SEMESTER VI

16PHU602A **QUANTUM MECHANICS** **L T P C**
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Objectives: This paper explains the shortcomings of classical physics in explaining different subatomic physics and the evolution of quantum mechanics.

UNIT I

Time dependent Schrodinger equation: Time dependent Schrodinger equation and dynamical evolution of a quantum state; Properties of Wave Function. Interpretation of Wave Function Probability and probability current densities in three dimensions; Conditions for Physical Acceptability of Wave Functions. Normalization. Linearity and Superposition Principles. Eigenvalues and Eigenfunctions. Position, momentum & Energy operators; commutator of position and momentum operators; Expectation values of position & momentum. Wave Function of a Free Particle.

UNIT II

Time independent Schrodinger equation-Hamiltonian, stationary states and energy eigenvalues; expansion of an arbitrary wavefunction as a linear combination of energy eigenfunctions; General solution of the time dependent Schrodinger equation in terms of linear combinations of stationary states; Application to the spread of Gaussian wavepacket for a free particle in one dimension; wave packets, Fourier transforms and momentum space wavefunction; Position-momentum uncertainty principle.

UNIT III

General discussion of bound states in an arbitrary potential- continuity of wave function, boundary condition and emergence of discrete energy levels; application to one-dimensional problem- square well potential; Quantum mechanics of simple harmonic oscillator-energy levels and energy eigenfunctions using Frobenius method.

UNIT IV

Quantum theory of hydrogen-like atoms: time independent Schrodinger equation in spherical polar coordinates; separation of variables for the second order partial differential equation; angular momentum operator and quantum numbers; Radial wavefunctions from Frobenius method; Orbital angular momentum quantum numbers l and m; s, p, d,.. shells (idea only)

UNIT V

Atoms in Electric and Magnetic Fields:- Electron Angular Momentum. Space Quantization. Electron Spin and Spin Angular Momentum. Larmor's Theorem. Spin Magnetic Moment. Stern-Gerlach Experiment. Normal Zeeman Effect: Electron Magnetic Moment and Magnetic Energy. Many electron atoms: Pauli's Exclusion Principle. Symmetric and Antisymmetric Wave Functions. Spin orbit coupling. Spectral Notations for Atomic States. Total Angular Momentum. Spin-orbit coupling in atoms-L-S and J-J couplings.

Reference Book

1. A Text book of Quantum Mechanics, P.M. Mathews and K. Venkatesan, 2nd Ed., 2010, McGraw Hill
2. Quantum Mechanics, Robert Eisberg and Robert Resnick, 2ndEdn., 2002, Wiley.
   Quantum Mechanics, Leonard I. Schiff, 3rdEdn. 2010, Tata McGraw Hill.
3. Quantum Mechanics, G. Aruldhas, 2ndEdn. 2002, PHI Learning of India.
4. Quantum Mechanics, Bruce Cameron Reed, 2008, Jones and Bartlett Learning
5. Introduction to Quantum Mechanics, D.J. Griffith, 2nd Ed. 2005, Pearson Education

KARPAGAM ACADEMY OF HIGHER EDUCATION

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(Established Under Section 3 of UGC Act 1956)
Coimbatore - 641021.
(For the candidates admitted from 2016 onwards)

DEPARTMENT OF PHYSICS

SUBJECT: Quantum Mechanics
SEMESTER: VI
SUBJET CODE: 16PHP602A **CLASS: III B.Sc Physics**

UNIT - I

Lecture hours (8)	Topics to be covered	P.No.
1	Time dependent Schroedinger equation and dynamical evolution of a quantum state, Properties of wave function, interpretation of wave function	T1:78-79, T1:79, T1:80-81
1	Probability and probability current densities in three dimension	T1:95-96
1	Condition for physics accessability of wave function, Normalization of wave function	T1:82-83, T1:83-84
1	Linearity and superposition principle, Eigenvalues and Eigen functions	T1:86-87
1	Position, momentum and Energy operators, Commutation of position and momentum operator	T1:90-91, T1:91-92, T1:92-93
1	Expectation values of position and momentum	
1	Wave function of a free particle	T1:94
1	Revision	

Textbooks

T1- A Textbook of Quantum Mechanics. P.M.Mathews and K. Vekatesan, 2nd Edition, 2010, McGraw Hill.
T2 – Qunatum Mechanics, G. Aruldhas, 2nd Edition, 2002, PHI Learning of India

Reference Book

R1 – Quantum Mechanics. Robert Eisberg and Robert Resnik, 2nd Edition, 2002, Wiley
R2 – Quantum Mechanics. Leonard. I. Schiff. 3rd Edition, 2010, Tata McGraw Hill

Unit - II

Lecture hours (8)	Topics to be covered	P.No.
1	Time independent Schroedinger equation, Hamiltonian, stationary states, energy eigen values	T1:76-77, T1:241, T1:243, T1:244
1	Expansion of arbitrary wavefunction as a linear combination of energy eigen function	T1:236-237
1	General solution of time dependent Schrodinger wave equation interms of linear combination of stationary states	T1:238-240
1	Application to the spread ofr Gaussian wavepacket for a free particle in one dimension	T1:133-135
1	Wave packets	T1:120-121
1	Fourier transforms and momentum space wave function	T1:220-221
1	Position-momentum uncertainty principle	T1:271-272
1	Revision	

Textbooks

T1- A Textbook of Quantum Mechanics. P.M.Mathews and K. Vekatesan, 2nd Edition, 2010, McGraw Hill.
T2 – Qunatum Mechanics, G. Aruldhas, 2nd Edition, 2002, PHI Learning of India

Reference Book

R1 – Quantum Mechanics. Robert Eisberg and Robert Resnik, 2nd Edition, 2002, Wiley
R2 – Quantum Mechanics. Leonard. I. Schiff. 3rd Edition, 2010, Tata McGraw Hill

UNIT - III

Lecture hours (6)	Topics to be covered	P.No.
1	General discussion of bound states in an arbitrary potential	T!:158-160
1	Contiunuty of wavefunction, boundary condition and emergence of discrete energy levels	T1:160
1	Application to one dimensional problem – square well potential	T1:161-163
1	Quantum mechanics of simple harmonic oscillator	T1:169-171
1	Energy levels and energy eigen functions usin Frobenius method	T1:192-193
1	Revision	

Textbooks

T1- A Textbook of Quantum Mechanics. P.M.Mathews and K. Vekatesan, 2nd Edition, 2010, McGraw Hill.
T2 – Qunatum Mechanics, G. Aruldhas, 2nd Edition, 2002, PHI Learning of India

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R2 – Quantum Mechanics. Leonard. I. Schiff. 3rd Edition, 2010, Tata McGraw Hill

UNIT - IV

Lecture hours (12)	Topics to be covered	P.No.
1	Quantum theory of hydrogen like atom	T1:221-222
1	Time independent Schroedinger equation in spherical polar coordinates	T1:223-225
1	Separation of variables for the second order partial differential equation	T1:225-227
1	Angular momentum operators and quantum numbers	T1:396-397
1	Radial wave functions from Frobenius method	T1:397-399
1	Orbital angular momentum quantum numbers l and m, s, d,…. Shells (ideas)	T1:400-401
1	Revision	

Textbooks

T1- A Textbook of Quantum Mechanics. P.M.Mathews and K. Vekatesan, 2nd Edition, 2010, McGraw Hill.
T2 – Qunatum Mechanics, G. Aruldhas, 2nd Edition, 2002, PHI Learning of India

Reference Book

R1 – Quantum Mechanics. Robert Eisberg and Robert Resnik, 2nd Edition, 2002, Wiley
R2 – Quantum Mechanics. Leonard. I. Schiff. 3rd Edition, 2010, Tata McGraw Hill

UNIT - V

Lecture hours (11)	Topics to be covered	P.No.
1	**Electron angular momentum, spin quantization, electron spin and spin angular momentum**	T1:380-381, T1:381-382, T1:382-383
1	Larmor's theorem, spin magnetic moment	T1:383, T1:384
1	Stern-Gerlach experiment, Normal Zeeman Effect	T1:385-386, T1:386-387
1	Electron magnetic moment and magnetic energy, many electron theorem and Pauli's exclusion principle	T1:387-388, T1:389-390
1	Symmetric and antisymmetric wave function, spin orbit coupling	T1:366-367, T1:367
1	Spectral notation for atomic states, Total angular momentum	T1:368, T1:368-369
1	Spin-orbit coupling in atoms, LS coupling, J-J coupling	T1:369-370, T1:370-371
1	Revision	
1	Old question paper discussion	
1	Old question paper discussion	
1	Old question paper discussion	

Textbooks

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UNIT I

Time dependent Schrodinger equation: Time dependent Schrodinger equation and dynamical evolution of a quantum state; Properties of Wave Function. Interpretation of Wave Function Probability and probability current densities in three dimensions; Conditions for Physical Acceptability of Wave Functions. Normalization. Linearity and Superposition Principles. Eigenvalues and Eigenfunctions. Position, momentum & Energy operators; commutator of position and momentum operators; Expectation values of position & momentum. Wave Function of a Free Particle.

Time dependent Schrodinger equation:

Although we were able to derive the single-particle time-independent Schrödinger equation starting from the classical wave equation and the de Broglie relation, the time-dependent Schrödinger equation cannot be derived using elementary methods and is generally given as a postulate of quantum mechanics. It is possible to show that the time-dependent equation is at least *reasonable* if not derivable, but the arguments are rather involved

The single-particle three-dimensional time-dependent Schrödinger equation is

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r})\psi(\mathbf{r},t) \tag{1}$$

where V is assumed to be a real function and represents the potential energy of the system *Wave Mechanics* is the branch of quantum mechanics with equation (1) as its dynamical law. Note that equation (1) does not yet account for spin or relativistic effects.

Of course the time-dependent equation can be used to derive the time-independent equation. If we write the wavefunction as a product of spatial and temporal terms, $\psi(\mathbf{r},t) = \psi(\mathbf{r})f(t)$, then equation (1) becomes

$$\psi(\mathbf{r})i\hbar\frac{df(t)}{dt} = f(t)\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) \tag{2}$$

or

$$\frac{i\hbar}{f(t)}\frac{df}{dt} = \frac{1}{\psi(\mathbf{r})}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) \tag{3}$$

Since the left-hand side is a function of t only and the right hand side is a function of $\mathbf{r}$ only, the two sides must equal a constant. If we tentatively designate this constant E (since the right-hand side clearly must have the dimensions of energy), then we extract two ordinary differential equations, namely

$$\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{iE}{\hbar} \tag{4}$$

and

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{5}$$

The latter equation is once again the time-independent Schrödinger equation. The former equation is easily solved to yield

$$f(t) = e^{-iEt/\hbar} \tag{6}$$

The Hamiltonian in equation (5) is a Hermitian operator, and the eigenvalues of a Hermitian operator must be real, so E is real. This means that the solutions $f(t)$ are purely oscillatory, since $f(t)$ never changes in magnitude (recall Euler's formula $e^{\pm i\theta} = cos\theta \pm i\ sin\theta$). Thus if

$$\psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-iEt/\hbar} \tag{7}$$

then the total wave function $\psi(\mathbf{r},t)$ differs from $\psi(\mathbf{r})$ only by a phase factor of constant magnitude. There are some interesting consequences of this. First of all, the quantity $|\psi(\mathbf{r},t)|^2$ is time independent, as we can easily show:

$$|\psi(\mathbf{r},t)|^2 = \psi^*(\mathbf{r},t)\psi(\mathbf{r},t) = e^{iEt/\hbar}\psi^*(\mathbf{r})e^{-iEt/\hbar}\psi(\mathbf{r}) = \psi^*(\mathbf{r})\psi(\mathbf{r}) \tag{8}$$

Secondly, the expectation value for any time-independent operator is also time-independent, if $\psi(\mathbf{r},t)$ satisfies equation (7). By the same reasoning applied above,

$$< A >= \int \psi^*(\mathbf{r},t)\hat{A}\psi(\mathbf{r},t) = \int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r}) \tag{9}$$

For these reasons, wave functions of the form (7) are called *stationary states*. The state $\psi(\mathbf{r},t)$ is ``stationary," but the particle it describes is not!

Of course equation (7) represents a particular solution to equation (1). The general solution to equation (1) will be a linear combination of these particular solutions, i.e.

$$\psi(\mathbf{r},t) = \sum_i c_i e^{-iE_i t/\hbar}\psi_i(\mathbf{r}) \tag{10}$$

Properties of wave functions

The quantity with which quantum mechanics is concerned is the wave function Ψ(r, t).

Properties:

1. Ψ(r, t) is complex. It can be written in the form Ψ(r, t) = A(r, t) + i B(r, t) where A and B are real functions.
2. Complex conjugate of Ψ is defined as Ψ* = A - iB
3. | Ψ| 2 = Ψ * Ψ = A 2+B 2 Therefore | Ψ| 2 = Ψ * Ψ is always positive and real.

4. While Ψ itself has no physical interpretation, | Ψ| 2 evaluated at a particular place at a particular time equals to the probability of finding the body there at that time.

5. Normalization If a wavefunction is not normalized, we can make it so by dividing it with a normalization constant. $\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dV = 1$. Eg

$$f(x) = \begin{cases} a(1-x) & x \geq 0 \\ a(1+x) & x < 0 \end{cases}$$

$$\therefore \int_{-\infty}^{\infty} |f(x)|^2 \, dx = 2\int_0^1 [a(1-x)]^2 dx$$

$$= 2a^2\left[-\frac{(1-x)^3}{3}\right]_0^1$$

$$= \frac{2}{3}a^2 \neq 1$$

$$\therefore \text{ f(x) is not normalixed, but } \psi(x) = \frac{f(x)}{\sqrt{\frac{2}{3}}a} \text{ is!}$$

5. Mathematical properties of Ψ: a. Ψ must be continuous and single-valued everywhere. b. ∂Ψ / ∂x, ∂Ψ / ∂y, ∂Ψ / ∂z must be continuous and single-valued everywhere. (There may be exception in some special situations, we will discuss this later.) c. Ψ must be normalizable. | Ψ| 2 must go 0 fast enough as x, y, or z →±∞ so that ∫ |Ψ| 2 dV remains finite.

Probability Interpretation of Wavefunction

After many false starts, physicists in the early 20th century eventually came to the conclusion that the only physical interpretation of a particle wavefunction that is consistent with experimental observations is probabilistic in nature (Dirac 1982). To be more exact, if $\psi(x,t)$ is the complex wavefunction of a given particle, moving in one dimension along the x-axis, then the probability of finding the particle between x and $x+dx$ at time t is

$$P(x,t) = |\psi(x,t)|^2 \, dx. \qquad (1105)$$

A probability is a real number lying in the range 0 to 1 . An event that has a probability 0 is impossible. On the other hand, an event that has a probability 1 is certain to occur. An event that has an probability $1/2$ (say) is such that in a very large number of identical trials the event occurs in half of the trials. We can interpret

$$P(t) = \int_{-\infty}^{\infty} |\psi(x,t)|^2\, dx \tag{1106}$$

as the probability of the particle being found anywhere between $x = -\infty$ and $x = +\infty$ at time t . This follows, via induction, from the fundamental result in probability theory that the probability of the occurrence of one or other of two mutually exclusive events (such as the particle being found in two non-overlapping regions) is the sum (or integral) of the probabilities of the individual events (Reif 2008). (For example, the probability of throwing a 1 on a six-sided die is $1/6$. Likewise, the probability of throwing a 2 is $1/6$. Hence, the probability of throwing a 1 or a 2 is $1/6 + 1/6 = 1/3$.) Assuming that the particle exists, it is certain that it will be found somewhere between $x = -\infty$ and $x = +\infty$ at time t . Because a certain event has probability 1 , our probability interpretation of the wavefunction is only tenable provided

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2\, dx = 1 \tag{1107}$$

at all times. A wavefunction that satisfies the previous condition--which is known as the *normalization condition*--is said to be properly normalized.

Suppose that we have a wavefunction, $\psi(x,t)$, which is such that it satisfies the normalization condition (1107) at time $t=0$. Furthermore, let the wavefunction evolve in time according to Schrödinger's equation, (1102). Our probability interpretation of the wavefunction only makes sense if the normalization condition remains satisfied at all subsequent times. This follows because if the particle is certain to be found somewhere on the x-axis (which is the interpretation put on the normalization condition) at time $t=0$ then it is equally certain to be found somewhere on the x-axis at a later time (because we are not considering any physical process by which particles can be created or destroyed). Thus, it is necessary for us to demonstrate that Schrödinger's equation preserves the normalization of the wavefunction.

Taking Schrödinger's equation, and multiplying it by ψ^* (the complex conjugate of the wavefunction), we obtain

$$\mathrm{i}\,\hbar\,\frac{\partial\psi}{\partial t}\,\psi^* = -\frac{\hbar^2}{2\,m}\,\frac{\partial^2\psi}{\partial x^2}\,\psi^* + U(x)\,|\psi|^2. \tag{1108}$$

The complex conjugate of the previous expression yields

$$-\mathrm{i}\,\hbar\,\frac{\partial\psi^*}{\partial t}\,\psi = -\frac{\hbar^2}{2\,m}\,\frac{\partial^2\psi^*}{\partial x^2}\,\psi + U(x)\,|\psi|^2. \tag{1109}$$

Here, use has been made of the readily demonstrated results $(\psi^*)^* = \psi$ and $\mathrm{i}^* = -\mathrm{i}$, as well as the fact that $U(x)$ is real. Taking the difference between the previous two expressions, we obtain

$$\mathrm{i}\,\hbar\left(\frac{\partial\psi}{\partial t}\,\psi^* + \frac{\partial\psi^*}{\partial t}\,\psi\right) = -\frac{\hbar^2}{2\,m}\left(\frac{\partial^2\psi}{\partial x^2}\,\psi^* - \frac{\partial^2\psi^*}{\partial x^2}\,\psi\right), \tag{1110}$$

which can be written

$$\mathrm{i}\,\hbar\,\frac{\partial|\psi|^2}{\partial t} = -\frac{\hbar^2}{2\,m}\,\frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial x}\,\psi^* - \frac{\partial\psi^*}{\partial x}\,\psi\right). \tag{1111}$$

Integrating in x, we get

$$\mathrm{i}\,\hbar\,\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2\,dx = -\frac{\hbar^2}{2\,m}\left[\frac{\partial\psi}{\partial x}\,\psi^* - \frac{\partial\psi^*}{\partial x}\,\psi\right]_{-\infty}^{\infty}. \tag{1112}$$

Finally, assuming that the wavefunction is localized in space: that is,

$$|\psi(x,t)| \to 0 \quad \text{as} \quad |x| \to \infty, \tag{1113}$$

we obtain

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2\,dx = 0. \tag{1114}$$

It follows, from the preceding analysis, that if a localized wavefunction is properly normalized at $t = 0$ (i.e., if $\int_{-\infty}^{\infty} |\psi(x,0)|^2\,dx = 1$) then it will remain properly normalized as it evolves in time according to Schrödinger's equation. Incidentally, a wavefunction that is not localized cannot be properly normalized, because its normalization integral $\int_{-\infty}^{\infty} |\psi|^2\,dx$ is necessarily infinite. For such a wavefunction, $|\psi(x,t)|^2\,dx$ gives the relative, rather than the absolute, probability of finding the particle between x and $x + dx$ at time t. In other words, [cf., Equation (1105)]

$$P(x,t) \propto |\psi(x,t)|^2\,dx.$$

Conditions for physical acceptability of wave functions:

1. The wave function ψ must be continuous. All its partial derivatives must also be continuous (partial derivatives are $\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}$). This makes the wave function “smooth”.
2. The wave function ψ must be quadraticallyintegrable. This means that the integral $\int \psi^* \psi\, d\tau$ must exist.
3. Since $\int \psi^* \psi\, d\tau$ is the probability density, it must be single valued.
4. The wave functions must form an orthonormal set. This means that

- the wave functions must be normalized.

$$\int_{-\infty}^{\infty} \psi_i^* \; \psi_i \, d\tau = 1$$

- the wave functions must be orthogonal.

$$\int_{-\infty}^{\infty} \psi_i^* \ \psi_j \, d\tau = 0$$

OR $$\int_{-\infty}^{\infty} \psi_i^* \ \psi_j \, d\tau = \delta_{ij} \text{ where } \delta_{ij} = 1 \text{ when } i = j \text{ and } \delta_{ij} = 0 \text{ when } i \neq j$$

δijcalledKronecker delta

5. The wave function must be finite everywhere.

6. The wave function must satisfy the boundary conditions of the quantum mechanical system it represents.

Linearity and The Superposition Principle

Though it is customary to view the superposition principle within the mathematical framework of Hilbert Spaces, it is in-structive to recall its purely operational meaning as elaborated by Dirac. He gives a very broad characterization of states as the embodiment of the collection of all possible measurement outcomes. Then superposition of states according to him is as follows: if A is a superpositionof two or more states, say, B,C,.., every outcome of a measurement on A must also be a possible outcome of the same measurement on any of B, CThough this characterization of superposition may seem adhoc, the customary, Hilbert Space based view is completely equivalent to it. but the Dirac characterization has the advantage of being purely operational and applicable even if there is no underlying Hilbert space structure. Being about superposition of states, it is like no other superposition principle in either physics or mathematics. Examples of the latter are superposition of sound waves, of electromagnetic waves, of vectors etc.. This was most emphatically stated by Dirac himself: 'It is important to remember, however, that the superposition that occurs in quantum mechanics is of an essentially different nature from any occurring in the classical theory' (The italics are Dirac's). He further stated that The analogies are thus liable to be misleading(p.11 §3of [1], and p.14 §4of [2]). In the current formulation of quantum theory, this principle is givena precise mathematical meaning through the Hilbert Space formalism(actually one needs the density matrix formalism for a more satisfactory description, but that discussion is somewhat beyond the scope of this presentation). According to this, every physical state is representable by a family of vectors in a Hilbert space. A typical such vector is symbolically denoted by |i. Vectors belonging to a given family differ only in phase. This is the so called ray representation of states. If P1, P2are two distinct physical states meaning their rays are distinct, and if |1i belongs to the ray of P1and |2ibelongs to the ray of P2, the principle of superposition of states states that the complex linear superposition

$$|\psi\rangle = \alpha|1\rangle + \beta|2\rangle$$

also represent quantum states of the system.

