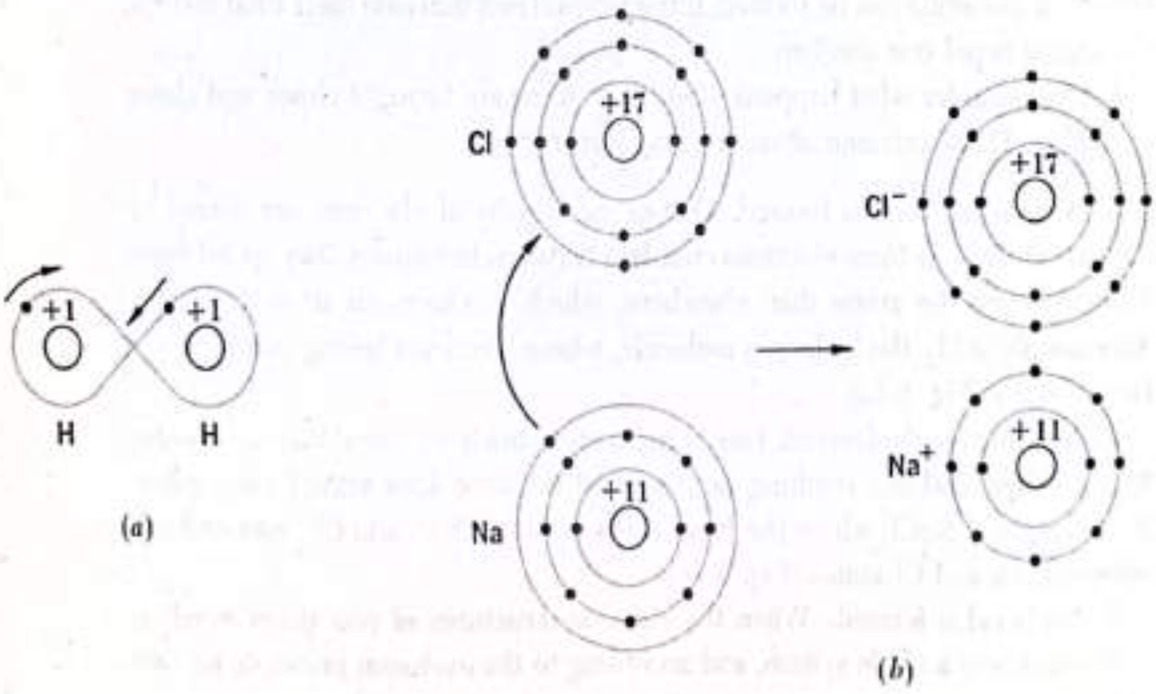
2. An *ionic bond* is formed. One or more electrons from one atom may transfer to the other, and the resulting positive and negative ions attract each other. An example is NaCl, where the bond exists between $Na^+$ and $Cl^-$ ions and not between Na and Cl atoms (Fig. 8-1*b*).

3. No bond is formed. When the electron structures of two atoms overlap, they constitute a single system, and according to the exclusion principle no two

electrons in such a system can exist in the same quantum state. If some of the interacting electrons are thereby forced into higher energy states than they occupied in the separate atoms, the system may have much more energy than before and be unstable. To visualize this effect, we may regard the electrons as fleeing as far away from one another as possible to avoid forming a single system, which leads to a repulsive force between the nuclei. (Even when the exclusion principle can be obeyed with no increase in energy, there will be an electrostatic repulsive force between the various electrons; this is a much less significant factor than the exclusion principle in influencing bond formation, however.)

Ionic bonds usually do not result in the formation of molecules. A molecule is an electrically neutral aggregate of atoms that is held together strongly enough to be experimentally observable as a particle. Thus the individual units that constitute gaseous hydrogen each consist of two hydrogen atoms, and we are entitled to regard them as molecules. On the other hand, the crystals of rock salt (NaCl) are aggregates of sodium and chlorine ions which, although invariably arranged in a certain definite structure (Fig. 8-2), do not pair off into discrete molecules consisting of one $Na^+$ ion and one $Cl^-$ ion; rock salt crystals may in fact be of almost any size. There are always equal numbers of $Na^+$ and $Cl^-$ ions in rock salt, so that the formula NaCl correctly represents its composition. However, these ions form molecules rather than crystals only in the gaseous state.

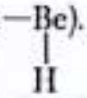
**FIGURE 8-1** (*a*) Covalent bonding. The shared electrons spend more time on the average between their parent nuclei and therefore lead to an attractive force. (*b*) Ionic bonding. Sodium and chlorine combine chemically by the transfer of electrons from sodium atoms to chlorine atoms; the resulting ions attract electrostatically.



## 8.10 ELECTRONIC SPECTRA OF MOLECULES

The energies of rotation and vibration in a molecule are due to the motion of its atomic nuclei, since the nuclei contain essentially all of the molecule's mass. The molecular electrons also can be excited to higher energy levels than those corresponding to the ground state of the molecule, though the spacing of these levels is much greater than the spacing of rotational or vibrational levels. Electronic transitions involve radiation in the visible or ultraviolet parts of the spectrum, with each transition appearing as a series of closely spaced lines, called a band, due to the presence of different rotational and vibrational states in each electronic state (see Fig. 4-12). All molecules exhibit electronic spectra, since a dipole moment change always accompanies a change in the electronic configuration of a molecule. Therefore homonuclear molecules, such as $H_2$ and $N_2$, which have neither rotational nor vibrational spectra because they lack permanent dipole moments, nevertheless have electronic spectra which possess rotational and vibrational fine structures that permit their moments of inertia and bond force constants to be ascertained.

Electronic excitation in a polyatomic molecule often leads to a change in its shape, which can be determined from the rotational fine structure in its band spectrum. The origin of such changes lies in the different characters of the wave functions of electrons in different states, which lead to correspondingly different types of bond. For example, a possible electronic transition in a molecule whose bonds involve *sp* hybrid orbitals is to a higher-energy state in which the bonds involve pure *p* orbitals. From the sketches earlier in this chapter we can see that, in a molecule such as $BeH_2$, the bond angle in the case of *sp* hybridization is 180° and the molecule is linear (H—Be—H), while the bond angle in the case of pure *p* orbitals is 90° and the molecule is bent



$$(\mathrm{H{-}\underset{\substack{|\\ \mathrm{H}}}{Be}}).$$

There are various ways in which a molecule in an excited electronic state can lose energy and return to its ground state. The molecule may, of course, simply emit a photon of the same frequency as that of the photon it absorbed, thereby returning to the ground state in a single step. Another possibility is *fluorescence;* the molecule may give up some of its vibrational energy in collisions with other molecules, so that the downward radiative transition originates from a lower vibrational level in the upper electronic state (Fig. 8-30). Fluorescent radiation is therefore of lower frequency than that of the absorbed radiation.

In molecular spectra, as in atomic spectra, radiative transitions between electronic states of different total spin are prohibited (see Sec. 7-11). Figure 8-31

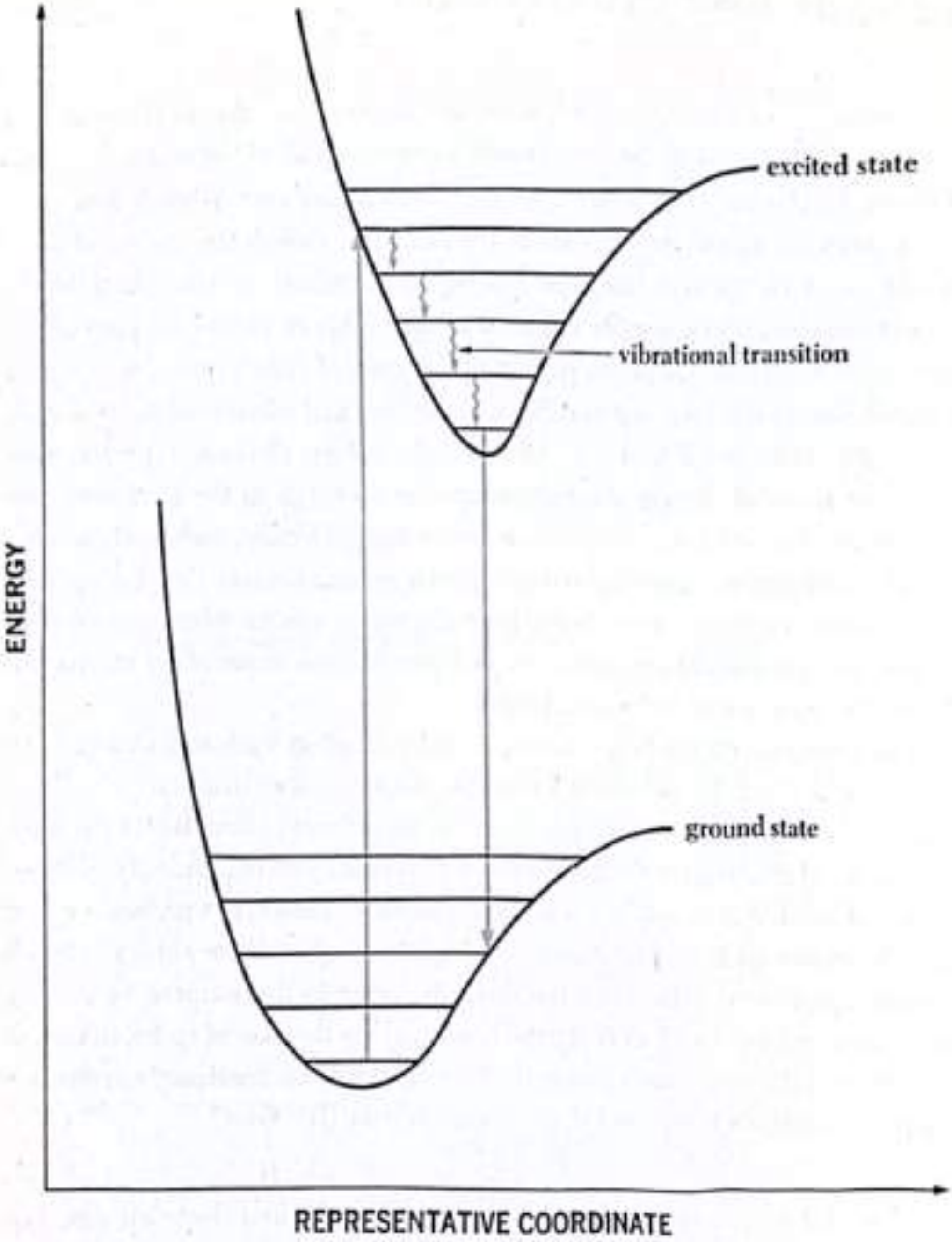
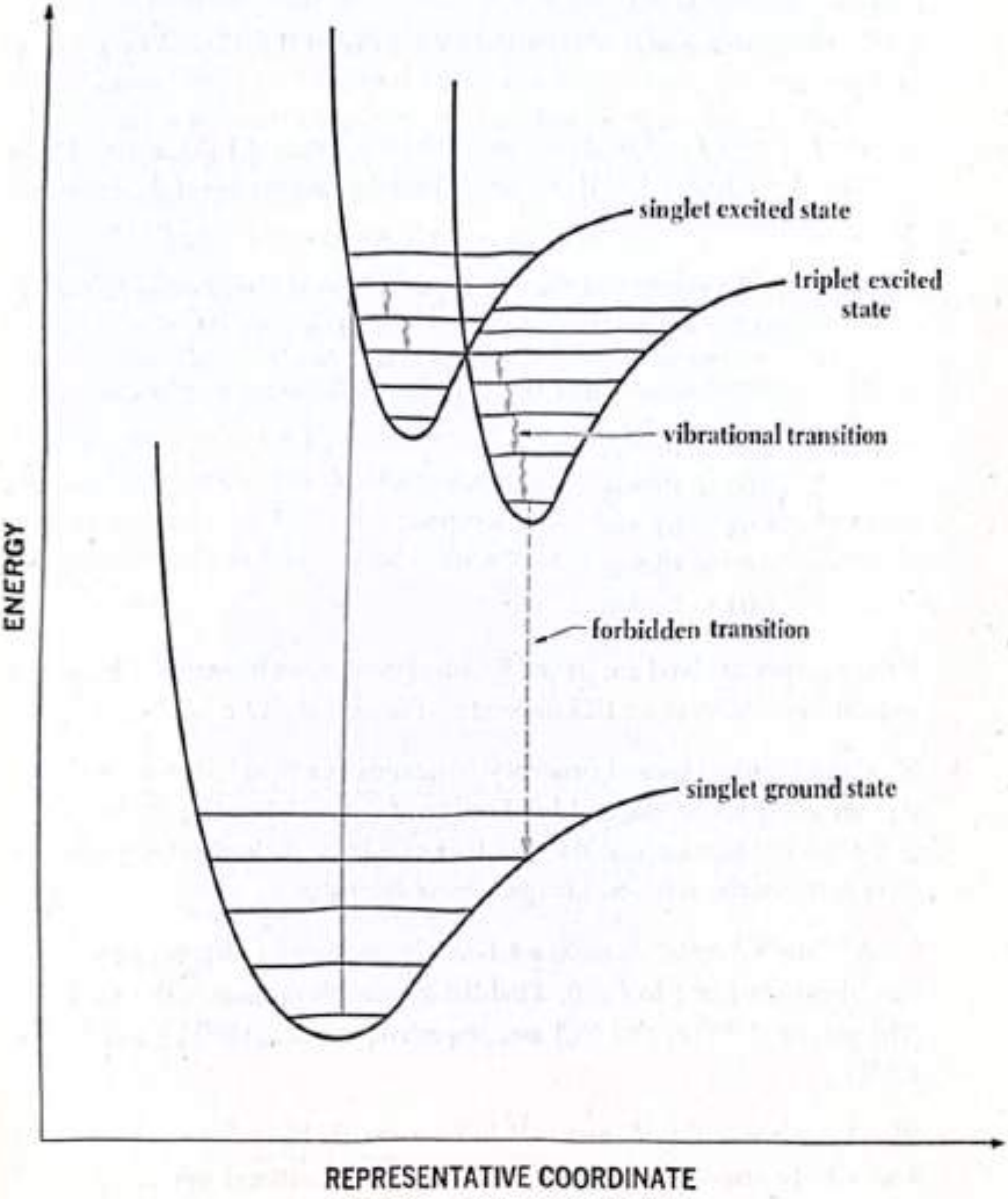