Eigenfunctions and Eigenvalues

An *eigenfunction* of an operator $\hat{A}$ is a function f such that the application of $\hat{A}$ on f gives f again, times a constant.

$$\hat{A}f = kf \tag{49}$$

where k is a constant called the *eigenvalue*. It is easy to show that if $\hat{A}$ is a linear operator with an eigenfunction g, then any multiple of g is also an eigenfunction of $\hat{A}$.
When a system is in an *eigenstate* of observable A (i.e., when the wavefunction is an eigenfunction of the operator $\hat{A}$) then the expectation value of A is the eigenvalue of the wavefunction. Thus if

$$\hat{A}\psi(\mathbf{r}) = a\psi(\mathbf{r}) \tag{50}$$

then

$$\begin{aligned} < A > &= \underline{\int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})d\mathbf{r}} \\ &= \underline{\int \psi^*(\mathbf{r})a\psi(\mathbf{r})d\mathbf{r}} \end{aligned} \tag{51}$$

$$
\begin{aligned}
&= a \int \psi^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} \\
&= a
\end{aligned}
$$

assuming that the wavefunction is normalized to 1, as is generally the case. In the event that $\psi(\mathbf{r})$ is not or cannot be normalized (free particle, etc.) then we may use the formula

$$< A >= \frac{\int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})}{d}\mathbf{r} \int \psi^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} \qquad (52)$$

What if the wavefunction is a combination of eigenstates? Let us assume that we have a wavefunction which is a linear combination of two eigenstates of $\hat{A}$ with eigenvalues a and b.

$$\psi = c_a\psi_a + c_b\psi_b \qquad (53)$$

where $\hat{A}\psi_a = a\psi_a$ and $\hat{A}\psi_b = b\psi_b$. Then what is the expectation value of A?

$$
\begin{aligned}
< A > &= \int \psi^* \hat{A}\psi \qquad (54) \\
&= \int [c_a\psi_a + c_b\psi_b]^* \hat{A} [c_a\psi_a + c_b\psi_b] \\
&= \int [c_a\psi_a + c_b\psi_b]^* [ac_a\psi_a + bc_b\psi_b] \\
&= a|c_a|^2 \int \psi_a^*\psi_a + bc_a^*c_b \int \psi_a^*\psi_b + ac_b^*c_a \int \psi_b^*\psi_a + b|c_b|^2 \int \psi_b^*\psi_b
\end{aligned}
$$

$$= a|c_a|^2 + b|c_b|^2$$

assuming that ψ_a and ψ_b are orthonormal (shortly we will show that eigenvectors of Hermitian operators are orthogonal). Thus the average value of A is a weighted average of eigenvalues, with the weights being the squares of the coefficients of the eigenvectors in the overall wavefunction.

1. In the "position representation" or "position basis", the position operator is represented by the variable x:

$$\hat{x} \doteq x$$

2. In the "position representation" or "position basis", the momentum operator is represented by the derivative with respect to x:

$$\hat{p} \doteq -i\hbar \frac{d}{dx}$$

3. This follows if you accept (2). The energy operator is:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V} \doteq -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

Now think about eigenfunctions of these operators

Commutator of position and momentum operators:

Operators (or variables in quantum mechanics) do not necessarily commute. We can see our first example of that now that we have a few operators. We define the commutator to be

$$\boxed{[p,x] \equiv px - xp}$$

(using p and x as examples.)

We will now compute the commutator between p and x. Because p is represented by a differential operator, we must do this carefully. Lets think of the commutator as a (differential) operator too, as generally it will be. To make sure that we keep all the $\frac{\partial}{\partial x}$ that we need, we will compute $[p,x]\psi(x)$ then remove the $\psi(x)$ at the end to see only the commutator.

$$\begin{aligned}
[p,x]\psi(x) &= px\psi(x) - xp\psi(x) = \frac{\hbar}{i}\frac{\partial}{\partial x}x\psi(x) - x\frac{\hbar}{i}\frac{\partial}{\partial x}\psi(x) \\
[p,x]\psi(x) &= \frac{\hbar}{i}\left(\psi(x) + x\frac{\partial\psi(x)}{\partial x} - x\frac{\partial\psi(x)}{\partial x}\right) = \frac{\hbar}{i}\psi(x)
\end{aligned}$$

So, removing the $\psi(x)$ we used for computational purposes, we get the commutator.

$$\boxed{[p,x]=\frac{\hbar}{i}}$$

Later we will learn to derive the uncertainty relation for two variables from their commutator. Physical variable with zero commutator have no uncertainty principle and we can know both of them at the same time.

We will also use commutators to solve several important problems.

We can compute the same commutator in momentum space.

$$\begin{aligned}[p,x]\phi &= [p,i\hbar\frac{d}{dp}]\phi=i\hbar\left(p\frac{d}{dp}\phi-\frac{d}{dp}p\phi\right)=i\hbar(-\phi)=\frac{\hbar}{i}\phi\\ [p,x] &= \frac{\hbar}{i}\end{aligned}$$

Expectation Values

To relate a quantum mechanical calculation to something you can observe in the laboratory, the "expectation value" of the measurable parameter is calculated. For the position x, the expectation value is defined as

$$\langle x\rangle=\int_{-\infty}^{\infty}\psi^*(x,t)x\,\psi(x,t)dx$$

This integral can be interpreted as the average value of x that we would expect to obtain from a large number of measurements. Alternatively it could be viewed as the average value of position for a large number of particles which are described by the same wavefunction. For example, the expectation value of the radius of the electron in the ground state of the hydrogen atom is the average value you expect to obtain from making the measurement for a large number of hydrogen atoms.

While the expectation value of a function of position has the appearance of an average of the function, the expectation value of momentum involves the representation of momentum as a quantum mechanical operator.

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^*(x,t) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x,t)\, dx$$

where

$$p_{operator} = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

is the operator for the x component of momentum.

Since the energy of a free particle is given by

$$E = \frac{p^2}{2m} \qquad then \qquad \langle E \rangle = \frac{\langle p^2 \rangle}{2m}$$

and the expectation value for energy becomes

$$\langle E \rangle_{free\ particle} = \int_{-\infty}^{\infty} \psi^* \frac{(-\hbar^2)}{2m} \frac{\partial^2}{\partial x^2} \psi\, dx$$

for a particle in one dimension.

In general, the expectation value for any observable quantity is found by putting the quantum mechanical operator for that observable in the integral of the wavefunction over space:

$$\langle Q \rangle = \int_{-\infty}^{\infty} \psi^* Q_{operator} \underset{\text{integral over all space}}{\psi\, dV}$$

Karpagam Academy of Higher Education
Department of Physics
III B.Sc Physics
Quantum Mechanics (16PHU602A)
Multiple Choice Questions

Question	Choice 1	Choice 2	Choice 3	Choice 4	Choice 5	Choice 6	Answer
Equation	$P= mv$	$P= dv$	$P= md$	$P= m^2v$			$P= mv$
Torque τ .	r x F	r^2 x F	r^2 x	r x F^2			r x F
Angular	moment o	torque x v	acceleratio	force x mass			moment of inertia x
Total angu	orbital ang	. spin angu	linear angu	torque			orbital angular mome
Angular	h(r xΔ)	ħ/I r x Δ	h(r^2 xΔ)	ħ/i r x Δ			ħ/i r x Δ
L x L=….	ihL	iħL	iħL^2	iħ ^{2}L			iħL
Total angu	$J^2 = J_x^2 +J$	$J^3 = J_x^3 +J$	$J^2 = J_x +J_y$	$J = J_x^2 +J_y^2 +J_z^2$			$J^2 = J_x^2 +J_y^2 +J_z^2$
Commutat	iħJ_x.	iħJ_z	iħJ_y	iħJ_{z+x+y}			iħJ_z
.[J^2 , J_y] =	1	2	0	3			0
.J_+ =……	$J_x + iJ_y$	$J_x - iJ_y$	$J_x^2 + iJ_y^2$	$J_x^2 - iJ_y^2$			$J_x + iJ_y$
J_- =…….	$J_x + iJ_y$	$J_x - iJ_y$	$J_x^2 + iJ_y^2$	$J_x^2 - iJ_y^2$			$J_x - iJ_y$
[J_x^2 ,J_x] =	$J_x [J_x J_x] +$	J_x	$J_x [J_x J_x] +$	J_x^2			$J_x [J_x J_x] + [J_x J_x] J_x$
.[J_z , J_+] =	ħJ_+	ħJ_x	ħJ_z	ħJ_xJ_y			ħJ_+
.[J^2 , J_+] i	1	2	4	0			0
[J_+ , J_-] is	ħJ	ħJ_z	ħJ^2	hJ			ħJ
Torque is	moment o	moment o	rate of cha	rate of change of distance			moment of force
Momentu	vector	scalar	dimension	product of vector and scalar			vector
In quantu	ħ/i r x Δ	ħ/i Δ	ħ/i r	ħ/i (r x Δ)^2			ħ/i r x Δ
The opera	. Hamilto	Ladder op	Hermitian	angular momentum operator			Ladder operator
[J_x^2 ,J_x] =	1	2	4	0			0
The opera	iħ∂/∂t	-iħ∂/∂t	iħ∂/∂x	–iħv			iħ∂/∂t
Operation	Another k	A bra vect	Another o	Phase vector			Another ket vector
Operation	A ket vect	Another o	Another b	Phase vector			Another bra vector
When an	box norma	plane norn	total norm	any of the above			box normalization
The orbita	s orbital	p orbital	d orbital	f orbital			s orbital
The orbita	s orbital	p orbital	d orbital	f orbital			p orbital
The orbita	s orbital	p orbital	d orbital	f orbital			d orbital
The orbita	s orbital	p orbital	d orbital	f orbital			f orbital
The quant	n and l	l and m	n, l and m	n and m			n, l and m
The value	0,1,2,3, …	1,2,3,4, …	±1, ±2, ±3	0, ±1, ±2, ±3, ±4 …			0, ±1, ±2, ±3, ±4 …
Which of	A linear co	A linear co	A linear co	A linear combination of degene			A linear combination
The corre	lh	lħ	[l(l+1)ħ]	$[l(l+1)]^{1/2}$ ħ.			$[l(l+1)]^{1/2}$ ħ.
The quant	angular m	spin angul	orbital ang	any of the above			orbital angular mome
An energy	2-fold	3-fold	(2l+1) fol	l-fold			(2l+1) fold

The poten	gravitatio	electroma	nuclear	Coulombic	Coulombic
The proba	probabilit	probabilit	radial pro	any of the above	radial probability den
For the gr	$P_{10} = 2a$, w	$dP_{10-}/dr =$	$dP_{10-}/dr =$	none of the above	$dP_{10-}/dr = 0$
For the gr	the Bohr r	twice the	half the B	No relation with Bohr radius.	the Bohr radius
The bindi	2.226 Me	2.226 eV	2.226 keV	Zero	2.226 MeV
The eigen	13.5 eV	2.75 eV	12.75 eV	3.5 eV	13.5 eV
The energ	$2Z^2E_H$	$2ZE_H$	$-\ 2ZE_H$	$-2Z^2E_H$	$-2Z^2E_H$
For n = 1,	$(Z/\pi a_0)^{1/2}$	$(Z^3/\pi a_0^3)^{1/}$	$(Z/\pi a_0)^{3/2}e$	$(Z/\pi a_0^3)^{1/2}e^{-\rho/2}$	$(Z^3/\pi a_0^3)^{1/2}\ e^{-\rho/2}$
The secul	principal	lower diag	upper diag	lower and upper diagonal	principal diagonal
The pertu	$eEr\cos\theta$	$er\cos\theta$	$-\ eEr\cos\theta$	$-\ er\cos\theta$	$-\ eEr\cos\theta$
The groun	$(1/\pi a_0^3)^{1/2}$	$(1/\pi a_0^3)^{1/2}$	$(1/\pi a_0^3)^{3/2}$	$(1/\pi a_0^3)^{3/2}\exp(r/a_0)$	$(1/\pi a_0^3)^{1/2}\exp(-r/a_0)$
The behav	electric qu	electric di	Zeeman e	Magnetic dipole moment	electric dipole mome
The Bohr	5.267 Å	0.05267 Å	0.5267 Å	52.67 Å	0.5267 Å
By expans	$\psi = 1$	$\psi = 0$	$\psi = \psi_0$	$\psi \neq \psi_0$	$\psi \neq \psi_0$
The orient	parallel	perpendic	anti-parall	none of the above	anti-parallel

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ıngular velocity
:ntum + spin angular momentum

of degenerate eigenfunctions of a degenerate level is also an eigen function, with the same eigen

:ntum quantum number

ısity

nt

value.

UNIT – II

Time independent Schrodinger equation-Hamiltonian, stationary states and energy eigenvalues; expansion of an arbitrary wavefunction as a linear combination of energy eigenfunctions; General solution of the time dependent Schrodinger equation in terms of linear combinations of stationary states; Application to the spread of Gaussian wavepacket for a free particle in one dimension; wave packets, Fourier transforms and momentum space wavefunction; Position-momentum uncertainty principle.

Time Dependent Schrodinger Equation

The time dependent Schrodinger equation for one spatial dimension is of the form

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

For a free particle where U(x) =0 the wavefunction solution can be put in the form of a plane wave

$$\Psi(x,t)=Ae^{ikx-i\omega t}$$

For other problems, the potential U(x) serves to set boundary conditions on the spatial part of the wavefunction and it is helpful to separate the equation into the time-independent Schrodinger equation and the relationship for time evolution of the wavefunction

$$H\Psi=i\hbar\frac{\partial\Psi}{\partial t}$$

Time evolution

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x)}{\partial x^2}+U(x)\Psi(x)=E\Psi(x)$$

Time independent equation

Hamiltonian, stationary state and energy eigen values:

In quantum mechanics, a Hamiltonian is an operator corresponding to the total energy of the system in most of the cases. It is usually denoted by *H*, also $\check{H}$ or $\hat{H}$. Its spectrum is the set of possible outcomes when one measures the total energy of a system. Because of its close relation to the time-evolution of a system, it is of fundamental importance in most formulations of quantum theory.

A stationary state is a quantum state with all observables independent of time. It is an eigenvector of the Hamiltonian.[1] This corresponds to a state with a single definite energy (instead of a quantum superposition of different energies). It is also called energy eigenvector, energy eigenstate, energy eigenfunction, or energy eigenket.

The wavefunction for a given physical system contains the measurable information about the system. To obtain specific values for physical parameters, for example energy, you operate on the wavefunction with the quantum mechanical operator associated with that parameter. The operator associated with energy is the Hamiltonian, and the operation on the wavefunction is the Schrodinger equation. Solutions exist for the time independent Schrodinger equation only for certain values of energy, and these values are called "eigenvalues*" of energy.

Corresponding to each eigenvalue is an "eigenfunction*". The solution to the Schrodinger equation for a given energy E_i involves also finding the specific function ψ_i which describes that energy state. The solution of the time independent Schrodinger equation takes the form

$$H_{op}\psi_i = E_i\psi_i$$

The eigenvalue concept is not limited to energy. When applied to a general operator Q, it can take the form

$$\underset{\text{operator}}{Q_{op}}\psi_i = \underset{\text{eigenvalue}}{q_i}\overset{\text{eigenfunction}}{\psi_i}$$

if the function ψ_i is an eigenfunction for that operator. The eigenvalues qi may be discrete, and in such cases we can say that the physical variable is "quantized" and that the index i plays the role of a "quantum number" which characterizes that state.

Energy eigenvalues

*"Eigenvalue" comes from the German "Eigenwert" which means proper or characteristic value. "Eigenfunction" is from "Eigenfunktion" meaning "proper or characteristic function".

Linear combination of separable solutions:

The general solution is a linear combination of separable solutions. As the timeindependent Schrodinger equation yields an infinite collection of solutions ψ1 (x), ψ2 (x), ψ3 (x), ... , each with its associated value of energy eigenvalue s E 1 , E 2 , E 3 .... ; thus there is a different wave function for each allowed energy:

$$\Psi_1(x,t)=\psi_1(x)e^{-iE_1t/\hbar}, \quad \Psi_2(x,t)=\psi_2(x)e^{-iE_2t/\hbar}, \ldots.$$

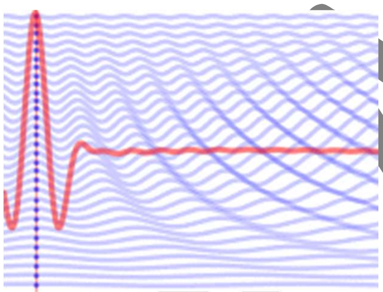
Now the (time-dependent) Schrodinger equation has the property that any linear combinations combinations of solutions solutions is itself a solution solution. Once we have found the separable separable solutions, then, we can immediately construct a much more general solution, of the form

$$\Psi(x,t)=\sum_{n=1}^{\infty}c_n\psi_n(x)e^{-iE_nt/\hbar}.$$

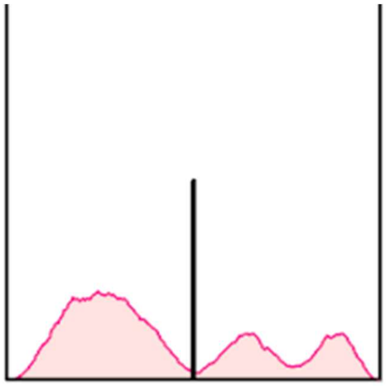
It so happens that every solution to the (time-dependent) Schrodinger equation can be written in this form--it is simply a matter of finding the right constants (c 1 , c 2, ...) so as to fit the initial conditions for the problem at hand.

Gaussian wave packets

Gaussian wave packets in quantum mechanics[edit]



Superposition of 1D plane waves (blue) that sum to form a quantum Gaussian wave packet (red) that propagates to the right while spreading. Blue dots follow each plane wave's phase velocity while the red line follows the central group velocity.



Position space probability density of an initially Gaussian state trapped in an infinite potential well experiencing periodic Quantum Tunneling in a centered potential wall.

The above dispersive Gaussian wave packet, unnormalized and just centered at the origin, instead, at t=0, can now be written in 3D, now in standard units:[3][4]

$$\psi(\mathbf{r},0)=e^{-\mathbf{r}\cdot\mathbf{r}/2a},$$

where a is a positive real number, the *square of the width of the wave packet*,

$$a=2\langle\mathbf{r}\cdot\mathbf{r}\rangle/3\langle 1\rangle=2(\Delta x)^2.$$

The Fourier transform is also a Gaussian in terms of the wavenumber, t=0, the k-vector, (with inverse width,

$$1/a=2\langle\mathbf{k}\cdot\mathbf{k}\rangle/3\langle 1\rangle=2(\Delta p_x/\hbar)^2$$

so that

$$\Delta x\Delta p_x=\hbar/2$$

i.e., it saturates the uncertainty relation),

$$\psi(\mathbf{k},0)=(2\pi a)^{3/2}e^{-a\mathbf{k}\cdot\mathbf{k}/2}.$$

Each separate wave only phase-rotates in time, so that the time dependent Fourier-transformed solution is

$$\begin{aligned}\Psi(\mathbf{k},t) &= (2\pi a)^{3/2} e^{-a\mathbf{k}\cdot\mathbf{k}/2} e^{-iEt/\hbar}\\ &= (2\pi a)^{3/2} e^{-a\mathbf{k}\cdot\mathbf{k}/2 - i(\hbar^2\mathbf{k}\cdot\mathbf{k}/2m)t/\hbar}\\ &= (2\pi a)^{3/2} e^{-(a+i\hbar t/m)\mathbf{k}\cdot\mathbf{k}/2}.\end{aligned}$$

The inverse Fourier transform is still a Gaussian, but now the parameter a has become complex, and there is an overall normalization factor.[5]

$$\Psi(\mathbf{r},t) = \left(\frac{a}{a+i\hbar t/m}\right)^{3/2} e^{-\frac{\mathbf{r}\cdot\mathbf{r}}{2(a+i\hbar t/m)}}.$$

The integral of Ψ over all space is invariant, because it is the inner product of Ψ with the state of zero energy, which is a wave with infinite wavelength, a constant function of space. For any energy eigenstate $\eta(x)$, the inner product,

$$\langle\eta|\psi\rangle = \int \eta(\mathbf{r})\psi(\mathbf{r})d^3\mathbf{r}$$

only changes in time in a simple way: its phase rotates with a frequency determined by the energy of η. When η has zero energy, like the infinite wavelength wave, it doesn't change at all.

The integral $\int|\Psi|^2 d^3r$ is also invariant, which is a statement of the conservation of probability. Explicitly,

$$P(r) = |\Psi|^2 = \Psi^*\Psi = \left(\frac{a}{\sqrt{a^2+(\hbar t/m)^2}}\right)^3 e^{-\frac{a\,\mathbf{r}\cdot\mathbf{r}}{a^2+(\hbar t/m)^2}},$$

in which $\sqrt{a}$ is the width of $P(r)$ at $t = 0$; r is the distance from the origin; the speed of the particle is zero; and the time origin $t = 0$ can be chosen arbitrarily.

The width of the Gaussian is the interesting quantity which can be read off from the probability density, $|\Psi|^2$,

$$\sqrt{\frac{a^2+(\hbar t/m)^2}{a}}.$$

This width eventually grows linearly in time, as $\hbar t/(m\surd a)$, indicating wave-packet spreading. For example, if an electron wave packet is initially localized in a region of atomic dimensions (i.e., 10^{-10} m) then the width of the packet doubles in about 10^{-16} s. Clearly, particle wave packets spread out very rapidly indeed (in free space):[6] For instance, after 1 ms, the width will have grown to about a kilometer.

This linear growth is a reflection of the (time-invariant) momentum uncertainty: the wave packet is confined to a narrow$\Delta x=\surd\boxed{a/2}$, and so has a momentum which is uncertain (according to the uncertainty principle) by the amount $\hbar/\surd\boxed{2a}$, a spread in velocity of $\hbar/m\surd\boxed{2a}$, and thus in the future position by $\hbar t\ /m\surd\boxed{2a}$. The uncertainty relation is then a strict inequality, very far from saturation, indeed! The initial uncertainty $\Delta x\Delta p=\hbar/2$ has now increased by a factor of $\hbar t/ma$ (for large t).

Fourier transformations:

$$\phi(\vec{k})=\left(\frac{1}{\sqrt{2\pi}}\right)^3\int_{r\text{ space}}\psi(\vec{r})e^{-\mathbf{ik\cdot r}}d^3\boldsymbol{r}$$

for momentum space and

$$\psi(\vec{r})=\left(\frac{1}{\sqrt{2\pi}}\right)^3\int_{k\text{ space}}\phi(\vec{k})e^{\mathbf{ik\cdot r}}d^3k$$

for position space.

1

The identification of one transform as the Fourier transform and the other as the inverse transform is a matter of definition. The Fourier transform predates quantum mechanics so the reason for the assignment has nothing to do with QM and everything to do with mathematics history.

In 1807 Fourier submitted a manuscript to the Institut de France containing, among other things, what we now call the Fourier cosine transform and its inverse. These are his transforms:

Fc(u)=2π∫∞0f(x)cos(ux)dxFc(u)=2π∫0∞f(x)cos (ux)dx f(x)=∫∞0Fc(u)cos(ux)du.f(x)=∫0∞Fc(u)cos (ux)du.

Cauchy's 1827 generalization of Fourier's relations entailed complex-valued functions, and an ineluctable sign asymmetry in form of the transforms. Trying to preserve symmetry does not help. As the article below notes, it may be shown that if the same sign is taken for both the forward and inverse formulae, "one formula is not exactly the inverse of the other one."

It is a long and helpful exercise to verify that f^f^ and ff inhabit dual spaces with a high degree of symmetry. For example, a function contains the same "energy" as its FT (Plancherel). Whether physics would be equally well served had a different convention been chosen is moot, even if we find particular instances that seem to point to the road not taken.

Karpagam Academy of Higher Education
Department of Physics
III B.Sc Physics
Quantum Mechanics (16PHU602A)
Multiple Choice Questions

Question	**Choice 1**	**Choice 2**	**Choice 3**	**Choice 4**	**Choice 5**	**Choice 6**	**Answer**
Time dependent theory is mostly used in	nuclear physics	crystallography	optics	mechanics			nuclear physics
Oscillating electric and magnetic field associated with light can induce transition is an example of	time independent theory	variation theory	harmonic perturbation	WKB approximation			harmonic perturbation
Transition probability per unit time when transitions are extended to continuum is given by τ, where τ is equal to	$2\pi \vert H_{ml}' \vert^2 \rho(E_m)$	$i\hbar \vert H_{ml}' \vert^2 \rho(E_m)$	$\vert H_{ml}' \vert \rho(E_m)$	$(2\pi/\hbar) \vert H_{ml}' \vert^2 \rho(E_m)$			$(2\pi/\hbar) \vert H_{ml}' \vert^2 \rho(E_m)$
The time dependent theory was developed by	Einstein	Schrödinger	Pauli	Dirac			Dirac
The transition probability per unit time is proportional to	density of final states	$\vert H_{ml}' \vert$	Time ‘t’	t^2			t^2
The validity of adiabatic approximation requires	smallness of $(\partial H/\partial t)$ but $E_m - E_s$ not too small	smallness of $(\partial H/\partial t)$ but $E_m - E_s$ large	large value of $(\partial H/\partial t)$ but $E_m - E_s$ small	large value of $(\partial H/\partial t)$ but $E_m - E_s$ not too small			smallness of $(\partial H/\partial t)$ but $E_m - E_s$ not too small
In sudden approximation, perturbation changes	at slow rate at narrow interval of time	at rapid rate in a very small interval of time	at rapid rate in large interval of time	at slow rate in large interval of time			at rapid rate in a very small interval of time
Frequency of radiation emitted during transition from m level to n level is	$E_m - E_n$	$(E_m - E_n)/\hbar$	$(E_m - E_n)/h$	$(E_n - E_m)/\hbar$			$(E_m - E_n)/h$
While calculating the first order perturbation the constant of integration is taken as zero in order that dm(t) to be zero at	$t = \infty$	$t = -\infty$	$t = 0$	$t = 2\pi$			$t = 0$

Height of the main curve in time dependent perturbation theory increase in proportion to	t^2	t	t^{-1}	t^3	t^2
The maximum value of Sin^2 [(ω_{ml}/2)/ ω_{ml}^2] occurs when ω_{ml} is	infinity	negative	zero	one	zero
The example for time dependent perturbation is	particle in a box	nuclear reactions and disintegration	harmonic oscillator	Stark effect	harmonic oscillator
Example for adiabatic approximation is	collision of gas molecules	harmonic oscillator	spectral analysis	interaction of electromagnetic waves	collision of gas molecules
Before the perturbation is applied to the system the first order transition constant $a_m^{(1}$ be zero at	$t = \infty$	$t = 0$	$t = -\infty$	$t = t^2$	$t = 0$
In adiabatic approximation the Hamiltonian varies slowly with	position	time	position and time	none of the above	time
The molecular velocities and electron velocities in atoms are respectively	10^6 m/s and 10^2 m/s	10^2 m/s and 10^6 m/s	10^4 m/s and 10^8 m/s	10^8 m/s and 10^4 m/s	10^2 m/s and 10^6 m/s
A most common way of inducing transitions between stationary states of quantum system is by applying	sudden perturbation	constant perturbation	harmonic perturbation	adiabatic perturbation	harmonic perturbation
The transition probability per unit time is proportional to	$\lvert H_{ml}' \rvert$	$\lvert H_{ml}' \rvert^2$	t	t^2	$\lvert H_{ml}' \rvert^2$
Time dependent perturbation theory is often called	harmonic perturbation	constant perturbation	variation of constants	sudden approximation	harmonic perturbation
In case of time dependent perturbation theory, H′ might be zero except during the period	$t_1 < t < t_2$	$0 < t < \infty$	$t_1 \le t \le t_2$	$t_1 < t \le t_2$	$t_1 < t \le t_2$
In time dependent theory, perturbation is effective during the period	$0 < t < \infty$	$t_1 < t < t_2$	$t_1 \le t < t_2$	$t_1 < t \le t_2$	$t_1 < t \le t_2$

In time dependent theory, perturbation is effective, when H′ might be	negative	zero	one	infinite	one
The Schrödinger time equation for the system, in case of time dependent perturbation theory	$(H + H')\psi = (h/2\pi i)\partial\omega/\partial t$	$(H + H')\psi = (\hbar/2\pi i)\partial\omega/\partial t$	$(H + H')\psi = -(h/2\pi i)\partial\omega/\partial t$	$(H + H')\psi = -(\hbar/2\pi i)\partial\omega/\partial t$	$(H + H')\psi = -(h/2\pi i)\partial\omega/\partial t$
Breadth of the main curve in time dependent perturbation theory decreases inversely as	t^2	$-t$	$-t^2$	t	$-t$
Example for transition between stationary states in atoms is	oscillating electric and magnetic fields	electric field	magnetic field	harmonic oscillator	harmonic oscillator
The energy is transferred from the perturbing source to the system, this process is known as	absorption	emission	approximation	transformation probability	emission
The energy is transferred to the perturbing source from the system, this process is known as	absorption	emission	approximation	transmission	emission
In adiabatic approximation the perturbation is turned on	fast	slowly	very slowly	very fast	very slowly
During the collision of gas molecules, the molecular velocities are low about	10 m/s	10^3 m/s	1 m/s	10^2 m/s	10^2 m/s
The gas molecules collide or approach each other, the process may be regarded as	adiabatic	isothermal	sudden approximation	perturbation	adiabatic
The condition of sudden approximation, by the help of uncertainty relation $\Delta E.\Delta T = \hbar$, is expressed as	$\Delta x.\Delta p \approx \hbar$	$\hbar/\Delta E >> t_0$	$\Delta x.\Delta t \approx \hbar$	$\Delta p.\Delta t \approx \hbar$	$\hbar/\Delta E >> t_0$
In sudden approximation the probability of transition from state k to state f will be given by	$\lvert a_f\rvert^2 = \lvert\langle f\vert H'\vert k\rangle\rvert^2/\hbar^2\omega_{fk}^2$	$\lvert a_f\rvert^2 = \lvert\langle f\vert H'\vert k\rangle\rvert/\hbar^2\omega_{fk}^2$	$\lvert a_f\rvert^2 = \lvert\langle f\vert H'\vert k\rangle\rvert/\hbar\omega_{fk}$	$\lvert a_f\rvert^2 = \lvert\langle f\vert H'\vert k\rangle\rvert^2/\hbar\omega_{fk}$	$\lvert a_f\rvert^2 = \lvert\langle f\vert H'\vert k\rangle\rvert^2/\hbar^2\omega_{fk}^2$
There is no transition between the states of the system then,	$\langle f\vert H(t)k\rangle = \infty$	$\langle f\vert H(t)k\rangle = 1$	$\langle f\vert H(t)k\rangle = 0$	$\langle k\vert H(t)f\rangle = 0$	$\langle f\vert H(t)k\rangle = 0$

The velocity of electrons in atoms are about	10^8 m/s	10^4 m/s	10^2 m/s	10^6 m/s	10^6 m/s
A particle executes a harmonic motion along x-axis and possesses a charge +e, dipole moment is	– ex	Ex	eE	– eE	eE

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UNIT III

General discussion of bound states in an arbitrary potential- continuity of wave function, boundary condition and emergence of discrete energy levels; application to one-dimensional problem- square well potential; Quantum mechanics of simple harmonic oscillator-energy levels and energy eigenfunctions using Frobenius method.

GENERAL DISCUSSION OF BOUND STATES IN AN ARBITRARY POTENTIAL:

In quantum physics, a bound state is a special quantum state of a particle subject to a potential such that the particle has a tendency to remain localised in one or more regions of space. The potential may be external or it may be the result of the presence of another particle; in the latter case, one can equivalently define a bound state as a state representing two or more particles whose interaction energy exceeds the total energy of each separate particle. One consequence is that, given a potential vanishing at infinity, negative-energy states must be bound. In general, the energy spectrum of the set of bound states is discrete, unlike free particles, which have a continuous spectrum.

Although not bound states in the strict sense, metastable states with a net positive interaction energy, but long decay time, are often considered unstable bound states as well and are called "quasi-bound states".[1] Examples include certain radionuclidesand electrets.

Let *H* be a complex separable Hilbert space, $U = \{U(t) \mid t \in \mathbb{R}\}$ be a one-parameter group of unitary operators on *H* and $\rho = \rho(t_0)$ be a statistical operator on *H*. Let *A* be an observable on *H* and $\mu(A, \rho)$ be the induced probability distribution of *A* with respect to *ρ* on the Borel σ-algebra of $\mathbb{R}$. Then the evolution of *ρ* induced by *U* is bound with respect to *A* if $\lim_{R\to\infty} \sup_{t \geq t_0} \mu(A, \rho(t))(\mathbb{R}_{>R}) = 0,$, where $\mathbb{R}_{>R} = \{x \in \mathbb{R} \mid x > R\}$

More informally, a bound state is contained within a bounded portion of the spectrum of *A*. For a concrete example: let $H = L^2(\mathbb{R})$ and let *A* be position. Given compactly-supported $\rho = \rho(0) \in H \text{ and } [-1, 1] \subseteq \mathrm{Supp}(\rho).$

If the state evolution of *ρ* "moves this wave package constantly to the right", e.g. if $[t-1, t+1] \in \mathrm{Supp}(\rho(t))$ for all t>=0, , then *ρ* is not bound state with respect to position.

If *ρ* does not change in time, i.e. *ρ(t)= ρ* for all t>=0, then *ρ* is bound with respect to position.

More generally: If the state evolution of *ρ* "just moves *ρ* inside a bounded domain", then *ρ* is bound with respect to position.

Continuity of wavefunction

Time-independent Schrödinger equation:

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

1. The wave function has to be continuous at all points, no exception.

2. The first derivative of the wave function $\frac{\partial}{\partial x}\psi(x)$ is continuous, only if V(x) is finite.

3. If V(x) is not finite at x=a:

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

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

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

$$\Rightarrow -\frac{\hbar^2}{2m}\left[\psi'(a+\varepsilon)-\psi'(a-\varepsilon)\right]+\int_{a-\varepsilon}^{a+\varepsilon}V(x)\psi(a)dx=0$$

$$\Rightarrow \left[\psi'(a+\varepsilon)-\psi'(a-\varepsilon)\right]=\frac{4m\psi(a)}{\hbar^2}\int_{a-\varepsilon}^{a+\varepsilon}V(x)dx$$

Boundary conditions for the wave functions:

The main equation of the non-relativistic quantum mechanics is the Schr¨odinger equation

$$H\psi=-\frac{\hbar^2}{2m}\Delta\psi+V(x)\psi=E\psi. \qquad (1)$$

Eq. (1) is not sufficient for the construction of the physically meaningful solutions. For bound states one uses the Hilbert space condition

$$\int |\psi(x)|^2 dx < \infty, \qquad (2)$$

which leads to the real eigenvalues of the Hamiltonian. Gamow solutions on the other hand are obtained if one assumes that the asymptotic behavior of the wave function ψ(x) is a purely outgoing wave. Such a boundary conditionleads to complex eigenvalues [1] of the Hamiltonian and the corresponding discrete solutions are interpreted as wave functions of unstable states. The other kind of the continuity conditions for the wave function ψ(x) is related to the form of the potential V (x). The wave function and its first derivative are assumed to be continuous at finite jumps of the potential. The only notable exception is when the potential becomes infinite and at such a point the wave function is assumed to vanish and its first derivative is not assumed to be continuous. In this paper we consider the potential wall in the form of the Dirac delta function [2, 3]

$\Omega\delta(x)$ (3)

in the presence of an infinite oscillator wall. We then present explicit solutions for such a system with the boundary condition in the form of the outgoing wave.This leads to the Gamow wave functions with complex eigenvalues of the Hamiltonian. From the explicit solution we can study the behavior of the wave function ψ(x) at the point x = 0, where the Dirac delta potential wall is present. We find that at this point the wave function is continuous and the first derivative has a finite jump. We generalize these results to an arbitrary form of the potential. The plan of the paper is the following. In Section 2 we present the case of the quantum unstable oscillator. In Section 3 we discuss the wave function of the quantum unstable oscillator and analyze its properties. In Section 4 we generalize the results obtained in In Section 3 and discuss the new boundary conditions for the wave function and draw conclusions from our results.

One- dimensional problem:

Bound States in One Dimension In this chapter we will concern ourselves with obtaining stationary state solution of the time independent Schr¨odinger Equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$
---(1)

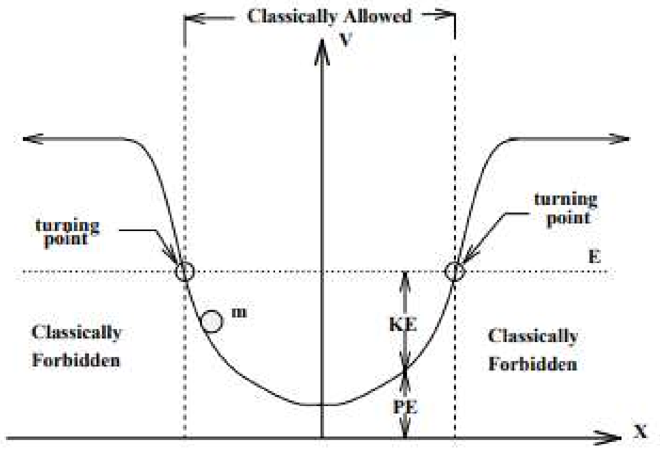
for particles (such as electrons) bound in one dimensional potential wells. In general these solutions can be chosen to be real rather than complex functions which can often be considerable simplification. To see this lets take the complex conjugate of the time independent SE given in Eq. (1):

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

Because all the factors which operate on $\psi(x)$ are real, they don't change under complex conjugation and hence $\psi(x)$ and $\psi*(x)$ are equally valid solutions of the same potential V (x) with the same energy E. Since the SE is a homogenous linear differential equation, we can always form new valid solutions by taking linear combinations of valid solutions. In particular, the solution $\psi r(x)$ which is constructed out of a general solutions $\psi(x)$ and $\psi*(x)$ according to

$$\psi_r(x) \propto \psi(x)+\psi^*(x) \qquad (3)$$

is an intrinsically real. Of course exp $(i\varphi) \times \psi r(x)$ is an equally valid solution with any complex phase φ that one cares to choose. We will generally choose real bound state solutions to the problems posed in this chapter. Some of the problems which we will address are a bit artificial but they are easily solvable and give considerable insight into perhaps more realistic but less tractable problems. I begin by describing the general "potential well" illustrated below in hopefully familiar classical terms.