FIGURE 8-30 The origin of fluorescence.

shows a situation in which the molecule in its singlet (S = 0) ground state absorbs a photon and is elevated to a singlet excited state. In collisions the molecule can undergo radiationless transitions to a lower vibrational level that may happen to have about the same energy as one of the levels in the triplet (S = 1) excited state, and there is then a certain probability for a shift to the triplet state to occur. Further collisions in the triplet state bring the molecule's energy below that of the crossover point, so that it is now trapped in the triplet state and ultimately reaches the $v = 0$ level. A radiative transition from a triplet to a singlet state is "forbidden" by the selection rules, which really means not that it is impossible to occur but that it has only a minute likelihood of doing so. Such transitions accordingly have very long half lives, and the resulting *phosphorescent radiation* may be emitted minutes or even hours after the initial absorption.

**FIGURE 8-31** The origin of phosphorescence. The final transition is delayed because it violates the selection rules for electronic transitions.



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Second stage
Lecture 12

# Modern Physics II

2024-2025

Lecture 12

## Molecular physics

1- Vibration of spectra
2- Electronic spectra

Preparation
Lecturer. Hala I. Jasim

spectra (Sec. 6.10), certain *selection rules* summarize the conditions for a radiative transition between rotational states to be possible. For a rigid diatomic molecule the selection rule for rotational transitions is

$$\Delta J = \pm 1 \tag{8.9}$$

In practice, rotational spectra are always obtained in absorption, so that each transition that is found involves a change from some initial state of quantum number $J$ to the next higher state of quantum number $J + 1$. In the case of a rigid molecule, the frequency of the photon absorbed is

$$\begin{aligned} \nu_{J \to J+1} &= \frac{\Delta E}{h} = \frac{E_{J+1} - E_J}{h} \\ &= \frac{\hbar}{2\pi I}(J + 1) \end{aligned} \tag{8.10}$$

**Rotational spectra**

where $I$ is the moment of inertia for end-over-end rotations. The spectrum of a rigid molecule therefore consists of equally spaced lines, as in Fig. 8-22. The frequency of each line can be measured, and the transition it corresponds to can often be ascertained from the sequence of lines; from these data the moment of inertia of the molecule can be readily calculated. (Alternatively, the frequencies of any two successive lines may be used to determine $I$ if the spectrometer used does not record the lowest-frequency lines in a particular spectral sequence.) In CO, for instance, the $J = 0 \to J = 1$ absorption line occurs at a frequency of $1.153 \times 10^{11}$ Hz. Hence

$$\begin{aligned} I_{\text{CO}} &= \frac{\hbar}{2\pi\nu}(J + 1) \\ &= \frac{1.054 \times 10^{-34}\ \text{J-s}}{2\pi \times 1.153 \times 10^{11}\ \text{s}^{-1}} \\ &= 1.46 \times 10^{-46}\ \text{kg-m}^2 \end{aligned}$$

Since the reduced mass of the CO molecule is $1.14 \times 10^{-26}$ kg, the bond length $R_{\text{CO}}$ is $\sqrt{I/m'} = 1.13$ Å. This is the way in which the bond length for CO quoted earlier in this section was determined.