By a potential well, we mean a graph of potential energy as a function of coordinate x. In this well picture, we indicate a constant energy level (total potential plus kinetic energy) for the particle of mass m by the horizontal "dotted line". The picture is meant to evoke conservation of energy ie the particle has the same total energy E = KE +PE independent of x. As a particle of mass m slides back and forth in x along the well much like a mass sliding down a frictionless valley, it constantly exchanges potential energy for kinetic energy while keeping a constant E. The (energy) distance between the energy level and the potential curve represents the kinetic energy since KE = E − V (x). Classically the kinetic energy is an intrinsically positive quantity because KE = mv2/2. The classical turning points are the two intersections of the energy level and the potential well where the particle has zero kinetic energy. In the region between the turning points E>V (x) and KE = E − V > 0. Since the kinetic energy is positive this is a perfectly reasonable or “allowed” region for the particle to exist. In the reason outside of the turning points, E< 0 which is a classically “forbidden” condition. Classically the particle can never be found outside of the interval between the classical turning points.

Think of the particle as released from rest down at the left turning point on the frictionless gravitational valley represented by th potential, the particle picks up maximum speed at the bottom of the well, slows down as it approaches the right turning point. It stops at the right turning point, turns around and heads back down the well valley. Turning points where the particle turns around and reverses are aptly named.

Square Potential Well

Consider a particle of mass m and energy E interacting with the simple square potential well

$$V(x) = \begin{cases} -V_0 & \text{for } -a/2 \le x \le a/2 \\ 0 & \text{otherwise} \end{cases}, \tag{372}$$

where $V_0 > 0$.

Now, if $E > 0$ then the particle is unbounded. Thus, when the particle encounters the well it is either reflected or transmitted. As is easily demonstrated, the reflection and transmission probabilities are given by Eqs. (327) and (328), respectively, where

$$k^2 = \frac{2mE}{\hbar^2}, \tag{373}$$

$$q^2 = \frac{2m(E+V_0)}{\hbar^2}. \tag{374}$$

Suppose, however, that $E < 0$. In this case, the particle is bounded (*i.e.*, $|\psi|^2 \to 0$ as $|x| \to \infty$). Is is possible to find bounded solutions of Schrödinger's equation in the finite square potential well (372)?

Now, it is easily seen that independent solutions of Schrödinger's equation (301) in the symmetric [*i.e.*, $V(-x) = V(x)$] potential (372) must be either totally symmetric [*i.e.*, $\psi(-x) = \psi(x)$], or totally anti-symmetric [*i.e.*, $\psi(-x) = -\psi(x)$]. Moreover, the solutions must satisfy the boundary condition

$$\psi \to 0 \qquad \text{as } |x| \to \infty. \tag{375}$$

Let us, first of all, search for a totally symmetric solution. In the region to the left of the well (*i.e.* $x < -a/2$), the solution of Schrödinger's equation which satisfies the boundary condition $\psi \to 0$ and $x \to -\infty$ is

$$\psi(x) = A\,e^{k\,x}, \tag{376}$$

where

$$k^2 = \frac{2m\,|E|}{\hbar^2}. \tag{377}$$

By symmetry, the solution in the region to the right of the well (*i.e.*, $x > a/2$) is

$$\psi(x) = A\,e^{-k\,x}. \tag{378}$$

The solution inside the well (*i.e.*, $|x| \leq a/2$) which satisfies the symmetry constraint $\psi(-x) = \psi(x)$ is

$$\psi(x) = B\cos(q\,x), \tag{379}$$

where

$$q^2 = \frac{2m\,(V_0 + E)}{\hbar^2}. \tag{380}$$

Here, we have assumed that $E > -V_0$. The constraint that $\psi(x)$ and its first derivative be continuous at the edges of the well (*i.e.*, at $x = \pm a/2$) yields

$$k = q\,\tan(q\,a/2). \tag{381}$$

Let $y = q\,a/2$. It follows that

$$E = E_0\,y^2 - V_0, \tag{382}$$

where

$$E_0 = \frac{2\,\hbar^2}{m\,a^2}. \tag{383}$$

Moreover, Eq. (381) becomes

$$\frac{\sqrt{\lambda - y^2}}{y} = \tan y, \tag{384}$$

with

$$\lambda = \frac{V_0}{E_0}. \tag{385}$$

Here, y must lie in the range $0 < y < \sqrt{\lambda}$: *i.e.*, E must lie in the range $-V_0 < E < 0$.

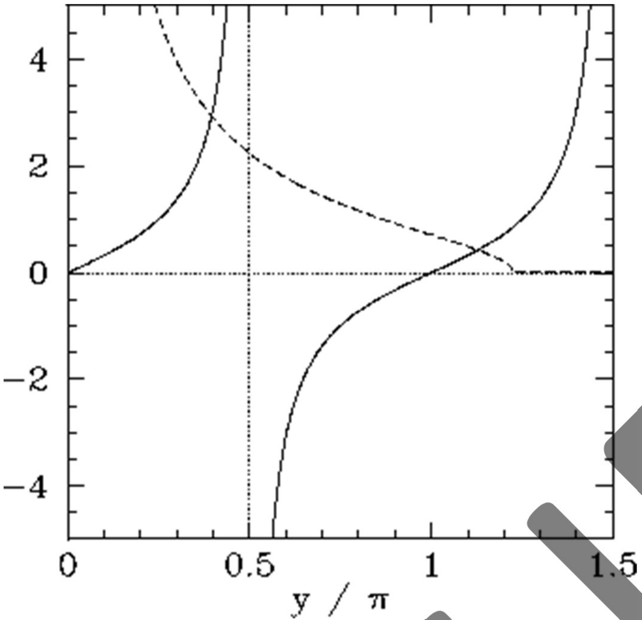


Figure: *The curves* $\tan y$ *(solid) and* $\sqrt{\lambda - y^2}/y$ *(dashed), calculated for* $\lambda = 1.5\pi^2$.

The latter curve takes the value 0 *when* $y > \sqrt{\lambda}$.

Now, the solutions to Eq. (384) correspond to the intersection of the curve $\sqrt{\lambda - y^2}/y$ with the curve $\tan y$. Figure 16 shows these two curves plotted for a particular value of λ. In this case, the curves intersect twice, indicating the existence of two totally symmetric bound states in the well. Moreover, it is evident, from the figure, that as λ increases (*i.e.*, as the well becomes deeper) there are more and more bound states. However, it is also evident that there is always at least one totally symmetric bound state, no matter how small λ becomes (*i.e.*, no matter how shallow the well becomes). In the limit $\lambda \gg 1$ (*i.e.*, the limit in which the well becomes very deep), the solutions to Eq. (384) asymptote to the roots of $\tan y = \infty$. This gives $y = (2\,j-1)\,\pi/2$, where j is a positive integer, or

$$q = \frac{(2\,j-1)\,\pi}{a}. \tag{386}$$

These solutions are equivalent to the odd-n infinite square well solutions specified by Eq. (307).

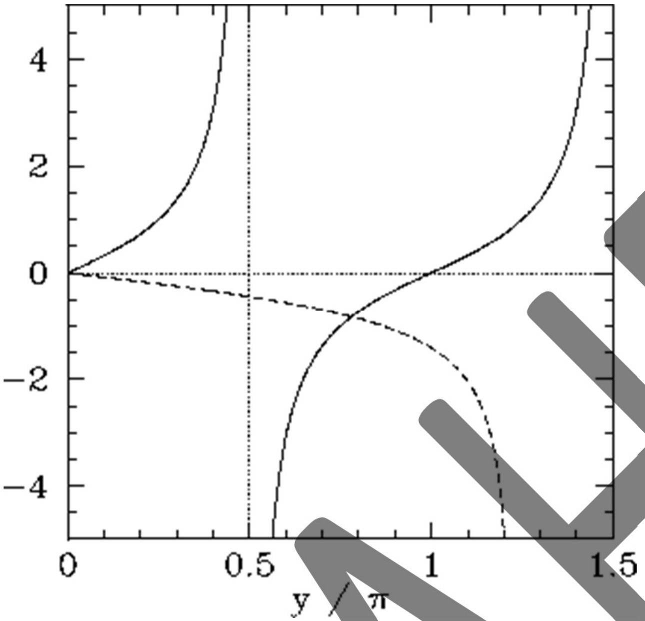


Figure: *The curves* $\tan y$ *(solid) and* $-y/\sqrt{\lambda - y^2}$ *(dashed), calculated for* $\lambda = 1.5\pi^2$.

For the case of a totally anti-symmetric bound state, similar analysis to the above yields

$$-\frac{y}{\sqrt{\lambda - y^2}} = \tan y. \tag{387}$$

The solutions of this equation correspond to the intersection of the curve $\tan y$ with the curve $-y/\sqrt{\lambda - y^2}$. Figure 17 shows these two curves plotted for the same value of λ as that used in Fig. 16. In this case, the curves intersect once, indicating the existence of a single totally anti-symmetric bound state in the well. It is, again, evident, from the figure, that as λ increases (*i.e.*, as the well becomes deeper) there are more and more bound states. However, it is also evident that when λ becomes sufficiently small [*i.e.*, $\lambda < (\pi/2)^2$] then there is no totally anti-symmetric bound state. In other words, a very shallow potential well always possesses a totally symmetric bound state, but does not generally possess a totally anti-symmetric bound state. In the limit $\lambda \gg 1$ (*i.e.*, the limit in which the well becomes very deep), the solutions to Eq. (387) asymptote to the roots of $\tan y = 0$. This gives $y = j\,\pi$, where j is a positive integer, or

$$q = \frac{2\,j\,\pi}{a}. \tag{388}$$

These solutions are equivalent to the even-n infinite square well solutions specified by Eq. (307).

Quantum Harmonic Oscillator: Schrodinger Equation

The Schrodinger equation for a harmonic oscillator may be obtained by using the classical spring potential

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2 \qquad \omega = \sqrt{\frac{k}{m}} = \text{ angular frequency}$$

$$\omega = 2\pi \cdot \text{frequency}$$

The Schrodinger equation with this form of potential is

$$\frac{-\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + \frac{1}{2}m\omega^2x^2\,\Psi(x) = E\Psi(x)$$

Since the derivative of the wavefunction must give back the square of x plus a constant times the original function, the following form is suggested:

$$\Psi(x) = Ce^{-\alpha x^2/2}$$

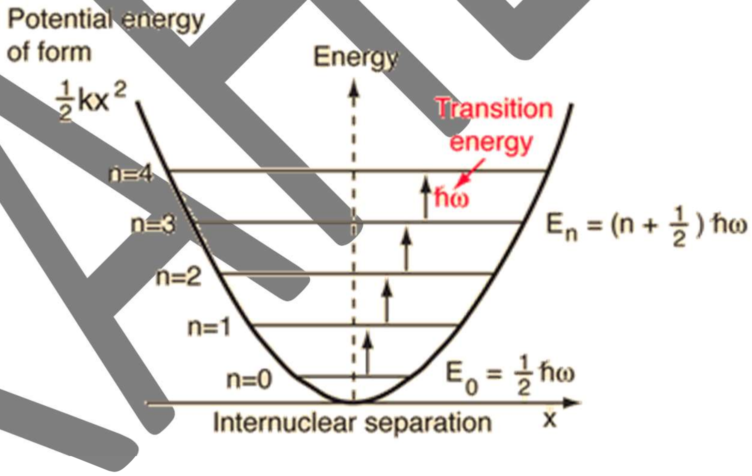
Note that this form (a Gaussian function) satisfies the requirement of going to zero at infinity, making it possible to normalize the wavefunction.

Substituting this function into the Schrodinger equation and fitting the boundary conditions leads to the ground state energy for the quantum harmonic oscillator:

$$E_0 = \frac{\hbar\omega}{2}$$

While this process shows that this energy satisfies the Schrodinger equation, it does not demonstrate that it is the lowest energy. One interesting way to show that is to demonstrate that that it is the lowest energy allowed by the uncertainty principle.

The general solution to the Schrodinger equation leads to a sequence of evenly spaced energy levels characterized by a quantum number n.



The wavefunctions for the quantum harmonic oscillator contain the Gaussian form which allows them to satisfy the necessary boundary conditions at infinity. In the wavefunction associated with a given value of the quantum number n, the Gaussian is multiplied by a polynomial of order n called a Hermite polynomial. The expressions are simplified by making the substitution

$$y = \sqrt{\alpha}\ x \qquad where \qquad \alpha = \frac{m\omega}{\hbar}$$

The general formula for the normalized wavefunctions is

$$\Psi_n(y) = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(y) e^{-y^2/2}$$

$H_n(y)$ = Hermite polynomial

The quantum harmonic oscillator is one of the foundation problems of quantum mechanics. It can be applied rather directly to the explanation of the vibration spectra of diatomic molecules, but has implications far beyond such simple systems. It is the foundation for the understanding of complex modes of vibration in larger molecules, the motion of atoms in a solid lattice, the theory of heat capacity, etc. In real systems, energy spacings are equal only for the lowest levels where the potential is a good approximation of the "mass on a spring" type harmonic potential. The anharmonic terms which appear in the potential for a diatomic molecule are useful for mapping the detailed potential of such systems.

ENERGY LEVELS AND ENERGY EIGENFUNCTIONS USING FROBENIUS METHOD

The exact solution of the Schr¨odinger equation can be obtained only for a few particular formsofpotentials,inothercasesonehastoresorttoapproximationsornumericaltechniques. Manyapproximation methods have been developed for solving problems in one-dimensional space.Approximate solutions to the Schr¨odinger equation have also been studied for sphericallysymmetricpotentials in *D*-dimensionalspace,bothbymethodselaboratedforone-dimensionalspace, e.g., the Hill determinant method [1], the variational approach [2], and by methods dedicated to *D*-dimensional problems, e.g., the shifted 1/*D*

expansion [3, 4]. Here we showthat highly accurate solutions to the Schr ¨odinger equation can be determined for varioustypes of spherically symmetric potentials with the use of the Fr¨obenius method (FM). Themethod consists in expanding the solution of a differential equation into power series [5],and was originally applied by Barakat and Rosner [6] to compute the spectrum of a one-dimensional quartic oscillator confined by impenetrable walls at

$x = \pm R$

. The energy eigenvalues of the system have been obtained numerically as zeros of a function,
calculatedfromitspowerseriesrepresentation. Moreover,ithasbeenshownthat thebound-stateenergiesof the confined system approach rapidly those of the unconfined oscillator for increasing*R*.

Low-lying eigenvalues for other one-dimensional potentials [7] have also been successfullycalculated in a similar way. Recently, a modified treatment of unconfined systems allowedfor a very accurate determination of the ground-state energy for the quartic oscillator [8]. In all the cases studied the potential was a finite function, and a solution was expanded aroundan ordinary point of the differential equation. Here we study the application of the FM for solving the radial Schr¨odinger equation, which requires that an expansion around a regular singular point be used.The outline of the present work is as follows. In section 2 the solution of the radialSchr¨odinger equation in the form of a generalized power series is discussed. The case of a spherically symmetric potential bounded by an impenetrable wall at

$r = R$

is studied insection 3. In this case, the energy eigenvalues can be easily determined by finding the roots of the polynomial, which is illustrated in the example of the confined harmonic and anharmonicoscillators and Hulth´en potential. The case of an unconfined system is studied in section 4,where a scheme for determining an arbitrarily large set of bound-state energies is developed.After demonstrating the performance of the method in the exactly solvable example of theKratzer potential, the results for the unconfined oscillator are presented for various choices of anharmonic parameters.

Karpagam Academy of Higher Education
Department of Physics
III B.Sc Physics
Quantum Mechanics (16PHU602A)
Multiple Choice Questions

Question	**Choice 1**	**Choice 2**	**Choice 3**	**Choice 4**	**Choice 5**
Hermitian operators have ____ eigen	real	imaginary	complex	infinity	
If two Hermitian operators operators	unitary	inverse	Hermitian	Identity	
The commutation relation [x,H] yields	–iħp	iħp	(–iħ/m)p	(iħ/m)p	
The commutation relation [p,H] yields	$-i\hbar k_x$	$i\hbar k_x$	$(-i\hbar/m)k_x$	$(i\hbar/m)k_x$	
If a is lowering operator and $a^\dagger$ raising	$H/\hbar\omega_o$ – ½	$H/\hbar\omega_o$ + ½	1	0	
If a is lowering operator and $a^\dagger$ raising	$H/\hbar\omega_o$ – ½	$H/\hbar\omega_o$ + ½	1	0	
If |a> and |b> are arbitrary kets then	<a|b>	|b><a|	[|a><b|]*	|a><b|	
If A and B are unitary operators, then	Hermitian	Unitary	Hamiltonia	Inverse	
The expectation value of observable p	<p> = ∫ψ^*pψdτ	<p> = ∫ψp	<p> = ∫ψ^*ψ	<p> = ∫ψpψ^*dτ	
In bra and ket space, any complete br	vector	number	operator	space	
In bra and ket space, any incomplete	vector	number	operator	space	
The development of classical mechani	Planck's radiation	Bohr's qua	Newton's t	Kepler's laws	
Classical mechanics could not explain	Spectrum of black	Stability of	Intensity of	All the above	
Old quantum theory explains _____	particle in a box	Pauli's excl	Spectral lin	Spin of the electrons	
The quantum concept was introduced	Schrodinger	Bohr	Planck	Einstein	
The idea of dual nature of light was pr	Plank	De Broglie	Einstein	Maxwell	
The value of Plank's constant is	6.62 X 10^{-34} JS^2	6.62 X 10^{-3}	6.62 X 10^{-3}	6.62 X 10^{-31} JS^2	
Wave mechanics described the behav	atomic system	interaction	electromag	all the above	
The wave equation for a moving parti	$\tilde{N}^2\psi + (1/v^2)\,\partial^2\psi/$	$\tilde{N}^2\psi - (1/v^2$	$\tilde{N}^2\psi + (v^2)$	$\tilde{N}^2\psi - (v^2)\,\partial^2\psi/\partial t^2 = 0$	
The equation which describes the mo	Hψ + Eψ = 0	Hψ = Eψ	Hψ = -iħ∂ψ	Hψ = (1/iħ)∂ψ/∂t	
The state functions in the Hilbert spac	linear vectors	state vecto	basis vecto	complex vectors	
The state functions in the Hilbert spac	column vector	basis vecto	linear vect	all the above	
The change of basis from one ortho-n	<p| = <n|<n|p>	<p| = <n|p	|p> = |n><	|p> = <n|p>	
If the condition pc = cp is satisfied the	Hermitian	Unitary	Inverse	Linear	
The eigen functions of Hermitian oper	orthogonal	normalized	orthogonal	neither orthogonal nor	
The eigen functions corresponding to	odd function	even functi	can be eve	none of the above	
The eigen function corresponding to t	odd function	even functi	can be eve	none of the above	
The eigen value of the even function	λ = 0	λ = 1	λ = ±1	λ = - 1	
The eigen value of the odd function o	λ = 0	λ = 1	λ = ±1	λ = -1	
The expectation value of operator in	∂/∂t <A_s> = 0	∂/∂t <A_s>	∂/∂t <A_s> =	∂/∂t <A_s> = -1	
In harmonic oscillator problem, the m	only upper diagon	only lower	only diagor	both upper and lower	
In harmonic oscillator problem, the m	only upper diagon	only lower	only diagor	both upper and lower	
In harmonic oscillator problem, the m	only upper diagon	only lower	only diagor	both upper and lower	

Prepared by Dr. B. Janarthanan, Associate Professor, Karpagam Academy of Higher Education

Choice 6	**Answer**
	real
	Hermitian
	$(i\hbar/m)p$
	$-i\hbar k_x$
	$H/\hbar\omega_o + ½$
	$H/\hbar\omega_o - ½$
	|b><a|
	Unitary
	$<p> = \int\psi^* p\psi d\tau$
	number
	vector
	Newton’s three laws of motion
	All the above
	particle in a box
	Planck
	Einstein
	$6.62 \text{ X } 10^{-34}$ JS
	all the above
	$\tilde{N}^2\psi + (1/v^2)\,\partial^2\psi/\partial t^2 = 0$
	$H\psi = E\psi$
	basis vectors
	column vector
	|p> = |n><n|p>
	Hermitian
normalizec	orthogonal
	can be even or odd
	odd function
	$\lambda = 1$
	$\lambda = -1$
	$\partial/\partial t <A_s> = 0$
diagonal ele	only upper diagonal elements
diagonal ele	only lower diagonal elements
diagonal ele	only diagonal elements

UNIT – IV

Quantum theory of hydrogen-like atoms: time independent Schrodinger equation in spherical polar coordinates; separation of variables for the second order partial differential equation; angular momentum operator and quantum numbers; Radial wavefunctions from Frobenius method; Orbital angular momentum quantum numbers l and m; s, p, d,.. shells (idea only)

Quantum theory of Hydrogen-like atoms:

Introduction

By now you're probably familiar with the Bohr model of the atom, which was a great help in classifying the position of fundamental atomic specta lines. However, Bohr lucked out in more ways than one. The hydrogen atom turns out to be one of the few systems in Quantum Mechanics that we are able to solve almost precisely. This has made it tremendously useful as a model for other Quantum Mechanical systems, and as a model for the behavior of atoms themselves.