## 8.9 VIBRATIONAL ENERGY LEVELS

When sufficiently excited, a molecule can vibrate as well as rotate. As before, we shall only consider diatomic molecules. Figure 8-23 shows how the potential energy of a molecule varies with the internuclear distance $R$. In the neighborhood

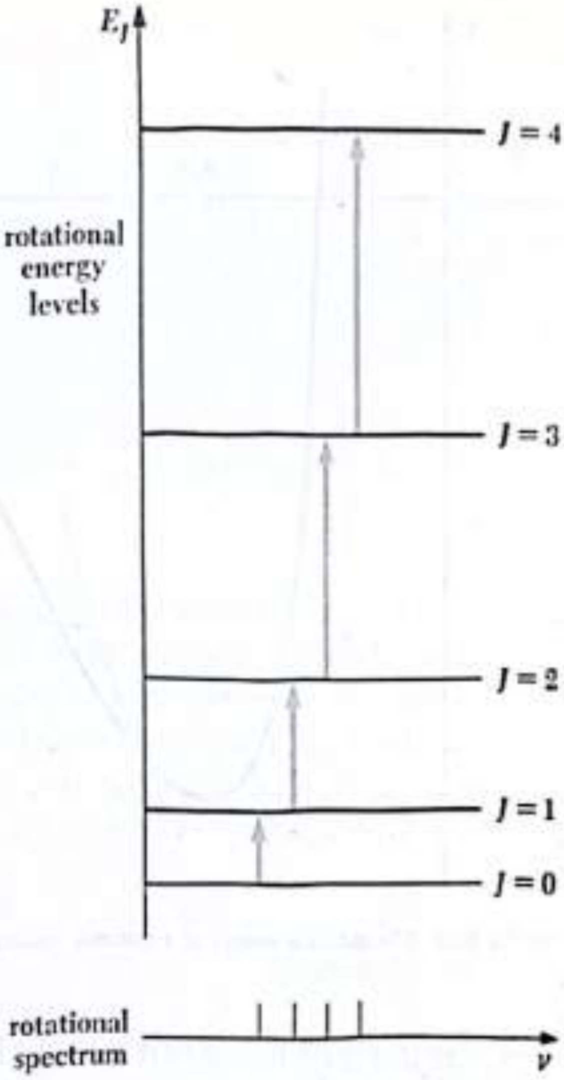


FIGURE 8-22 Energy levels and spectrum of molecular rotation.

of the minimum of this curve, which corresponds to the normal configuration of the molecule, the shape of the curve is very nearly a parabola. In this region, then,

$$V = V_0 + \tfrac{1}{2}k(R - R_0)^2 \tag{8.11}$$

where $R_0$ is the equilibrium separation of the atoms. The interatomic force that gives rise to this potential energy may be found by differentiating $V$:

$$F = -\frac{dV}{dR}$$

$$= -k(R - R_0) \tag{8.12}$$

The force is just the restoring force that a stretched or compressed spring exerts—a Hooke's law force—and, as with a spring, a molecule suitably excited can undergo simple harmonic oscillations.

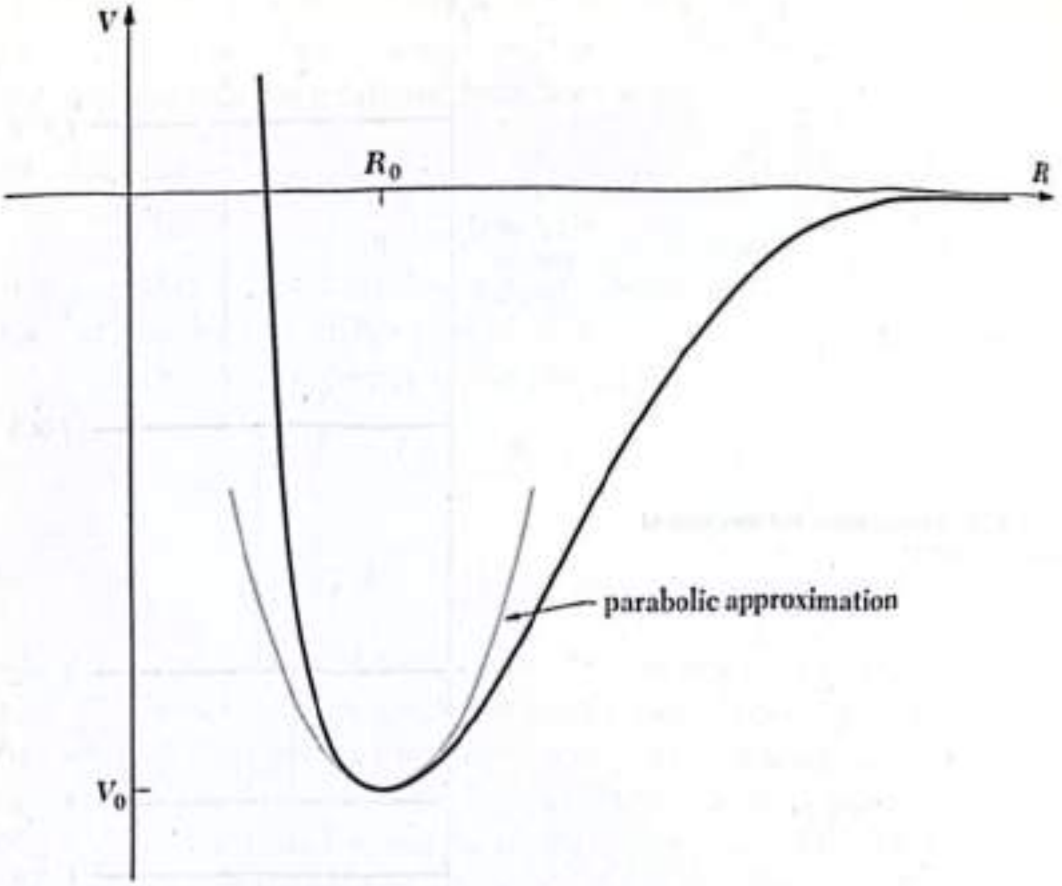


FIGURE 8-23 The potential energy of a diatomic molecule as a function of internuclear distance.

Classically, the frequency of a vibrating body of mass $m$ connected to a spring of force constant $k$ is

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \tag{8.13}$$

What we have in the case of a diatomic molecule is the somewhat different situation of two bodies of masses $m_1$ and $m_2$ joined by a spring, as in Fig. 8.24. In the absence of external forces the linear momentum of the system remains constant, and the oscillations of the bodies therefore cannot affect the motion of their center of mass. For this reason $m_1$ and $m_2$ vibrate back and forth relative to their center of mass in opposite directions, and both reach the extremes of their respective motions at the same times. The frequency of oscillation of such a two-body oscillator is given by Eq. 8.13 with the reduced mass $m'$ of Eq. 8.5

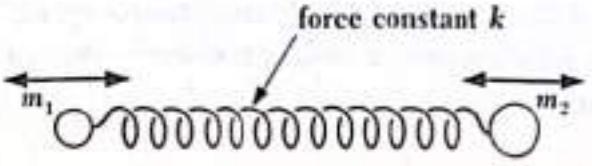


FIGURE 8-24 A two-body oscillator.

substituted for $m$:

8.14 $$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m'}}$$ **Two-body oscillator**

When the harmonic-oscillator problem is solved quantum mechanically, as was done in Chap. 5, the energy of the oscillator is found to be restricted to the values

8.15 $$E_v = (v + \tfrac{1}{2})\,h\nu_0$$

where $v$, the *vibrational quantum number*, may have the values

$$v = 0, 1, 2, 3, \ldots$$

The lowest vibrational state ($v = 0$) has the finite energy $\frac{1}{2}h\nu_0$, not the classical value of 0; as discussed in Chap. 5, this result is in accord with the uncertainty principle, because if the oscillating particle were stationary, the uncertainty in its position would be $\Delta x = 0$ and its momentum uncertainty would then have to be infinite—and a particle with $E = 0$ cannot have an infinitely uncertain momentum. In view of Eq. 8.14 the vibrational energy levels of a diatomic molecule are specified by

8.16 $$E_v = (v + \tfrac{1}{2})\,\hbar\sqrt{\frac{k}{m'}}$$ **Vibrational energy levels**

Let us calculate the frequency of vibration of the CO molecule and the spacing between its vibrational energy levels. The force constant $k$ of the bond in CO is 187 N/m (which is 10 lb/in.—not an exceptional figure for an ordinary spring) and, as we found in Sec. 8.8, the reduced mass of the CO molecule is $m' = 1.14 \times 10^{-26}$ kg. The frequency of vibration is therefore

$$\begin{aligned}\nu_0 &= \frac{1}{2\pi}\sqrt{\frac{k}{m'}}\\ &= \frac{1}{2\pi}\sqrt{\frac{187\ \text{N/m}}{1.14 \times 10^{-26}\ \text{kg}}}\\ &= 2.04 \times 10^{13}\ \text{Hz}\end{aligned}$$

The separation $\Delta E$ between the vibrational energy levels in CO is

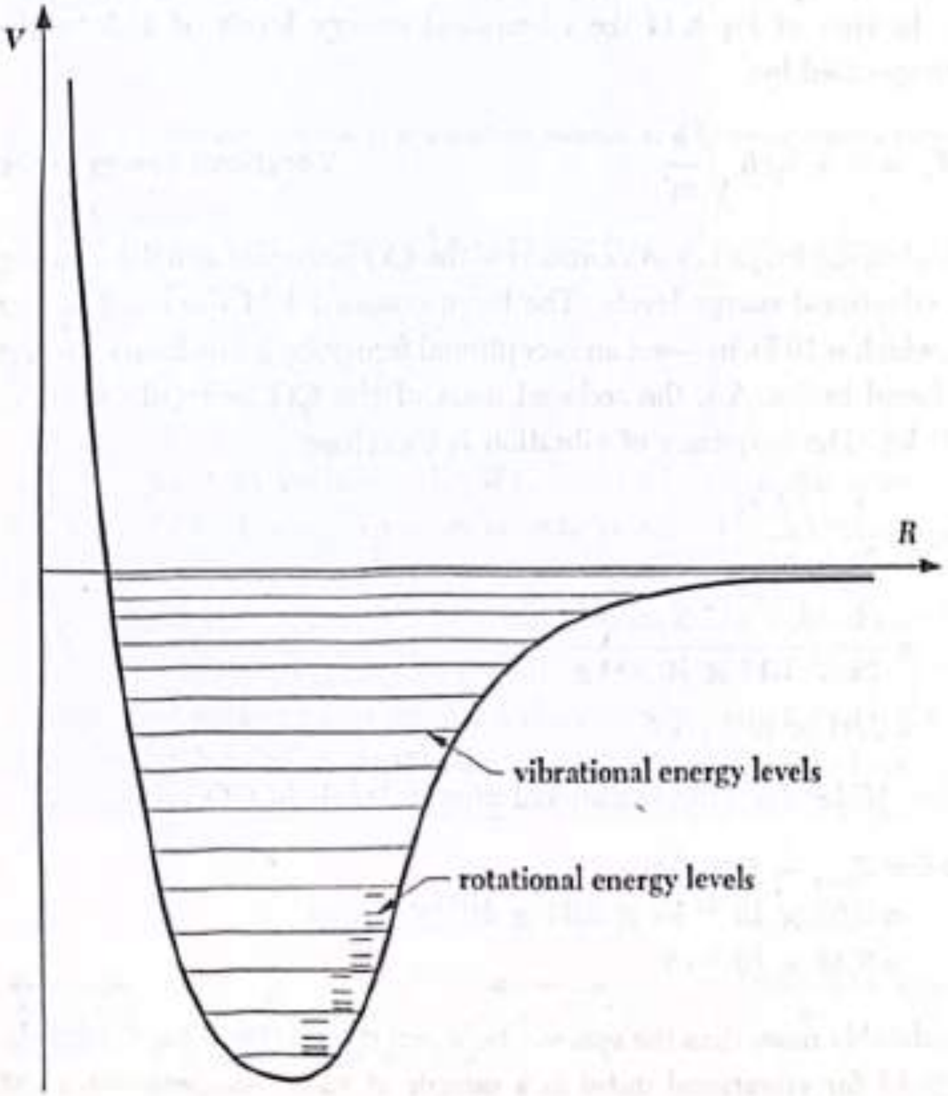
$$\begin{aligned}\Delta E &= E_{v+1} - E_v = h\nu_0\\ &= 6.63 \times 10^{-34}\ \text{J-s} \times 2.04 \times 10^{13}\ \text{s}^{-1}\\ &= 8.44 \times 10^{-2}\ \text{eV}\end{aligned}$$

which is considerably more than the spacing between its rotational energy levels. Because $\Delta E > kT$ for vibrational states in a sample at room temperature, most of the molecules in such a sample exist in the $v = 0$ state with only their zero-point energies. This situation is very different from that characteristic of rotational states, where the much smaller energies mean that the majority of the molecules in a room-temperature sample are excited to higher states.