Fundamentals

We can assume that the hydrogen atom is governed by the Coulomb potential, namely:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

such that, $H\Psi = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$

Obviously, simply by inspection, we can see that the Hydrogen Atom is a spherical system. Hence it makes more sense to deal with the Hydrogen atom in spherical coordinates. One should remember at this point that, via Separation of variables, you can obtain the solution to the spherical Laplacian in three-dimensional space:

$$\nabla^2 f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2}$$

the solutions to this function when we use separation of variables inside a Hamiltonian gives us two different functions, the Radial Wave functions (not useful now, but good to know):

$$A \cdot J_l\left(Z_{nl}\frac{r}{a}\right)$$

where J_l are the spherical Bessel functions of type l, and Z_{nl} are the zeroes of said Bessel functions.

The other component, the angular component are the Spherical harmonics which are explored in detail on Wikipedia.

Schrodinger Equation, Spherical Coordinates

If the potential of the physical system to be examined is spherically symmetric, then the Schrodinger equation in spherical polar coordinatescan be used to advantage. For a three-dimensional problem, the Laplacianin spherical polar coordinates is used to express the Schrodinger equation in the condensed form

$$\frac{-\hbar^2}{2m}\nabla^2\Psi + U(r,\theta,\phi)\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

Expanded, it takes the form

$$\frac{-\hbar^2}{2\mu}\frac{1}{r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2\Psi}{\partial\phi^2}\right]$$
$$+U(r)\Psi(r,\theta,\phi) = E\,\Psi(r,\theta,\phi)$$

separation of variables second order partial differential equations:

Classification of 2nd order PDEs in two variables Most physical systems are governed by second order partial differential equations, or PDEs. Such equations fall into three basic types. Consider the equation for u(x, y) auxx + buxy + cuyy = f , (1) where the functions a, b, c and f do not depend on uxx, uxy or uyy. They may, however, depend on x, y, u, ux and uy. The Characteristic Equation of (1) is dy dx = b ± √b2 − 4ac 2a . (2) Equation (1) is classified as hyperbolic, parabolic or elliptic according to: If □ □□ □□ b2 − 4ac > 0 2 real roots, (1) is hyperbolic b2 − 4ac = 0 1 real root, (1) is parabolic b2 − 4ac < 0 0 real roots, (1) is elliptic. □ □□ □□ . (3) For hyperbolic equations, (2) is an ODE for y(x) which can be integrated to define two sets of curves (one for the + sign, one for the −), called the characteristics of (1). Characteristics are curves along which information travels at a finite speed. They are associated with "time-like" behaviour, and a characteristic speed. In contrast elliptic problems have no "time-like" variable; x and y behave like space coordinates. Hyperbolic Equations: A typical example is the one-dimensional wave equation for u(x, t), utt = c2uxx where c is the constant wave speed. (4) Hyperbolic equations should be solved with two initial conditions (at t = 0, say). Elliptic Equations: These have no characteristics; no lines along which information travels. A typical elliptic equation is Laplace's equation for u(x, y) ∇2u ≡ uxx + uyy = 0 in D, (5) where D is some region of (x, y)-space. This equation requires one boundary condition (say u = f) on the boundary of D. Parabolic Equations: A typical example is the diffusion equation for u(x, t) ut = Kuxx where K > 0 is the constant diffusivity. (6) Parabolic equations require one initial condition and it is vital that we move "forwards in time." Physically, parabolic equations describe the smoothing out of an initial configurationtowards an equilibrium. Many different initial conditions give rise to almost the same final state. This is why running the process backwards in time is an ill-posed problem. You can't un-stir a cup of tea!

Exact Solutions by "Separation of Variables" Consider the example problem of the flow of heat in a bar, ut = uxx in 0 < x < 1, t > 0 with u(0, t) = u(1, t) = 0, u(x, 0) = u0(x)) (7) We look for separable solutions of the PDE of the form u(x, t) = X(x)T(t), so that XT0 = X00T or T0 T = X00 X = −ω2, say. (8) As T0 /T is a function of t only, while X00/X is a function of x only, both functions must be a constant, which we take to be negative. Then the functions X(x) and T(t) take the forms X = A cosωx + B sin ωx, and T = Ce−ω2t . (9) If we require X to obey the boundary conditions in (7), namely X(0) = X(1) = 0, we obtain non-zero solutions only if A = 0 and ω = mπ, for some integer m, so that u = Bm sin(mπx) e−m2π2t , for some constant Bm. As (7) is a linear problem, we may combine solutions to obtain a more general solution in the form u(x, t) = X∞ m=1 Bmsin(mπx) e−m2π2t . (10) The initial condition will be satisfied if u(x, 0) = X∞ m=1 Bmsin(mπx) = u0(x) . (11) Thus all we need do to obtain the solution of (7) is to expand the initial condition u = u0(x) in a Fourier series, and substitute the appropriate values of the constants Bm into (10). Using the orthogonality relations, we find Bn = 2 Z 1 0 u0(x) sin(nπx)dx .

Angular Momentum Operators

In classical mechanics, the vector angular momentum, **L**, of a particle of position vector $\mathbf{r}$ and linear momentum $\mathbf{p}$ is defined as

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}. \tag{526}$$

It follows that

$$L_x = y\,p_z - z\,p_y, \tag{527}$$

$$L_y = z\,p_x - x\,p_z, \tag{528}$$

$$L_z = x\,p_y - y\,p_x. \tag{529}$$

Let us, first of all, consider whether it is possible to use the above expressions as the definitions of the operators corresponding to the components of angular momentum in quantum mechanics, assuming that the x_i and p_i (where $x_1 \equiv x$, $p_1 \equiv p_x$, $x_2 \equiv y$, *etc.*) correspond to the appropriate quantum mechanical position and momentum operators. The first point to note is that expressions (527)-(529) are *unambiguous* with respect to the order of the terms in multiplicative factors, since the various position and momentum operators appearing in them all *commute* with one another [see Eqs. (483)]. Moreover, given that the x_i andthe p_i are Hermitian operators, it is easily seen that the L_i are also *Hermitian*. This is important, since only Hermitian operators can represent physical variables in quantum mechanics (see Sect. 4.6). We, thus, conclude that Eqs. (527)-(529) are plausible definitions for the quantum mechanical operators which represent the components of angular momentum.

Let us now derive the commutation relations for the L_i. For instance,

$$\begin{aligned}[L_x, L_y] &= [y\,p_z - z\,p_y, z\,p_x - x\,p_z] = y\,p_x\,[p_z, z] + x\,p_y\,[z, p_z] \\ &= \mathrm{i}\hbar\,(x\,p_y - y\,p_x) = \mathrm{i}\hbar\,L_z,\end{aligned} \tag{530}$$

where use has been made of the definitions of the L_i [see Eqs. (527)-(529)], and commutation relations (481)-(483) for the x_i and p_i. There are two similar commutation relations: one for L_y and L_z, and one for L_z and L_x. Collecting all of these commutation relations together, we obtain

$$[L_x, L_y] = \mathrm{i}\hbar\,L_z, \tag{531}$$

$$[L_y, L_z] = \mathrm{i}\hbar\,L_x, \tag{532}$$

$$[L_z, L_x] = \mathrm{i}\hbar\,L_y. \tag{533}$$

By analogy with classical mechanics, the operator L^2, which represents the *magnitude squared* of the angular momentum vector, is defined

$$L^2 = L_x^2 + L_y^2 + L_z^2. \tag{534}$$

Now, it is easily demonstrated that if A and B are two general operators then

$$[A^2, B] = A\,[A, B] + [A, B]\,A. \tag{535}$$

Hence,

$$\begin{aligned}[L^2, L_x] &= [L_y^2, L_x] + [L_z^2, L_x] \\ &= L_y\,[L_y, L_x] + [L_y, L_x]\,L_y + L_z\,[L_z, L_x] + [L_z, L_x]\,L_z \\ &= \mathrm{i}\hbar\,(-L_y\,L_z - L_z\,L_y + L_z\,L_y + L_y\,L_z) = 0,\end{aligned} \tag{536}$$

where use has been made of Eqs. (531)-(533). In other words, L^2 commutes with L_x. Likewise, it is easily demonstrated that L^2 also commutes with L_y, and with L_z. Thus,

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0. \tag{537}$$

Recall, from Sect. 4.10, that in order for two physical quantities to be (exactly) measured *simultaneously*, the operators which represent them in quantum mechanics must *commute* with one another. Hence, the commutation relations (531)-(533) and (537) imply that we can only simultaneously measure the magnitude squared of the angular momentum vector, L^2, together with, at most, *one* of its Cartesian components. By convention, we shall always choose to measure the z-component, L_z.

Finally, it is helpful to define the operators

$$L_\pm = L_x \pm \mathrm{i}\, L_y. \tag{538}$$

Note that L_+ and L_- are not Hermitian operators, but are the Hermitian conjugates of one another (see Sect. 4.6): *i.e.*,

$$(L_\pm)^\dagger = L_\mp, \tag{539}$$

Moreover, it is easily seen that

$$\begin{aligned} L_+ L_- = (L_x + \mathrm{i}\, L_y)(L_x - \mathrm{i}\, L_y) = L_x^2 + L_y^2 - \mathrm{i}\,[L_x, L_y] = L_x^2 + L_y^2 + \hbar \\ = L^2 - L_z^2 + \hbar\, L_z. \end{aligned} \tag{540}$$

Likewise,

$$L_- L_+ = L^2 - L_z^2 - \hbar\, L_z, \tag{541}$$

giving

$$[L_+, L_-] = 2\hbar\, L_z. \tag{542}$$

We also have

$$[L_+, L_z] \;=\; [L_x, L_z] + \mathrm{i}\,[L_y, L_z] = -\mathrm{i}\,\hbar\, L_y - \hbar\, L_x = -\hbar\, L_+, \tag{543}$$

and, similarly,

$$[L_-, L_z] = \hbar\, L_-. \tag{544}$$

Quantum numbers

A number which occurs in the theoretical expression for the value of some quantized property of a subatomic particle, atom, or molecule and can only have certain integral or half-integral values.

A quantum number is a value that is used when describing the energy levels available to atoms and molecules. An electron in an atom or ion has four quantum numbers to describe its state and yield solutions to the Schrödinger wave equation for the hydrogen atom.

There are four quantum numbers:

- n - principal quantum number - describes the energy level
- ℓ - azimuthal or angular momentum quantum number - describes the subshell
- m_ℓ or m - magnetic quantum number - describes the orbital of the subshell
- m_s or s - spin quantum number - describes the spin

Quantum Number Values

According to the Pauli exclusion principle, no two electrons in an atom can have the same set of quantum numbers. Each quantum number is represented by either a half-integer or integer value.

- The principal quantum number is an integer that is the number of the electron's shell. The value is 1 or higher (never 0 or negative).
- The angular momentum quantum number is an integer that is the value of the electron's orbital (e.g., s=0, p=1). ℓ is greater than or equal to zero and less than or equal to n-1.

- The magnetic quantum number is the orientation of the orbital with integer values ranging from -ℓ to ℓ. So, for the p orbital, where ℓ=1, m could have values of -1, 0, 1.
- The spin quantum number is a half-integer value that is either -1/2 (called "spin down") or 1/2 (called "spin up").

Quantum Number Example

For the outer valence electrons of a carbon atom, the electrons are found in the 2p orbital. The four quantum numbers used to describe the electrons are n=2, ℓ=1, m=1, 0, or -1, and s=1/2 (the electrons have parallel spins).

Not Just for Electrons

While quantum numbers are commonly used to describe electrons, they may be used to describe the nucleons (protons and neutrons) of an atom or elementary particles.

Radial Wavefunction

The potential, in this case, represents the electrostatic field set up by the nucleus of the Hydrogen atom, as felt by the electron:

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r}. \qquad (24.1)$$

This goes into the usual (with u(r) = r R(r) as before)

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[U(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} - E\right]u = 0 \qquad (24.2)$$

where we are associating m with the mass of the electron. We just made a pretty dramatic approximation. We know that the two-particle problem canbe reduced to a stationary center, provided we use the reduced mass of the system. On the one had, that is fine – but on the other: What do we mean by a two-particle problem in quantum mechanics? For now, just imagine the nucleus doesn’t have much “kinetic” energy, so that it remains pretty much fixed (what about the energy associated with having it around at all? Its relativistic “rest energy” is still there, but we are not doing relativistic quantum mechanics yet). If we write the above out, we have:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} - E\right]u = 0. \qquad (24.3)$$

As with the infinite square well, it makes sense to let κ = √ −2 m E ~ (negative inside the square root, now – bound states will have E < 0 and we want to make κ real). We want to define a new "coordinate" ρ ≡ κ r. The advantage is to render the coordinate variable itself unitless. Whenever we want to consider limiting cases of an equation or more generally, a physical setting, we need a point of comparison. What does it mean to be "far away" from a distribution of charge, for example? That clearly depends on how large the distribution itself is. By re-parametrizing using a fundamental length in the problem, we have allowed for easier classification of limits. For example, on the E&M side, suppose we have a dipole moment with a certain length d. Then "far away" means that a field point at a distance r from the origin is large compared to d: r d. Now suppose we wrote everything in our problem in terms of the new length r˜ ≡ r/d. We have eliminated the explicit comparison with d and can refer to "small ˜r" unambiguously as ˜r ∼ 0, making for easier Taylor expansion, etc. The point is, κ has units of 1/length and involves the fundamental (and as yet unknown) energy scale, it is a natural choice for constructing ρ = κ r, a unitless quantity. In the above, we just replace r −→ ρ/κ, and d dr −→ κ d dρ . Performing this simple change of variables, multiplying by 2 m ~2 in the process, we have

$$-\frac{d^2u(\rho)}{d\rho^2}+\left[-\frac{m\,e^2}{2\,\pi\,\epsilon_0\,\hbar^2\,\kappa\,\rho}+\frac{\ell\,(\ell+1)}{\rho}+1\right]u(\rho)=0. \qquad (24.4)$$

We have another scale defined by ρ0 ≡ m e2 2 π 0 ~2 κ (there are, evidently, two energy scales of interest to us here, hence two lengths – we could have writtenρ in terms of ρ = (ρ0 κ) r), and with this, we can write the final form:

$$\frac{d^2u}{d\rho^2}=\left[1-\frac{\rho_0}{\rho}+\frac{\ell\,(\ell+1)}{\rho^2}\right]u. \qquad (24.5)$$

As for limiting cases, we can take ρ −→ ∞, which gives us growing and decaying exponentials as solutions:

$$\frac{d^2u}{d\rho^2}=u\longrightarrow u(\rho)=A\,e^{-\rho} \qquad (24.6)$$

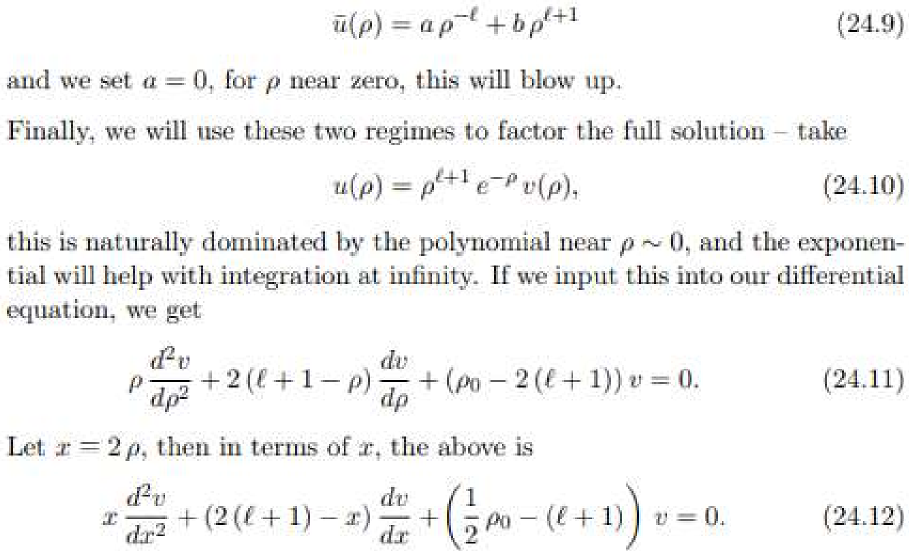
where we have thrown out the growing exponential, that will not be normalizable. On the other hand, when the barrier-term dominates, for small ρ, we have (using ¯u to distinguish from the actual solution)

$$\frac{d^2\bar{u}}{d\rho^2} = \frac{\ell\,(\ell+1)}{\rho^2}\,\bar{u}, \qquad (24.7)$$

and we can solve this by consider a generic polynomial (always a good ansatz for ODE's of the above flavor): ¯u(ρ) = a ρp , then

$$a\,p\,(p-1)\,\rho^{p-2} = a\,(\ell\,(\ell+1))\,\rho^{-2}\,a\,\rho^{p} \qquad (24.8)$$

and then we have a solution for p (p − 1) = ` (` + 1), or p = −`, p = ` + 1. The general solution is a linear combination:



$$\bar{u}(\rho) = a\,\rho^{-\ell} + b\,\rho^{\ell+1} \qquad (24.9)$$

and we set $a = 0$, for ρ near zero, this will blow up.