The higher vibrational states of a molecule do not obey Eq. 8.15 because the parabolic approximation to its potential-energy curve becomes less and less valid with increasing energy. As a result, the spacing between adjacent energy levels of high $v$ is less than the spacing between adjacent levels of low $v$, which is shown in Fig. 8-25. This diagram also shows the fine structure in the vibrational levels caused by the simultaneous excitation of rotational levels.

The selection rule for transitions between vibrational states is $\Delta v = \pm 1$ in the harmonic oscillator approximation. This rule is easy to understand. An oscillating dipole whose frequency is $\nu_0$ can only absorb or emit electromagnetic radiation of the same frequency, and all quanta of frequency $\nu_0$ have the energy

FIGURE 8-25 The potential energy of a diatomic molecule as a function of interatomic distance, showing vibrational and rotational energy levels.



$h\nu_0$. The oscillating dipole accordingly can only absorb $\Delta E = h\nu_0$ at a time, in which case its energy increases from $(v + \frac{1}{2})h\nu_0$ to $(v + \frac{1}{2} + 1)h\nu_0$, and it can only emit $\Delta E = h\nu_0$ at a time, in which case its energy decreases from $(v + \frac{1}{2})h\nu_0$ to $(v + \frac{1}{2} - 1)h\nu_0$. Hence the selection rule $\Delta v = \pm 1$.

Pure vibrational spectra are observed only in liquids where interactions between adjacent molecules inhibit rotation. Because the excitation energies involved in molecular rotation are considerably smaller than those involved in vibration, the freely moving molecules in a gas or vapor nearly always are rotating, regardless of their vibrational state. The spectra of such molecules do not show isolated lines corresponding to each vibrational transition, but instead a large number of closely spaced lines due to transitions between the various rotational states of one vibrational level and the rotational states of the other. In spectra obtained using a spectrometer with inadequate resolution, the lines appear as a broad streak called a vibration-rotation band.

To a first approximation, the vibrations and rotations of a molecule take place independently of each other, and we can also ignore the effects of centrifugal distortion and anharmonicity. Under these circumstances the energy levels of a diatomic molecule are specified by

$$E_{v,J} = (v + \tfrac{1}{2})\hbar\sqrt{\frac{k}{m'}} + J(J+1)\frac{\hbar^2}{2I} \tag{8.17}$$

Figure 8.26 shows the $J = 0, 1, 2, 3$, and $4$ levels of a diatomic molecule for the $v = 0$ and $v = 1$ vibrational states, together with the spectral lines in absorption that are consistent with the selection rules $\Delta v = +1$ and $\Delta J = \pm 1$. The $v = 0 \rightarrow v = 1$ transitions fall into two categories, the *P branch* in which $\Delta J = -1$ (that is, $J \rightarrow J - 1$) and the *R branch* in which $\Delta J = +1$ ($J \rightarrow J + 1$). From Eq. 8.17 the frequencies of the spectral lines in each branch are given by

$$\begin{aligned}\nu_P &= E_{1,J-1} - E_{0,J}\\ &= \frac{1}{2\pi}\sqrt{\frac{k}{m'}} + [(J-1)J - J(J+1)]\frac{\hbar}{4\pi I}\\ &= \nu_0 - J\frac{\hbar}{2\pi I} \qquad J = 1, 2, 3, \ldots \qquad \textbf{\textit{P} branch}\end{aligned} \tag{8.18}$$

and

$$\begin{aligned}\nu_R &= E_{1,J+1} - E_{0,J}\\ &= \frac{1}{2\pi}\sqrt{\frac{k}{m'}} + [(J+1)(J+2) - J(J+1)]\frac{\hbar}{4\pi I}\\ &= \nu_0 + (J+1)\frac{\hbar}{2\pi I} \qquad J = 0, 1, 2, \ldots \qquad \textbf{\textit{R} branch}\end{aligned} \tag{8.19}$$