Finally, we will use these two regimes to factor the full solution – take

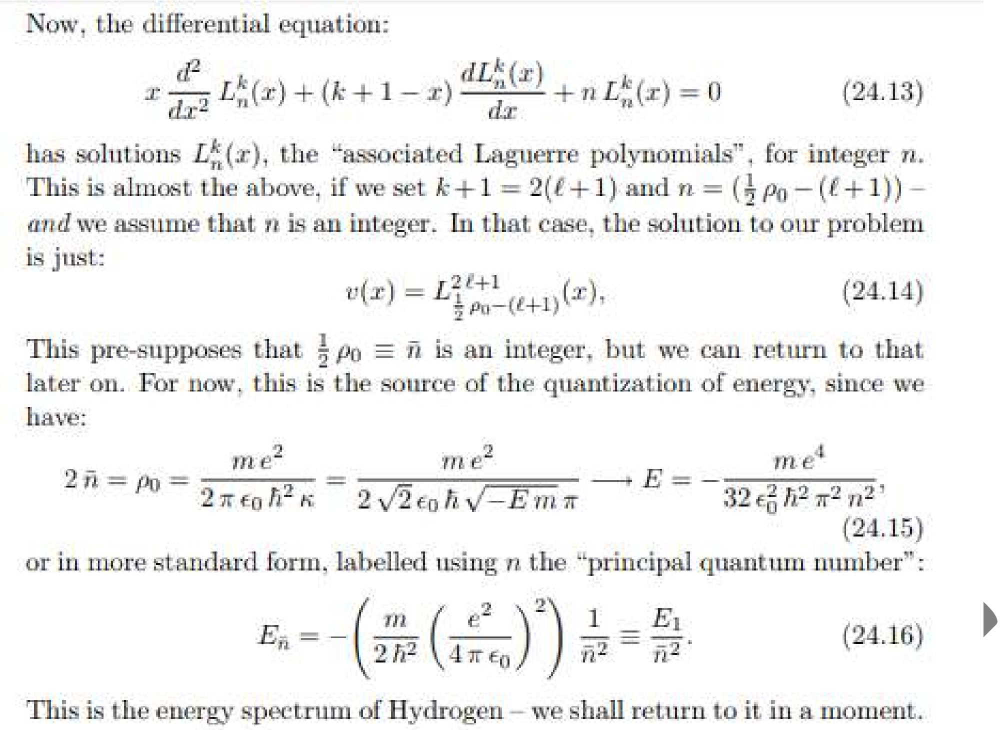
$$u(\rho) = \rho^{\ell+1}\,e^{-\rho}\,v(\rho), \qquad (24.10)$$

this is naturally dominated by the polynomial near $\rho \sim 0$, and the exponential will help with integration at infinity. If we input this into our differential equation, we get

$$\rho\,\frac{d^2v}{d\rho^2} + 2\,(\ell+1-\rho)\,\frac{dv}{d\rho} + (\rho_0 - 2\,(\ell+1))\,v = 0. \qquad (24.11)$$

Let $x = 2\,\rho$, then in terms of x, the above is

$$x\,\frac{d^2v}{dx^2} + (2\,(\ell+1) - x)\,\frac{dv}{dx} + \left(\frac{1}{2}\,\rho_0 - (\ell+1)\right)\,v = 0. \qquad (24.12)$$



Now, the differential equation:

$$x\,\frac{d^2}{dx^2}\,L_n^k(x) + (k+1-x)\,\frac{dL_n^k(x)}{dx} + n\,L_n^k(x) = 0 \qquad (24.13)$$

has solutions $L_n^k(x)$, the "associated Laguerre polynomials", for integer n. This is almost the above, if we set $k+1 = 2(\ell+1)$ and $n = (\frac{1}{2}\,\rho_0 - (\ell+1))$ – *and* we assume that n is an integer. In that case, the solution to our problem is just:

$$v(x) = L^{2\,\ell+1}_{\frac{1}{2}\,\rho_0-(\ell+1)}(x), \qquad (24.14)$$

This pre-supposes that $\frac{1}{2}\,\rho_0 \equiv \bar{n}$ is an integer, but we can return to that later on. For now, this is the source of the quantization of energy, since we have:

$$2\,\bar{n} = \rho_0 = \frac{m\,e^2}{2\,\pi\,\epsilon_0\,\hbar^2\,\kappa} = \frac{m\,e^2}{2\,\sqrt{2}\,\epsilon_0\,\hbar\,\sqrt{-E\,m}\,\pi} \longrightarrow E = -\frac{m\,e^4}{32\,\epsilon_0^2\,\hbar^2\,\pi^2\,n^2}, \qquad (24.15)$$

or in more standard form, labelled using n the "principal quantum number":

$$E_{\bar{n}} = -\left(\frac{m}{2\,\hbar^2}\left(\frac{e^2}{4\,\pi\,\epsilon_0}\right)^2\right)\frac{1}{\bar{n}^2} \equiv \frac{E_1}{\bar{n}^2}. \qquad (24.16)$$

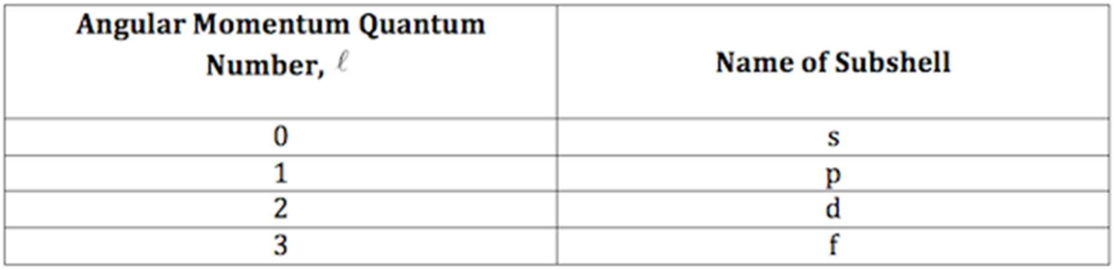
This is the energy spectrum of Hydrogen – we shall return to it in a moment.

Angular Momentum Quantum Number

There are four quantum numbers that make up the address for an electron. Of the four quantum numbers, our focus for this lesson is the **angular momentum quantum number**, which is also known as the **secondary quantum number** or **azimuthal quantum number**.

The angular momentum quantum number is a quantum number that describes the 'shape' of an orbital and tells us which subshells are present in the principal shell. We can think about it this way: each of our homes has its own architecture. In the subatomic level, the 'home' of electrons is an orbital, and each orbital has its own shape. The symbol that is used when we refer to the angular momentum quantum number looks like this:

Electrons occupy a region called 'shells' in an atom. The angular momentum quantum number, *l*, divides the shells into subshells, which are further divided into orbitals. Each value of *l* corresponds to a particular subshell. The lowest possible value for *l* is 0. This following table shows which subshells correspond to the angular momentum quantum number:



Angular Momentum Quantum Number, ℓ	Name of Subshell
0	s
1	p
2	d
3	f

The angular momentum quantum number can also tell us how many nodes there are in an orbital. A **node** is an area in an orbital where there is 0 probability of finding electrons. The value of *l* is equal to the number of nodes. For example, for an orbital with an angular momentum of $l = 3$, there are 3 nodes.

Karpagam Academy of Higher Education
Department of Physics
III B.Sc Physics
Quantum Mechanics (16PHU602A)
Multiple Choice Questions

Question	**Choice 1**	**Choice 2**	**Choice 3**	**Choice 4**	**Choice 5**	**Choice 6**	**Answer**
A system o	momentun	space	positional	phase-space			positional
The field la	Lagrangian	Hamiltonia	Volume	Surface			Lagrangian
The Har	a. dF/dt	a. dF/dt	a. dF/dt	a. dF/dt = ∂F/∂x + {F, H}			a. dF/dt = ∂F/∂t + {I
In the eq	total	partial	kinetic	none of the above			total
The Lagran	y(t)	dy/dt	q_i(t)	none of the above			q_i(t)
The field la	Ñy	dy/dt	q(r,t)	y(r,t)			y(r,t)
The appear	finite	infinite	constant	a and c			infinite
The variati	d∫L dt = 0	d∫L dt = 1	d∫L dt = -1	d∫L dt = y(r,t)			d∫L dt = 0
The mome	y	L	Ñy	dy			dy
The functic	time	momentun	space co-oı	none of the above			none of the above
The dF/dt	-∂F/∂t + {F,	-∂F/∂t – {F,	∂F/∂t + {F,	∂F/∂t – {F, H}			∂F/∂t + {F, H}
If H does r	equation	constant	lagrangian	Hamiltonian equation			constant
According t	quantum	classical	skew herm	Heisenberg			Heisenberg
According t	1	-1	0	2			0
The functic	∫ f(r) d(r, r')	-∫ f(r) d(r, r'	-∫ f(r) d(r, r'	∫ f(r) d(r, r') d^2r			∫ f(r) d(r, r') d^3r
The equati	dF/dt = -∂F	dF/dt = ∂F/	dF/dt = ∂F/	dF/dt = -∂F/∂t - 1/iħ [F, H]			dF/dt = ∂F/∂t + 1/iħ [F,
The field q	wave quan	second qua	wave funct	none of the above			second quantisation
If the comr	ak*ak3	ak*ak2	ak*ak	$a_k^* a_k$			$a_k^* a_k$
The sates (	……..n_k,….>	-l n_1, n_2, l	…….-n_k,….>	……..N_k,….>			l n_1, n_2, n_3, ……..n_k,….>
The a_k^* is ca	none of tl	creation	number	destruction			number
The a_k i	creation	number	a and b	destruction			destruction
The N_k is ca	number	creation	destructior	none of the above			number
The numbe	equation o	constant of	lagrangian	Hamiltonian motion			constant of motion
The rate c	dN_k/dt = iħ	dN_k/dt = -iħ	dN_k/dt = [a	iħ dN_k/dt = [a_k^*, a, H]			iħ dN_k/dt = [a_k^*, a, H]
The necess	0	–1	1	none of the above			0
If U_k and	H = Σ N_k E_k^2	H = Σ N_k E_k^3	H = Σ N_k E_k	H = Σ N_k E_k^4			H = Σ N_k E_k
Accordir	$a_k a_l + a_l a_k$ =	$a_k a_l + a_l a_k$ =	$a_k a_l + a_l a_k$ =	$a_k a_l - a_l a_k = 0$			$a_k a_l + a_l a_k = 0$
If the eige	variational	lagrangian	Hamiltonia	Exclusion			Exclusion
The eigen	spherical	polarized	plane	circular			plane
H is formal	harmonic	simple harı	sinusoidal	none of the above			harmonic
The mome	–(c/4p) E(r,	(c/p) E(r,t)	–(c/p) E(r,t	(c/4p) E(r,t) X H(r,t)			(c/4p) E(r,t) X H(r,t)
According t	–ħkc and ħ	ħkc and ħK	–ħkc and -ħ	ħkc and –ħK			ħkc and ħK
According t	ħK	–ħK	hn	h			hn
The quanti	classical	quantum	a and b	none of the above			classical
The Hamilt	-p	p	0	p			p
A physical s	finite	infinite	constant	none of the above			infinite
A transitior	doubly	triply	singly	none of the above			doubly

The electrc sound ultrasonic \ ultrasonic \ infrasonic wave ultrasonic wave

Prepared by Dr. B. Janarthanan, Associate Professor, Karpagam Academy of Higher Education

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UNIT – V

Atoms in Electric and Magnetic Fields:- Electron Angular Momentum. Space Quantization. Electron Spin and Spin Angular Momentum. Larmor's Theorem. Spin Magnetic Moment. Stern-Gerlach Experiment. Normal Zeeman Effect: Electron Magnetic Moment and Magnetic Energy. Many electron atoms: Pauli's Exclusion Principle. Symmetric and Antisymmetric Wave Functions. Spin orbit coupling. Spectral Notations for Atomic States. Total Angular Momentum. Spin-orbit coupling in atoms-L-S and J-J couplings.

Atoms in Electromagnetic Fields

Our goal in this chapter is to understand how atoms interact with electromagnetic fields. There will be several stages to our understanding. We start by looking at atoms in constant, background electromagnetic fields. Because these fields break various symmetries of the problem, we expect to see a splitting in the degeneracies of states. The splitting of the atomic spectrum due to an electric field is called the Stark effect. The splitting due to a magnetic field is called the Zeeman effect. We deal with each in turn. We then move on to look at what happens when we shine light on atoms. Here the physics is more dramatic: the atom can absorb a photon, causing the electron to jump from one state to a higher one. Alternatively the electron can decay to lower state, emitting a photon as it falls. We will begin with a classical treatment of the light but, ultimately, we will need to treat both light and atoms in a quantum framework.

8.1 The Stark Effect

Consider the hydrogen atom, where the electron also experience a constant, background electric field. We'll take the electric field to lie in the z direction, E = Ezˆ. The Hamiltonian is H = ~2 2m r2 e2 4⇡✏0r + eEz (8.1) The total potential energy, V (z) = eEze2/4⇡✏0r z V(z) Figure 81: is sketched in the diagram. The first thing to note is that the potential is unbounded below as z ! 1. This means that all electron bound states, with wavefunctions localised near the origin, are now unstable. Any electron can tunnel through the barrier to the left, and then be accelerated by the electric field to z ! 1. However, we know from our WKB analysis in Section 6.2.5 that the probability rate for tunnelling is exponentially suppressed by the height of the barrier (see, for example, (6.30)). This means that the lowest lying energy levels will have an extremely long lifetime.

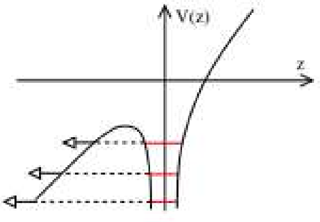


Figure 81:

If you want some numbers, the strength of a typical electric field is around E ⇠ 10 eV cm1. We know that the ground state of hydrogen is E0 ⇠ 13.6 eV and the Bohr radius is a0 ⇠ 5⇥109 cm, which suggests that the typical electric field inside the atom is around Eatom⇠ 109 eV cm1, which is eight orders of magnitude greater than the applied electric field. On general, ground we expect that the tunnelling probability is suppressed by a factor of e108 . At this point is doesn't really matter what our units are, this is going to be a very small number. The states which are well bound are stable for a very long time. Only those states very close to threshold are in danger of being destabilised by the electric field. For this reason, we'll proceed by ignoring the instability

8.2 The Zeeman E↵ect

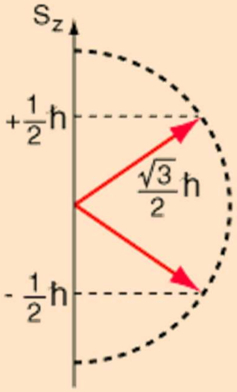
The splitting of energy levels due to a background magnetic field is called the Zeeman e↵ect. It was discovered in 1896 by Pieter Zeeman who, like many great scientists, ignored what his boss told him to do and instead followed his nose. For this, he was fired. The award of the Nobel prize six years later may have gone some way towards making amends. The addition of a magnetic field results in two extra terms in the Hamiltonian. The first arises because the electron is charged and so, as explained in more detail in Section 1, the kinetic terms in the Hamiltonian become H = 1 2m(p + eA) 2 1 4⇡✏0 Ze2 r (8.9) where A is the vector potential and the magnetic field is given by B = r ⇥ A. We take the magnetic field to lie in the z-direction: B = Bzˆ and work in symmetric gauge A = B 2 (y, x, 0) We can now expand out the square in (8.9). The cross terms are p · A = A · p = B(xpyypx)/2. Note that, even when viewed as quantum operators, there is no ordering ambiguity. Moreover, we recognise the combination in brackets as the component of the angular momentum in the z-direction: Lz = xpyypx. We can then write the Hamiltonian as H = 1 2m p2 + eB · L + e2 B2 (x2 + y2) 1 4⇡✏0 Ze2 r (8.10)

Note that the B · L term takes the characteristic form of the energy of a magnetic dipole moment μ in a magnetic field. Here μL = e 2m L is the dipole moment that arises from the orbital angular momentum of the electron. The second term that arises from a magnetic field is the coupling to the spin. We already saw this in Section 1.5 and again in Section 7.1.3 H = g e 2m B · S where the g-factor is very close to g ⇡ 2. Combining the two terms linear in B gives the so-called Zeeman Hamiltonian HZ = e 2m B · (L + 2S) (8.11) Note that it's not quite the total angular momentum J = L + S that couples to the magnetic field. There is an extra factor of g = 2 for the spin. This means that the appropriate dipole moment is μtotal = e 2m(L + 2S) (8.12) The terms linear in B given in (8.11) are sometimes called the paramagnetic terms; these are responsible for the phenomenon of Pauli paramagnetism that we met in the Statistical Physics lectures. The term in (8.10) that is quadratic in B is sometimes called the diamagnetic tem; it is related to Landau diamagnetism that we saw in Statistical Physics. In what follows, we will work with magnetic fields that are small enough so that we can neglect the diamagnetic B2 term. In terms of dimensionless quantities, we require that eBa2 0/~ ☒ 1 where a0, the Bohr radius, is the characteristic size of the atom. In practical terms, this means B .10 T or so.

Space quantization :

Quantization in respect to direction in spacethe space quantization of an atom in a magnetic field whose quantum states correspond to a limited number of possible angles between the directions of the angular momentum and the magnetic intensity.

Electron Spin



An electron spin s = 1/2 is an intrinsic property of electrons. Electrons have intrinsic angular momentum characterized by quantum number 1/2. In the pattern of other quantized angular momenta, this gives total angular momentum

$$S = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\hbar = \frac{\sqrt{3}}{2}\hbar$$

The resulting fine structure which is observed corresponds to two possibilities for the z-component of the angular momentum.

$$S_z = \pm\frac{1}{2}\hbar$$

This causes an energy splitting because of the magnetic moment of the electron

$$\mu_S = -\frac{e}{2m}gS$$

Spin "up" and "down" allows two electrons for each set of spatial quantum numbers.

$$n, \ell, m_\ell$$

Two types of experimental evidence which arose in the 1920s suggested an additional property of the electron. One was the closely spaced splitting of the hydrogen spectral lines, called fine structure. The other was the Stern-Gerlach experiment which showed in 1922 that a beam of silver atoms directed through an inhomogeneous magnetic field would be forced into two beams. Both of these experimental situations were consistent with the possession of an intrinsic angular momentumand a magnetic moment by individual electrons. Classically this could occur if the electron were a spinning ball of charge, and this property was called electron spin.

Quantization of angular momentum had already arisen for orbital angular momentum, and if this electron spin behaved the same way, an angular momentum quantum number s = 1/2 was required to give just two states. This intrinsic electron property gives:

Z-component of angular momentum: $S_Z = m_S \hbar\ , \quad m_S = \pm\frac{1}{2}$

Magnetic moment: $\mu_S = -\frac{e}{2m} gS$

Pin Angular Momemtum:

Spin angular momentum is a specific type of angular momentum possessed by some nuclei. As such, it obeys all the relations given for angular momentum under the quantum mechanics of rotation, here. i.e. there are two quantum numbers associated with the spin angular momentum momentum that determine its properties.

All nuclei have a spin quantum number, I, which may be integral (including zero) or half-integral, but never negative. The value of I is characteristic of a given nucleus, and may vary between isotopes. Thus all ^{1}H hydrogen nuclei have I = ½ , but all ^{2}H deuterium nuclei have I = 1.

The magnitude of the spin angular momentum is determined by the quantum number I, and is given by:

$$\text{Magnitude of spin angular momentum} = \hbar\sqrt{\left(I(I+1)\right)}$$

Thus all nuclei with I> 0 have spin angular momentum.

Further, all nuclei with a spin angular momentum (i.e. all nuclei with nonzero I) have a magnetic moment with constant magnitude and an orientation determined by a second quantum number, m_I. (To say that a nucleus has a magnetic moment means that in some ways it behaves like a small bar magnet.)

The quantum number m_I properly determines the component of the spin angular momentum on an arbitrary axis, normally termed the z axis (The arbitrary axis may be defined, for example, by the field direction of an external electric or magnetic field.):

z-component of spin angular momentum = $m_I\hbar$

where m_I can take values from I to -I. (m_I = I, I – 1, I – 2 … -I)

This property indicates that for a given I, the spin (and thus the magnetic moment) of a nucleus can adopt 2I + 1 different orientations relative to a defined axis. A proton (^{1}H hydrogen nucleus) has I = ½ , and thus its spin may adopt 2 different orientations (m_I = -½ or m_I = +½).

A large number of the nuclei that are studied by nuclear magnetic resonance (NMR) spectroscopy have I = ½, as they give rise simpler spectra than nuclei with I >½ ,but **any nucleus with nonzero I may be studied by NMR**. Spin ½ nuclei that are commonly studied include ^{1}H (the most popular nucleus for NMR studies), ^{13}C, ^{19}F and ^{31}P.

The state with m_I = +½ is denoted α , while the state with m_I = -½ is denoted β.

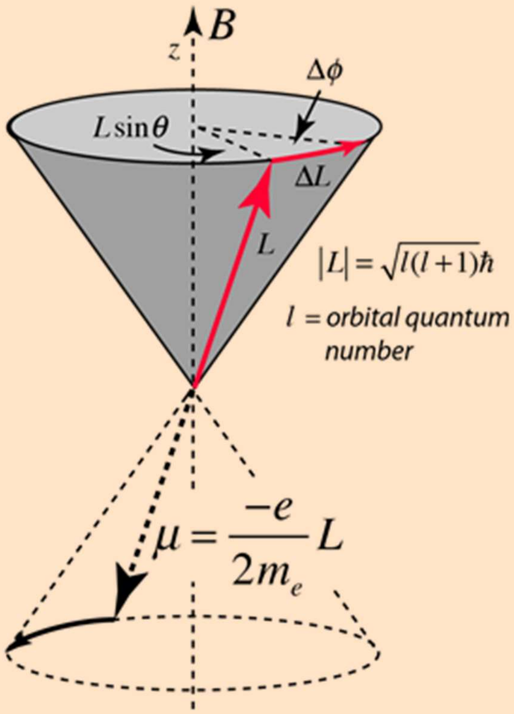
Note that two very common isotopes, ^{12}C and ^{16}O, have I = 0, so have no spin angular momentum, no magnetic moment, and hence are invisible in NMR studies.

Larmor Precession

When a magnetic moment μ is placed in amagnetic field B, it experiences a torque which can be expressed in the form of a vector product

$$\tau = \mu \ \ x \ \ B$$

For a static magnetic moment or a classical current loop, this torque tends to line up the magnetic moment with the magnetic field B, so this represents its lowest energy configuration. But if the magnetic moment arises from the motion of an electron in orbit around a nucleus, the magnetic moment is proportional to the angular momentum of the electron. The torque exerted then produces a change in angular momentum which is perpendicular to that angular momentum, causing the magnetic moment to precess around the direction of the magnetic field rather than settle down in the direction of the magnetic field. This is called Larmor precession.



When a torque is exerted perpendicular to the angular momentum L, it produces a change in angular momentum ΔL which is perpendicular to L, causing it to precess about the z axis. Labeling the precession angle as φ, we can describe the effect of the torque as follows:

$$\tau = \frac{\Delta L}{\Delta t} = \frac{L\sin\theta\Delta\phi}{\Delta t} = |\mu B\sin\theta| = \frac{e}{2m_e} LB\sin\theta$$

The precession angular velocity (Larmor frequency) is

$$\omega_{Larmor} = \frac{d\phi}{dt} = \frac{e}{2m_e}B$$

These relationships for a finite current loop extend to the magnetic dipoles of electron orbits and to the intrinsic magnetic moment associated with electron spin. There is also a characteristic Larmor frequency for nuclear spins.

In the case of the electron spin precession, the angular frequency associated with the spin transition is usually written in the general form

ω = □B

where □ is called the gyromagetic ratio (sometimes the magnetogyric ratio). This angular frequency is associated with the "spin flip" or spin transition, involving an energy change of 2μB. An example for magnetic field 1 Tesla follows.

$$\omega_{electron\,spin} = \frac{2\mu_e B}{\hbar} = \frac{2\cdot 2\cdot \frac{1}{2}(5.79x10^{-5}eV/T)(1T)}{6.58x10^{-16}eV\cdot s} = 1.7608x10^{11}s^{-1}$$

$$\nu = \frac{\omega}{2\pi} = 28.025\,GHz \quad \textit{Larmor frequency}$$

$$\omega_{proton\,spin} = \frac{2\mu_p B}{\hbar} = \frac{2(2.79)(3.15x10^{-8}eV/T)(1T)}{6.58x10^{-16}eV\cdot s} = 2.6753x10^{8}s^{-1}$$

$$\nu = \frac{\omega}{2\pi} = 42.5781\,MHz \quad \textit{Larmor frequency}$$

The characteristic frequencies associated with electron spin are employed in electron spin resonance (ESR) experiments, and those associated with the nuclear spin in nuclear magnetic resonance (NMR) experiments.

Spin magnetic moment

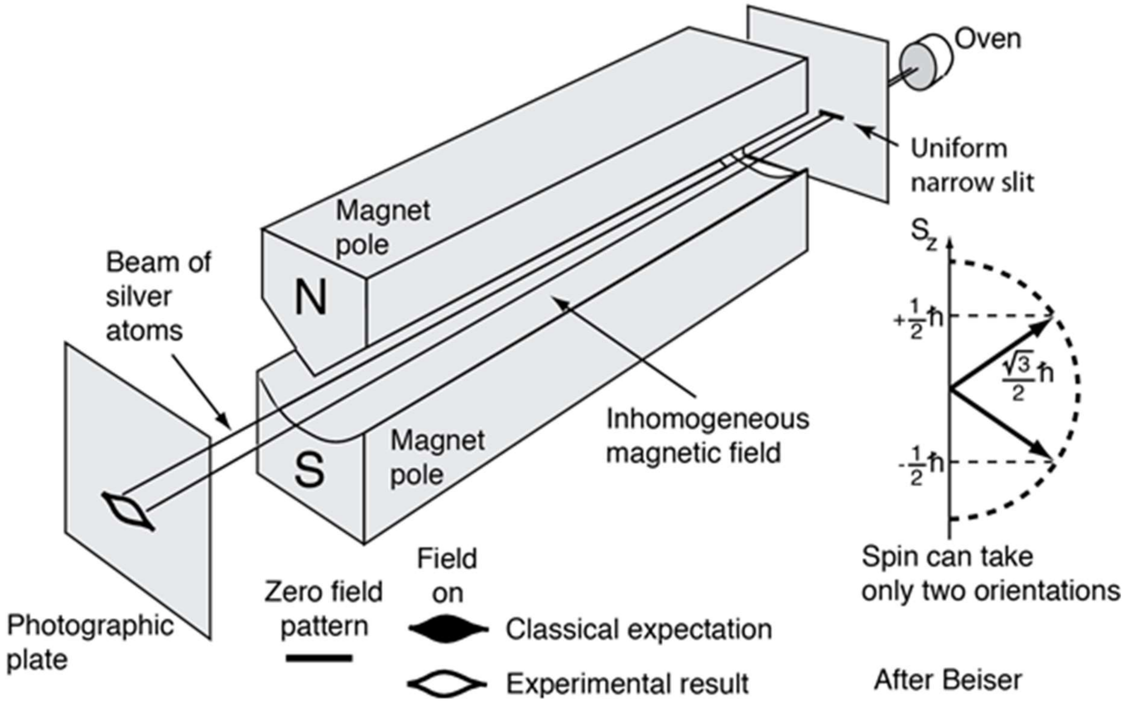
In physics, mainly quantum mechanics and particle physics, a **spin magnetic moment** is the magnetic moment caused by the spin of elementary particles. For example, the electron is an elementary spin-1/2 fermion.Quantum electrodynamics gives the most accurate prediction of the anomalous magnetic moment of the electron.

"Spin" is a non-classical property of elementary particles, since classically the "spin angular momentum" of a material object is really just the total *orbital* angular momenta of the object's constituents about the rotation axis. Elementary particles are conceived as concepts which have no axis to "spin" around (see wave–particle duality).

In general, a magnetic moment can be defined in terms of an electric current and the area enclosed by the current loop. Since angular momentum corresponds to rotational motion, the magnetic moment can be related to the orbital angular momentum of the charge carriers in the constituting current. However, in magnetic materials, the atomic and molecular dipoles have magnetic moments not just because of their quantized orbital angular momentum, but, due to the spin of elementary particles constituting them (electrons, and the quarks in the protons and neutrons of the atomic nuclei). A particle may have a spin magnetic moment without having an electric charge. For example, the neutron is electrically neutral but has a non-zero magnetic moment because of its internal quark structure.

Stern-Gerlach experiment:

From the time of Ampere onward, molecular currents were regarded as giving rise to magnetic moments. In the nuclear model of the atom the electron orbits the nucleus. This circular current results in a magnetic moment. The atom behaves as if it were a tiny magnet. In the Stern-Gerlach experiment a beam of silver atoms passed through an inhomogeneous magnetic field (Figure 12). In Larmor's classical theory there was no preferential direction for the direction of the magnetic moment and so one predicted that the beam of silver atoms would show a maximum in the center of the beam. In Sommerfeld's quantum theory an atom in a state with angular momentum equal to one (L=1)(L=1) would have a magnetic moment with two components relative to the direction of the magnetic field, ±eh/4me±eh/4me. (Bohr had argued that only two spatial components were allowed). In an inhomogeneous magnetic field, HH, the force on the magnetic moment μμ will be μzxμzx (Gradient of the magnetic field in the zz direction), where μz=±eh/4meμz=±eh/4me, where ee is the charge of the electron, meme is its mass, hh is Planck's constant, and zz is the field direction. Thus, depending on the orientation of the magnetic moment relative to the magnetic field there will be either an attractive or repulsive force and the beam will split into two components, exhibiting spatial quantization. There will be a minimum at the center of the beam. "According to quantum theory μzμz can only be ±(e/2me)(h/2π)±(e/2me)(h/2π). In this case the spot on the receiving plate will therefore be split into two, each of them having the same size but half the intensity of the original spot" (Stern 1921, p. 252, JM) This difference in prediction between the Larmor and Sommerfeld theories was what Stern and Gerlach planned to use to distinguish between the two theories. Stern remarked that "the experiment, if it can be carried out, (will result) in a clear-cut decision between the quantum-theoretical and the classical view" (Stern 1921, FW).



Sommerfeld's theory also acted as an enabling theory for the experiment. It provided an estimate of the size of the magnetic moment of the atoms so that Stern could begin calculations to see if the experiment was feasible. Stern calculated, for example, that a magnetic field gradient of 10^4 Gauss per centimeter would be sufficient to produce deflections that would give detectable separations of the beam components. He asked Gerlach if he could produce such a gradient. Gerlach responded affirmatively, and said he could do even better. The experiment seemed feasible. A sketch of the apparatus is shown in Figure 12. The silver atoms pass through the inhomogeneous magnetic field. If the beam is spatially quantized, as Sommerfeld predicted, two spots should be observed on the screen. (The sketch shows the beam splitting into three components, which would be expected in modern quantum theory for an atom with angular momentum equal to one). I note that Sommerfeld's theory was incorrect, illustrating the point that an enabling theory need not be correct to be useful.

A preliminary result reported by Stern and Gerlach did not show splitting of the beam into components. It did, however, show a broadened beam spot. They concluded that although they had not demonstrated spatial quantization, they had provided "evidence that the silver atom possesses a magnetic moment." Stern and Gerlach made improvements in the apparatus, particularly in replacing a round beam slit by a rectangular one that gave a much higher intensity. The results are shown in Figure 13 (Gerlach and Stern 1922a). There is an intensity minimum in the center of the pattern, and the separation of the beam into two components is clearly seen. This result seemed to confirm Sommerfeld's quantum-theoretical prediction of spatial quantization. Pauli, a notoriously skeptical physicist, remarked, "Hopefully now even the incredulous Stern will be convinced about directional quantization" (in a letter from Pauli to Gerlach 17 February 1922). Pauli's view was shared by the physics community. Nevertheless the Stern-Gerlach result posed a problem for the Bohr-Sommerfeld theory of the atom. Stern and Gerlach had assumed that the silver atoms were in an angular momentum state with angular momentum equal to one $(L=1)(L=1)$. In fact, the atoms are in an $L=0L=0$ state, for which no splitting of the beam would be expected in either the classical or the quantum theory. Stern and Gerlach had not considered this possibility. Had they done so they might not have done the experiment. The later, or new, quantum theory developed by Heisenberg, Schrodinger, and others, predicted that for an $L=1L=1$state the beam should split into three components as shown in Figure 12. The magnetic moment of the atom would be either 0 or ±eh/(4πxm)±eh/(4πxm). Thus, if the silver atoms were in an L=1L=1 state as Stern and Gerlach had assumed, their result, showing two beam components, also posed a problem for the new quantum theory. This was solved when Uhlenbeck and Goudsmit (1925, 1926) proposed that the electron had an intrinsic angular momentum or spin equal to h/4πh/4π. This is analogous to the earth having orbital angular momentum about the sun and also an intrinsic angular momentum due to its rotation on its own axis. In an atom the electron will have a total angular momentum J=L+SJ=L+S, where LLis the orbital angular momentum and SS is the spin of the electron. For silver atoms in an L=0L=0 state the electron would have only its spin angular momentum and one would expect the beam to split into two components. Goudsmit and Uhlenbeck suggested the idea of electron spin to explain features in atomic spectra such as the anomalous Zeeman effect, the splitting of spectral lines in a magnetic field into more components than could be accommodated by the Bohr-Sommerfeld theory of the atom. Although the Stern-Gerlach results were known, and would certainly have provided strong support for the idea of electron spin, Goudsmit and Uhlenbeck made no mention of the result.

The Stern-Gerlach experiment was initially regarded as a crucial test between the classical theory of the atom and the Bohr-Sommerfeld theory. In a sense it was, because it showed clearly that spatial quantization existed, a phenomenon that could be accommodated only within a quantum mechanical theory. It decided between the two classes of theories, the classical and the quantum mechanical. With respect to the particular quantum theory of Bohr and Sommerfeld, however, it wasn't crucial, although it was regarded as such at the time, because that theory predicted no splitting for a beam of silver atoms in the ground state (L=0)(L=0). The theory had been wrongly applied. The two-component result was also problematic for the new quantum theory, which also predicts no splitting for an angular momentum zero state and three components for an L=1L=1 state. Only after the suggestion of electron spin did the Stern-Gerlach result confirm the new theory.

Although the interpretation of the experimental result was incorrect for a time, the result itself remained quite robust through the theory change from the old to the new quantum theory. It is important to remember that experimental results do not change when accepted theory changes, although certainly, as we have seen, their interpretation may change. Gerlach and Stern emphasized this point themselves.

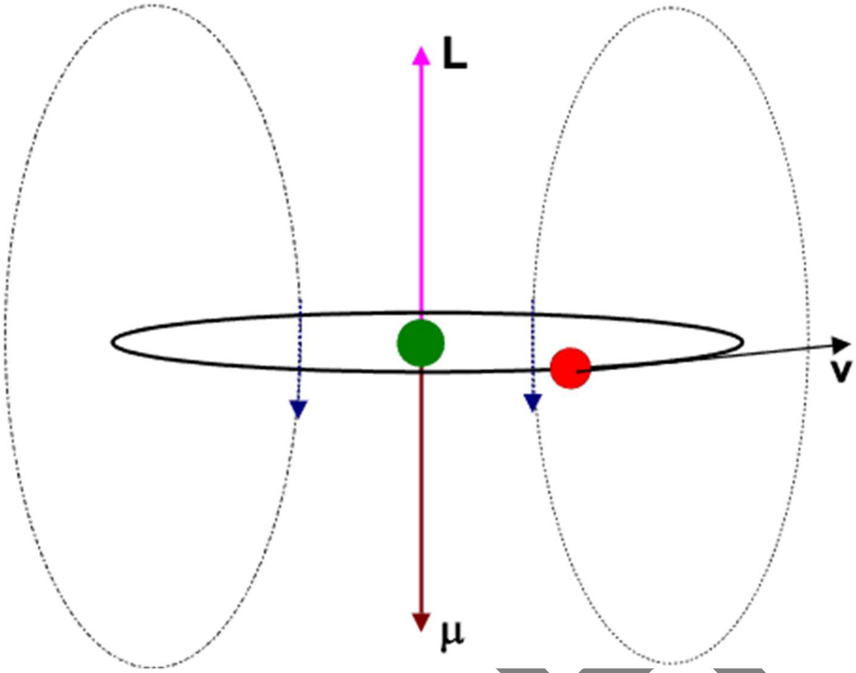
Apart from any theory, it can be stated, as a pure result of the experiment, and as far as the exactitude of our experiments allows us to say so, that silver atoms in a magnetic field have only *two discrete* values of the component of the magnetic moment in the direction of the field strength; both have the same absolute value with each half of the atoms having a positive and a negative sign respectively (Gerlach and Stern 1924, pp. 690–691, FW)

Experimental results, as well as experiments, also have a life of their own, independent of theory.

Normal Zeeman effect

In an experiment performed by the Dutch physicist Peter Zeeman in 1896, it was observed that each spectral line in the excitation spectrum for an atom placed in a magnetic field split into number of additional lines. Furthermore, the difference in energy between the new lines and the original line was found to be directly proportional to the strength of the external field. This effect came to be known as Zeeman effect. It could only be explained using quantum mechanics which says that the orbital angular momentum is quantized both in magnitude and direction:

$|\mathbf{L}| = \sqrt{l(l+1)}\,\hbar$ and $L_z = m_l\,\hbar$



The circulating electron would create a magnetic field and hence give rise to a magnetic dipole moment μ_{L}. It is left for the students to derive the relation betwen μ_{L} and the orbital angular momentum ($\mathbf{L}$) of the electron:

$$\mu_{\mathrm{L}} = -\frac{e}{2m}\mathbf{L}$$

Now if the current loop is placed in an external manetic field (along the z direction (say)), then the torque τ on the magnetic dipole is

$$\tau = \mu_{\mathrm{L}} \times \mathbf{B}$$

and the coresponding potential energy is given by

$$\begin{aligned} E_B &= -\mu_{\mathrm{L}} \cdot \mathbf{B} \\ &= \frac{e}{2m}\mathbf{L} \cdot \mathbf{B} \\ &= \frac{e}{2m}L_z B \end{aligned}$$

According to quantum mechanics $L_z = m_l \hbar$. Therefore the total energy is

$$\begin{aligned} E &= E_0 + E_B \\ &= E_0 + \frac{e}{2m} m_l \hbar B \\ &= E_0 + m_l \mu_B B \end{aligned}$$

E_0 is the energy in the absence of the field and $\mu_B = \frac{e}{2m}\hbar$ is called the Bohr magneton, having dimensions the same as the dipole moment μ.

Thus each energy level splits into $2l + 1$ levels, since m_l=-l to +l in integral steps.

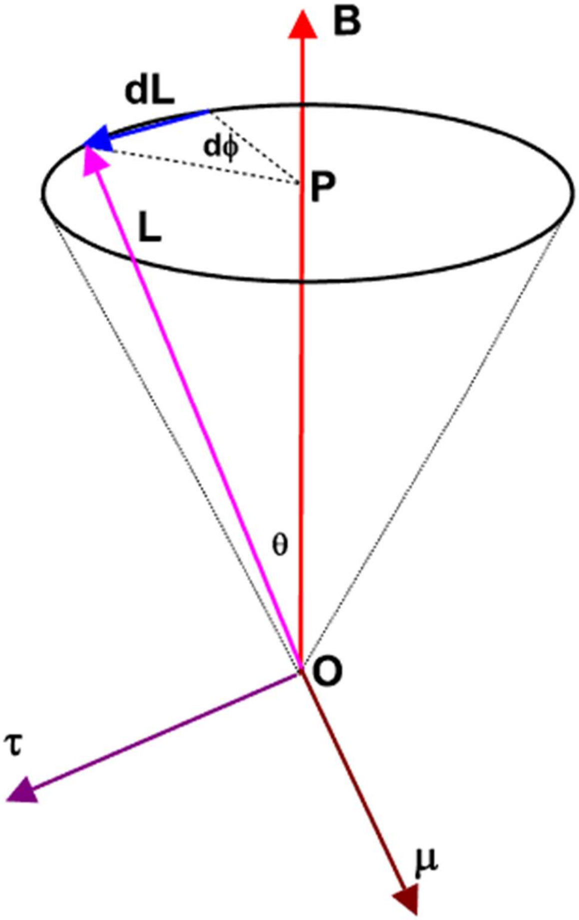
The emission spectrum of the atom placed in the external magnetic field $\mathbf{B}$ will however show only two additional lines apart from the original line. This is because the selection rules for electric dipole transitions are

$$\begin{aligned} \Delta l &= \pm 1 \\ \Delta m_l &= \pm 1 or 0 \end{aligned}$$

The frequency or wavelength of the three lines can be obtained from the relations

$$\begin{aligned} \Delta E &= \Delta E_0 and \\ \Delta E &= \Delta E_0 \pm \mu_B B \end{aligned}$$

The two symmetricaly placed lines on either side of the zero-field line are shifted in energy by $\mu_B B$. These three lines constitute what is known as a triplet.



The magnetic dipole moment μ of the electron is antiparallel to the orbital angular momentum $\mathbf{L}$. Both precess around the constant magnetic field $\mathbf{B}$ with an angular frequency of precession proportional to the field-strength and given by

$$\omega_p = \frac{e}{2m}B.$$

This precession is called ***Larmor precession***. ω_p is also equal to the frequency shift of the Zeeman lines originating from the external field from the field-free line.