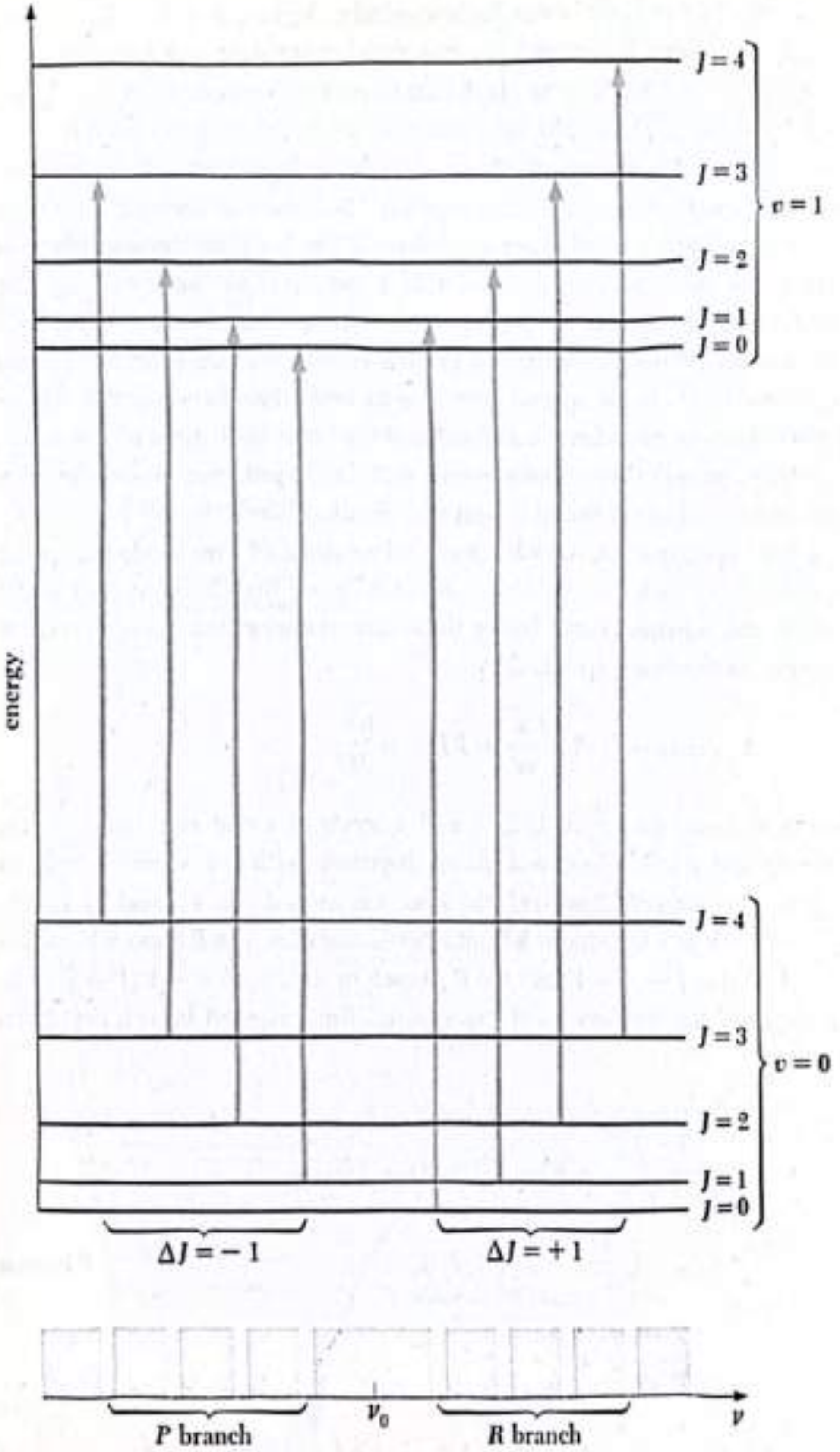
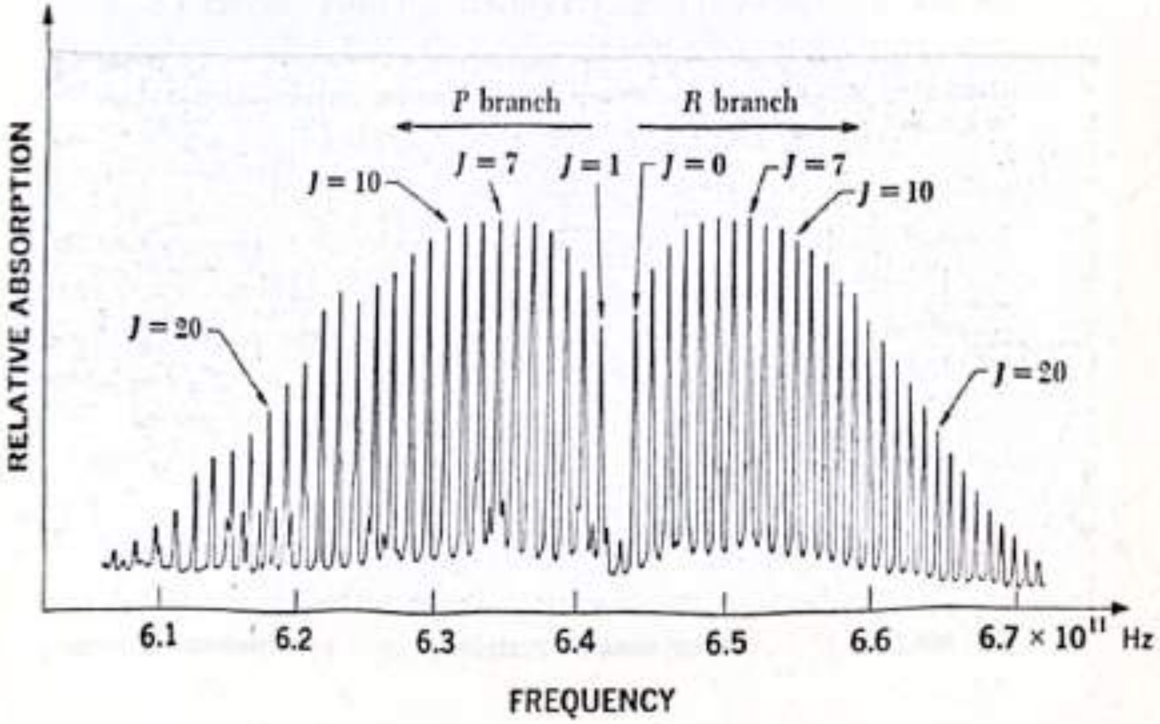