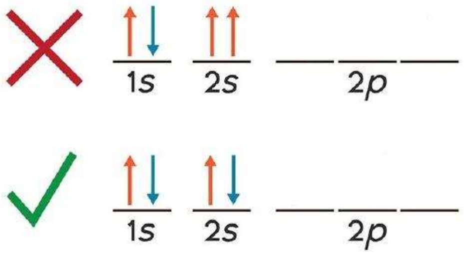
Note that for $(2l + 1)$ different values of m_l we have $(2l + 1)$ different values of the projection of $\mathbf{L}$, viz., $L_z = m_l \hbar$ or $(2l + 1)$ different values of θ. This aspect is referred to as space quantization of the orbital angular momentum in the presence of an external field.

Many electron atoms:

Pauli's Exclusion Principle:

The Pauli Exclusion Principle states that, in an atom or molecule, no two electrons can have the **same** four electronic quantum numbers. As an orbital can contain a maximum of only two electrons, the two electrons must have opposing spins. This means if one is assigned an up-spin (+1/2), the other must be down-spin (-1/2).

Electrons in the same orbital have the same first three quantum numbers, e.g., n=1n=1, l=0l=0, ml=0ml=0 for the 1*s* subshell. Only two electrons can have these numbers, so that their spin moments must be either ms=−1/2ms=−1/2 or ms=+1/2ms=+1/2. If the 1*s* orbital contains only one electron, we have one msms value and the electron configuration is written as $1s^1$ (corresponding to hydrogen). If it is fully occupied, we have two msms values, and the electron configuration is $1s^2$ (corresponding to helium). Visually these two cases can be represented as



Symmetric / antisymmetric wave functions

We have to construct the wave function for a system of identical particles so that it reflects the requirement that the particles are indistinguishable from each other. Mathematically, this means interchanging the particles occupying any pair of states should not change the probability density ($|\Psi|^2$) of the system. This simple statement has the enormous consequence of dividing all particles in nature into one of two classes.

An example for two non-interacting identical particles will illustrate the point. The probability density of the the two particle wave function $\Psi(\mathbf{r_1}, \mathbf{r_2})$ must be identical to that of the the wave function $\Psi(\mathbf{r_2}, \mathbf{r_1})$ where the particles have been interchanged.

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\Psi(\mathbf{r}_2, \mathbf{r}_1)|^2 \tag{55}$$

We can achieve this in two ways.

$$\text{Symmetric case :} \quad \Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1) \tag{56}$$

or

$$\text{Anti-symmetric case :} \quad \Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1) \tag{57}$$

It turns out that particles whose wave functions which are symmetric under particle interchange have integral or zero intrinsic spin, and are termed bosons. Particles whose wave functions which are anti-symmetric under particle interchange have half-integral intrinsic spin, and are termed fermions. Experiment and quantum theory place electrons in the fermion category. Any number of bosons may occupy the same state, while no two fermions may occupy the same state. This result, which establishes the behaviour of many-electron atoms, is proved below.

Spin Orbit Coupling

The spin angular momentum of electron can interact with its orbital angular momentum. This lead to splitting of different energy levels which can lead to different transition energies. This effect is known as spin orbit coupling. In simple words we can explain it as how a particles spin and orbital angular momentum interact together.

The total angular momentum is obtained due to the interaction between spin and orbital angular momentum. The value of this total momentum is maximum when both the spin and orbital momentum is parallel. We can get the total angular momentum due to the following coupling equation

$J = (L+S), (L+S-1), \ldots\ldots, (L-S)$

Here, J represents the total angular quantum number, L gives the orbital quantum number and S represents spin quantum number.

We can observe splitting in hydrogen atom emission spectra due to the spin orbit coupling. The electron here has an intrinsic spin given as

$s = \frac{1}{2}, m_s = \pm\frac{1}{2}$

The orbital spin of electron is,

$l = -l \ldots\ldots\ldots\ldots +l$

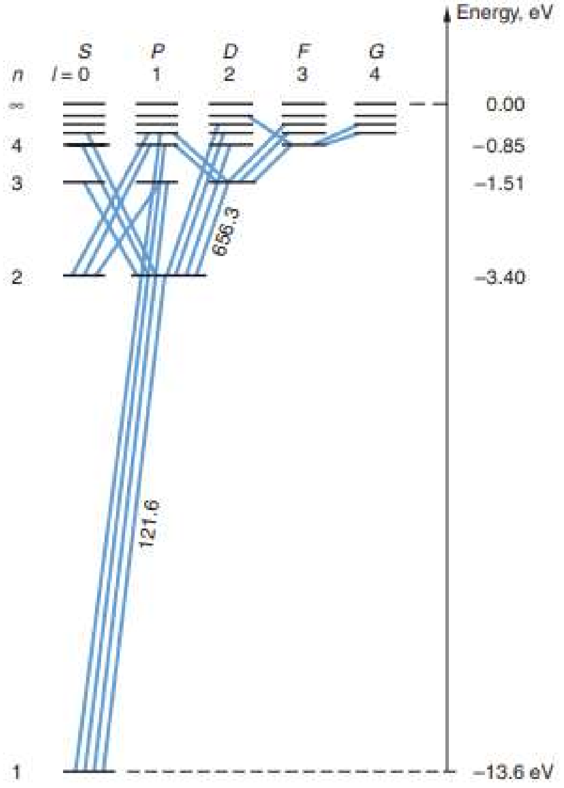
Both the spin and orbital momentum couple together and the total angular momentum can be obtained in hydrogen atom. This lead to the splitting in its emission spectra. Spin orbital coupling also has many other application. The magneto crystalline anisotropy caused due to this interaction.

The spin orbit coupling of electrons in semiconductor is found have variety of technological applications. The neutrons and protons spin orbital coupling in atom is of great importance as it gives a great contribution towards the total interaction energy

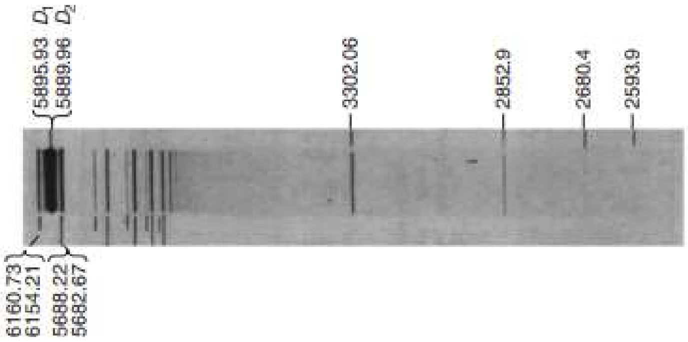
The neutral particles can also show spin orbit coupling since it has both the spin and orbital angular momenta.

Spectroscopic Notation

The absorption spectrum of hydrogen consists of those transitions whereby electrons in the ground state of the atom absorb energy from the incident light's continuous spectrum and are raised to certain of the various hydrogen excited states. In emission these are the lines of the Lyman series (see Figure SN-1). In the early days of atomic spectroscopy the spectrum of hydrogen, the simplest of the atoms, was much studied and its spectrum served as a benchmark relative to which the spectra of other, more complex atoms were compared and analyzed in the search for understanding of atomic structure. When the absorption spectra of the alkali metals (lithium, sodium, potassium, etc.) were obtained, it was at once apparent that they closely resembled the hydrogen absorption spectrum. That is, like hydrogen, they consisted of series of lines with regularly decreasing separations and intensities. Thus, they were accorded the distinction of being called the principal series. In the emission spectra of the alkali elements other series appeared in addition to the principal series of the absorption spectrum. The lines of one of the additional spectra appeared quite sharp on the photographic plates used to record them and so was given the name the sharp series. The lines of one of the other series seen in emission, less intense than those of the sharp series, appeared rather fuzzy or diffuse, so its name became the diffuse series (see Figure SN-2). Further in the infrared and lees intense than the diffuse series was the fundamental series (originally called the Bergmann series after its discoverer). The wave numbers (=1>wavelengths) of the spectral lines of each series were determined empirically from differences between a series-specific limiting term and a running term, the latter proportional to 1 divided by the square of an integer in a way similar to the Rydberg formula. Quantum theory subsequently associated each of the spectroscopic terms with an allowed energy state of the atom. For the spectra of the alkali elements the principal series in absorption corresponded to transitions from the ground energy state (the lowest S term) to the various

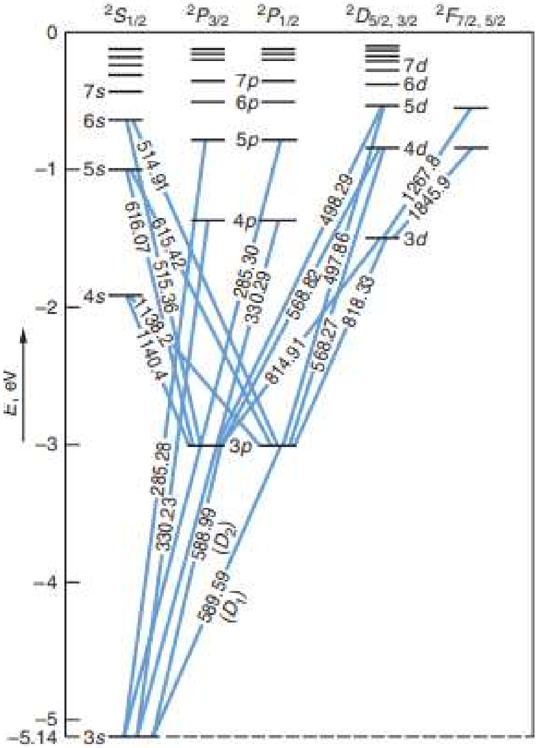


SN-1 Energy-level diagram for the hydrogen atom. The hydrogen absorption spectrum, the principal series, consists of those lines originating on the 1*s* state. In emission these are the spectral lines of the Lyman series.



SN-2 A portion of the emission spectrum of sodium. The delineating marks above the spectrum identify the lines of the principal series. Below the spectrum the shorter marks indicate the lines of the sharp series, the longer marks the lines of the diffuse series. The several wavelength values shown are in angstroms. Note that the very intense Na D lines are part of the principal series. [Adapted from G. Hertzberg, Atomic Spectra and Atomic Structure (New York: Prentice-Hall, 1937).]

principal (P term) energy states and just the reverse for the principal emission spectrum. The sharp series corresponded to transitions from the higher sharp (S terms) energy states—the running terms—to the lowest principal (P term) state, the limiting term for the sharp series (see Figure SN-3). Similarly, the diffuse emission spectrum was the result of transitions from the higher diffuse (D terms) energy states to the lowest principal (P term) state, the same limiting term as for the sharp series. Finally, the fundamental emission spectrum was the result of transitions from the higher fundamental (F terms) energy states to the lowest D term state, the limiting term for the fundamental series. In Figure SN-3 the principal emission series of sodium consists of those transitions originating on p states and ending on the 3s level (the lowest S term). The sharp series consists of those transitions originating on the 4s and higher s states and ending on the 3p state (the lowest P term). Similarly, the diffuse series is made up of those transitions from the d states to the 3p state and the fundamental series from the f states to the 3d state. The concept of spectral "terms" and the use of series names such as principal, sharp, and so on has now passed from common use, replaced by the quantitative understanding of atomic structure provided by quantum mechanics. However, the notational shorthand used by the early spectroscopists was adapted and modified to describe succinctly all atomic states, not just those of the alkali elements, and ultimately the quantum states of molecules, nuclei, and particles. The notation "code" is easy to learn and, as you will discover, convenient to use. For single electrons we have 1. For single-electron states the letter code s p d f g h . . . is used in one-to-one correspondence with the values of the orbital angular momentum quantum number /: 0 1 2 3 4 5. . . . For example, an electron with / = 2 is said to be a d electron or in a d state. 2. The single-electron (Bohr) energy levels are called shells, labeled K L M N O . . . in one-to-one correspondence with the values of the principal quantum number n: 1 2 3 4 5. . . . For example, an electron with n □ 3 in an atom is said to be in the M shell. (This notation is less commonly used.) For atomic states that may contain one or more electrons the notation includes the principal quantum number and the angular momenta quantum numbers. The total orbital angular momentum quantum number is denoted by a capital letter in the same sequence as in rule 1 above; that is, S P D F . . . correspond to / values 0 1 2 3. . . .



SN-3 Energy-level diagram for sodium (Na). The spectroscopic series notation was related by quantum theory to the principal and angular momentum quantum numbers. Wavelengths of the transitions shown are in nanometers.

The value of n is written as a prefix and the value of the total angular momentum quantum number j by a subscript. The magnitude of the total spin quantum number s appears as a left superscript in the form 2s 1 1. Thus, a state with / = 1, a P state, would be written as n2s+1 Pj For example, the ground state of the hydrogen atom (n □ 1, / = 0, s = 1>2) is written 12 S1 2, read “one doublet S one-half.” The n □ 2 state can have / = 0 or / = 1, so the spectroscopic notation for these states is 22 S1 2, 22 P3>2, and 22 P1 2. (The principal quantum number and spin superscript are sometimes not included if they are not needed in specific situations.) Appropriate versions of the notation are used to describe the quantum states of molecular constituents, the protons and neutrons in nuclei, and the states of fundamental particles.

LS-coupling and jj-coupling

Spin-orbit interaction in multi-electron atoms

• We now have two effects to consider:

• 1: Interaction between ~s and ~l for every electron - ~j = ~l + ~s

• 2: Angular part of the electrostatic interaction between the electrons -(~l1 +~l2 +~l3 + ··· = L~ ~s1 + ~s2 + ~s3 + ··· = S~

• Both these effects have to be included in a total Hamiltonian H = HCF + Hres + HSO The parts of the Hamiltonian

• The central field Hamiltonian HCF = X N i=1 Hi = X N i=1 1 2 r2 ri + VCF(ri) = X N i=1 1 2 r2 ri Z ri + S(ri) - kinetic energy of all electrons - Coulomb attraction to the nucleus for all electrons - the central (radial) part of the Coulomb repulsion between all electrons LectureNotesPh

• The residual Coulomb Hamiltonian Hres = X N j>i 1 rij X N i=1 S(ri) - The angular (residual) part of the Coulomb interaction between electrons - coupling of the angular momenta of the individual electrons

• The spin-orbit Hamiltonian HSO = X N i=1 ⇠(ri)~li · ~si- the sum of all spin-orbit interactions

Karpagam Academy of Higher Education
Department of Physics
III B.Sc Physics
Quantum Mechanics (16PHU602A)
Multiple Choice Questions

Question	**Choice 1**	**Choice 2**	**Choice 3**
The basis of all molecular approximation is the large ratio of _	electro	electron	electro
The energy associated with the motion of then nuclei is much ___	larger	smaller	varied
The period of nuclear motion is of the order of _________ divid	ђ	e	–ђ
The nuclear periods are _________ than the electronic periods	smaller	stable	longer
The nuclear motion are classified into translation and rotational	quasi-rigic	stable	unstable
Molecular energy levels are classified into _____________ vibrat	static	rigid	translation
The energy E_e associated with the motion of a valence is of order	–ђ^2/ma^2	–ђ^2/ma^2	–ђ^2/ma^2 +
The only nuclear coordinates R_j of the hydrogen molecule is th	R	r	–R
The linear combination of unperturbed degenerate wave function	heteropola	nuclei	homopola
The property of degeneracy is known as ______________.	resonance	doublet se	doublet in
An interaction between two resonant (degenerate) states in quant	eigen func	eigen valu	wave
The wave function based on a simple product of two ground state	alkali aton	helium atc	hydrogen
In case of hydrogen molecule, the equilibrium value for r_{AB} is the	0.74 A°	0.8 A°	1.06 A°
The ground state of a hydrogen molecule is ___________	a triplet st	a mixture	neither a s
The interaction between valence electrons give rise to _______ fo	bonding	electrostat	coloumbic
Heitler and London theory of hydrogen molecule helps us to deve	covalent	chemical	ionic
The spin functions of two electrons are a(1) and a(2), then the tota	either one	wavelengt	a and b
The complete wavefunction of an electron is the product of ____	unperturbe	perturbed	orbital
The symmetric orbital functions of an electron will be associated	skew symı	symmetric	a and b
The antisymmetric orbital function will be associated with _____	symmetric	skew symı	antisymme
If r_{12} is the distance between two electrons, then the interaction be	$-e^2/r_{12}{}^2$	$-e^2/r_{12}$	$-2e^2/r_{12}{}^2$
If the system consists of two hydrogen nuclei ‘a’ and ‘b’ and two	$e^2/r_{ab} + e^2/$	$e^2/r_{ab} + e^2/$	$e^2/r_{ab} + e^2/$
___________theory is also an approximation method for explair	vander wa	valence bc	scattering
The attraction of two hydrogen atom give rise to the formation of	stable	unstable	colloidal
If we assume both the hydrogen atom are in ground state, then bot	imaginary	integer	real
The schroedinger equation for hydrogen molecule is given by __	Ñ$_1{}^2$y + Ñ$_2$	Ñ$_1{}^2$y + Ñ$_2$	Ñ$_1{}^2$y + Ñ$_2$
If the co-ordinates of 1st electron is (x_1,y_1,z_1) and of 2nd electron	$\surd(x_2-x_1)^2$ -	$(x_2-x_1)^2$ +	$\surd(x_2-x_1)^2$ -
The SP^3 hybridisation leads to ________________ equivalent bo	3	4	6
The ground state of a hydrogen atom is ____________.	a triplet	a mixture	neither sin
If the spins of electron in two atoms are parallel then the atoms __	singlet	a. attra	coagulate
If the spins of the electrons in two atoms are antiparallel, then twc	repel	a. attra	coagulate
If two spins S_1 and S_2 of the electron combine to give a resultant s	doublet	triplet	multiplet
If two spins S_1 and S_2 of the electron combine to give a resultant	triplet	doublet	singlet
Hartree-Fock method incorporates the effect of _________ symm	skew	anti	exchange
The molecular wave function as a linear combination of atomic oı	LCAO	Exchange	MO

The effect of exchange symmetry has been incorporated in ____	Hartree-F	Hartree’s	Thomas –
The effect of exchange symmetry has been incorporated in _____	109°28’	180°	0°
In case of hydrogen molecule ion, the minimum potential energy	2.78 eV	4.72 eV	3.14 eV
Resonance is the property of __________	degenerac	doublet	singlet
The symmetric spin function will be associated with __________	skew sym	hermitian	antisymm

Prepared by Dr. B. Janarthanan, Associate Professor, Karpagam Academy of Higher Education

Choice 4	Choice 5	Choice 6	Answer
nuclear mass to electron mas			nuclear mass to electron mass
none of the above			smaller
–e			ђ
a and b			longer
neutral			quasi-rigid
electronic			electronic
$ђ^2/ma^2 + 1$			$–ђ^2/ma^2$
R^2			R
atomic			homopolar
none of the above			resonance
wave function			eigen value
hydrogen atom.			hydrogen atom.
1.32 A^o			0.8 A^o
a singlet state			a singlet state
a. repulsive			bonding
a. none of the above			chemical
two			two
none of the above.			orbital
antisymmetric			antisymmetric
b and c			symmetric
$–3e^2/r_{12}^2$			$–e^2/r_{12}$
$e^2/r_{ab} + e^2/r_{12}- e^2/r_{a1}- e^2/r_{b1}- e^2/r_a$			$e^2/r_{ab} + e^2/r_{12}- e^2/r_{a1}- e^2/r_{b1}- e^2/r_{a2}- e^2/r_{b2}$
partial wave.			valence bond
suspension			stable
none of the above			real
$Ñ_1^2y + Ñ_2^2y - (2m/ ђ^2) (E-V) y =$			$Ñ_1^2y + Ñ_2^2y + (2m/ ђ^2) (E-V) y = 0$
$\sqrt{}(x_2-x_1)^2 + (y_2-y_1)^2 - (z_2-z_1)^2$			$\sqrt{}(x_2-x_1)^2 - (y_2-y_1)^2 - (z_2-z_1)^2$
2			3
singlet			singlet
none of the above			singlet
none of the above			a. attract
singlet			singlet
multiplet			triplet
none of the above			exchange
none of the above			LCAO

None of the above	Hartree’s self consistent method
120°	109°28’
1.76 eV	1.76 eV
triplet	degeneracy
triplet	antisymmetric