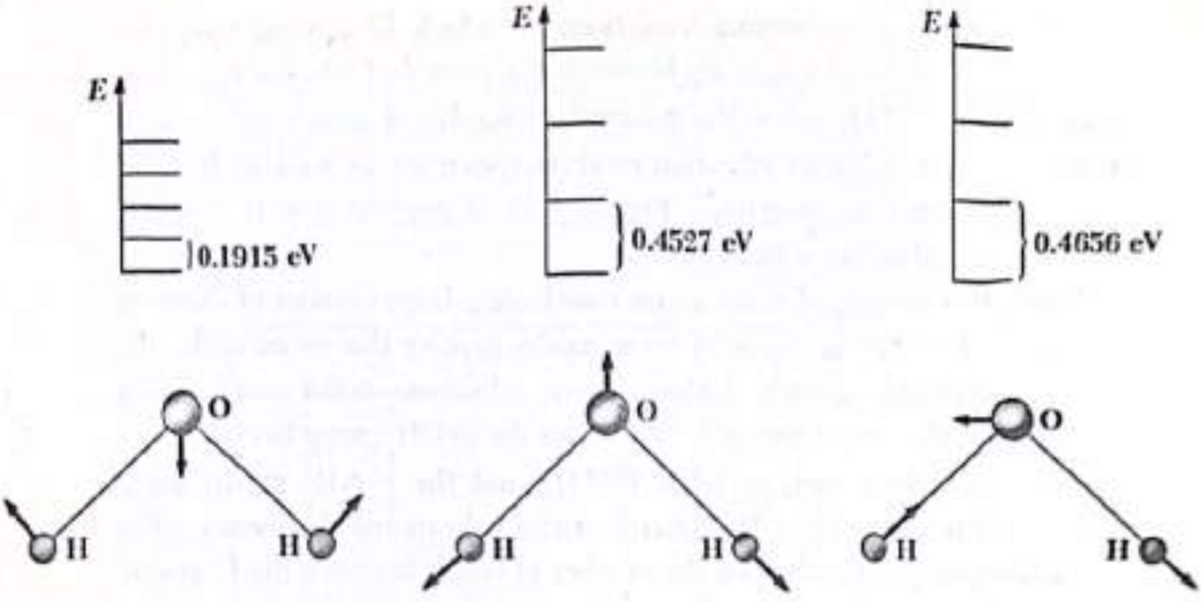
FIGURE 8-26 The rotational structure of the $v = 0 \to v = 1$ transitions in a diatomic molecule. There is no line at $\nu = \nu_0$ (the $Q$ branch) because of the selection rule $\Delta J = \pm 1$.

There is no line at $\nu = \nu_0$ because transitions for which $\Delta J = 0$ are forbidden in diatomic molecules. The spacing between the lines in both the $P$ and the $R$ branch is $\Delta\nu = \hbar/2\pi I$; hence the moment of inertia of a molecule can be ascertained from its infrared vibration-rotation spectrum as well as from its microwave pure-rotation spectrum. Figure 8-27 shows the $v = 0 \rightarrow v = 1$ vibration-rotation absorption band in CO.

A molecule that consists of many atoms may have a large number of different normal modes of vibration. Some of these modes involve the entire molecule, but others involve only groups of atoms whose vibrations occur more or less independently of the rest of the molecule. Thus the —OH group has a characteristic vibrational frequency of $1.1 \times 10^{14}$ Hz and the $-NH_2$ group has a frequency of $1.0 \times 10^{14}$ Hz. The characteristic vibrational frequency of a carbon-carbon group depends upon the number of bonds between the C atoms: the $>C-C<$ group vibrates at about $3.3 \times 10^{13}$ Hz, the $>C=C<$ group vibrates at about $5.0 \times 10^{13}$ Hz, and the $-C{\equiv}C-$ group vibrates at about $6.7 \times 10^{13}$ Hz (Figs. 8-28 and 8-29). (As we would expect, the greater the number of carbon-carbon bonds, the larger the value of the force constant $k$ and the higher the frequency.) In each case the frequency does not depend on the particular molecule or the location in the molecule of the group. This independence makes vibrational spectra a valuable tool in determining molecular

**FIGURE 8-27** The $v = 0 \rightarrow v = 1$ vibration-rotation absorption band in CO under high resolution. The lines are identified by the value of $J$ in the initial rotational state.



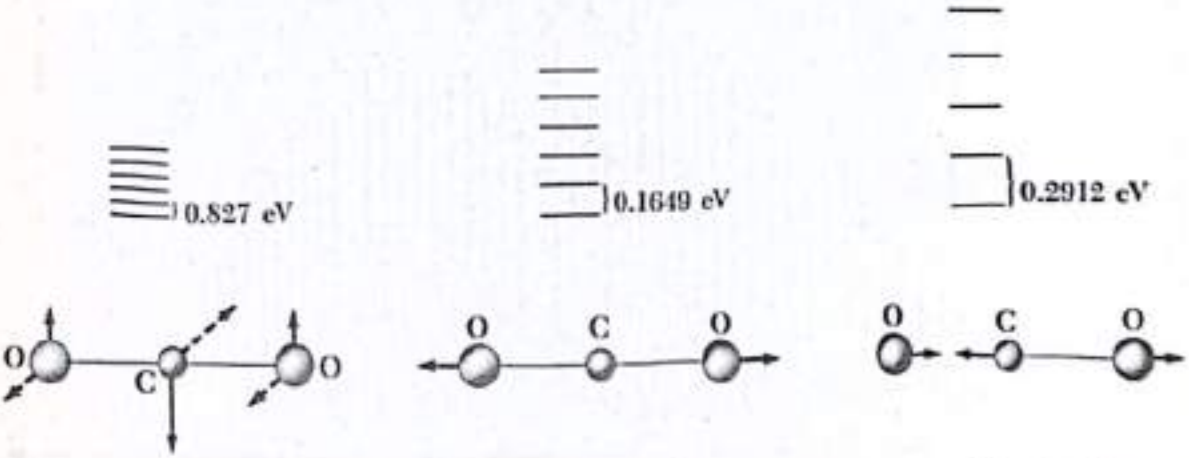


symmetric bending symmetric stretching asymmetric stretching

FIGURE 8-28 The normal modes of vibration of the $H_2O$ molecule and the energy levels of each mode.

structures. An example is thioacetic acid, whose structure might conceivably be either $CH_3CO{-}SH$ or $CH_3CS{-}OH$. The infrared absorption spectrum of thioacetic acid contains lines at frequencies equal to the vibrational frequencies of the $\rangle C{=}O$ and $-SH$ groups, but no lines corresponding to the $\rangle C{=}S$ or $-OH$ groups, so the former alternative is the correct one.

FIGURE 8-29 The normal modes of vibration of the $CO_2$ molecule and the energy levels of each mode. The symmetric bending mode can occur in two perpendicular planes.



symmetric bending symmetric stretching asymmetric stretching