e-Module and e-Content Developed by the Faculty Members

Relativistic Quantum Mechanics

by

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Notations

In the four dimensional space-time manifold, commonly known as the Minkowski space, the four vectors are defined by

$$x^\mu = (ct, \mathbf{x}),$$

$$x_\mu = (ct, -\mathbf{x}). \qquad (\mu = 0, 1, 2, 3)$$

The contravariant and the covariant vectors are related to each other through the metric tensor of the four dimensional manifold, namely,

$$x_\mu = \eta_{\mu\nu} x^\nu,$$

$$x^\mu = \eta^{\mu\nu} x_\nu.$$

$$\eta^{\mu\nu} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$\eta_{\mu\nu} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}.$$

The operator implying differentiation with respect to a contravariant (covariant) coordinate vector component transforms as a component of a covariant (contravariant) vector,

$$\left.\begin{aligned}\partial^{\mu} \equiv \frac{\partial}{\partial x_{\mu}} &= \left(\partial^0, \partial^1, \partial^2, \partial^3\right) = \left(\frac{\partial}{\partial x_0}, -\vec{\nabla}\right) \\ \partial_{\mu} \equiv \frac{\partial}{\partial x^{\mu}} &= \left(\partial_0, \partial_1, \partial_2, \partial_3\right) = \left(\frac{\partial}{\partial x^0}, \vec{\nabla}\right)\end{aligned}\right\}$$

where $\vec{\nabla} = \left(\frac{\partial}{\partial x^1}, \frac{\partial}{\partial x^2}, \frac{\partial}{\partial x^3}\right) = \left(\partial_1, \partial_2, \partial_3\right) = \left(-\partial^1, -\partial^2, -\partial^3\right)$ is the 3-divergence.

(thus $\vec{\nabla}.\vec{A} = \partial_k A^k$).

We may then define a 4-divergence of a 4-vector A^{μ} by

$$\partial_{\mu} A^{\mu} = \partial^{\mu} A_{\mu} = \frac{\partial A^0}{\partial x^0} + \vec{\nabla}.\vec{A} = \frac{\partial A^0}{\partial x^0} + \vec{\nabla}_i.A^i$$

In this notation the 4-dimensional d'Alembertian operator is the contraction

$$\Box^2 \equiv \partial_{\mu}\partial^{\mu} = \frac{\partial^2}{\partial x^0 \partial x_0} - \nabla^2 = \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2$$

and is a scalar under Lorentz transformations.

Klein-Gordon equation

The relativistic relation between the energy and momentum of a free particle is

$$E^2 = \vec{p}^2 c^2 + m^2 c^4$$

Substituting $E = i\hbar\frac{\partial}{\partial t}; \quad \vec{p} = -i\hbar\vec{\nabla}$, we have

$$-\hbar^2 \frac{\partial^2 \psi}{\partial t^2} = -\hbar^2 c^2 \nabla^2 \psi + m^2 c^4 \psi$$

Simplifying the above equation we get $\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 + \frac{m^2 c^2}{\hbar^2}\right)\psi = 0$

$$\left(\Box^2 + \frac{m^2 c^2}{\hbar^2}\right)\psi = 0, \qquad \text{where } \Box^2 \equiv \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2$$

This equation is known as Klein-Gordon equation.

There is no way in which the Pauli spin matrices can be included in Klein-Gordon equation without destroying the invariance of the theory. This is because the spin matrices transform like the components of three dimensional vector, rather than a four dimensional vector.

Thus the Klein-Gordon relativistic equation represents a particle that has no spin.

Solution of Klein-Gordon equation is of the form

$$\psi = N\exp\left(i(\vec{p}\cdot\vec{x} - Et)\right)$$

where N is the normalization constant and

$$E = \pm\left(p^2 c^2 + m^2 c^4\right)^{1/2}$$

In addition to the acceptable $E > 0$ solutions, we also have negative energy solution. A second problem is that $E < 0$ solutions are associated with a negative probability density. The negative energy solutions cannot be simply discarded as these correspond to *antiparticles*.

Plane wave solutions

Klein-Gordon equation also has plane wave solutions which are characteristic of free particle solutions. In fact, the functions

$$e^{\mp ik\cdot x} = e^{\mp ik_\mu x^\mu} = e^{\mp ik^\mu x_\mu} = e^{\mp i(k_0 t - \mathbf{k}\cdot\mathbf{x})}$$

with $k^\mu = (k^0, \mathbf{k})$ are eigenfunctions of the energy-momentum operator,

$$p^\mu e^{\mp ik\cdot x} = i\partial^\mu e^{\mp ik\cdot x} = i\frac{\partial}{\partial x_\mu} e^{\mp ik\cdot x} = \pm\ \hbar k^\mu e^{\mp ik\cdot x}$$

so that $\pm k^\mu$ are the eigenvalues of the energy-momentum operator. This shows that the plane waves define a solution of the Klein-Gordon equation provided

$$k^2 - m^2\mathbf{c}^2 = (k^0)^2 - \mathbf{k}^2 - m^2\mathbf{c}^2 = 0$$

$$k^0 = \pm E = \pm\sqrt{\mathbf{k}^2 + m^2\mathbf{c}^2}$$

Klein-Gordon equation and its complex conjugate

$$(\Box^2 + \frac{m^2\mathbf{c}^2}{\mathbf{h}^2})\psi = 0$$

$$(\Box^2 + \frac{m^2\mathbf{c}^2}{\mathbf{h}^2})\psi^* = 0$$

would imply

$$\psi^*\Box^2\psi - \psi\Box^2\psi^* = 0$$

$$\partial_\mu(\psi^*\partial^\mu\psi - \psi\,\partial^\mu\psi^*) = 0$$

$$\frac{\partial}{\partial t}\left(\psi^*\frac{\partial\psi}{\partial t} - \psi\ \frac{\partial\psi^*}{\partial t}\right) - \nabla\cdot(\psi^*\nabla\psi - \psi\ \nabla\psi^*) = 0$$

Defining the probability current density four vector as

$$J^{\mu} = (j^0, \mathbf{J}) = (\rho, \mathbf{J})$$

where

$$\begin{aligned} \mathbf{J} &= \frac{1}{2im}\left(\psi^* \boldsymbol{\nabla}\psi - \psi \ \boldsymbol{\nabla}\psi^*\right) \\ \rho &= \frac{i}{2m}\left(\psi^* \frac{\partial \psi}{\partial t} - \psi \ \frac{\partial \psi^*}{\partial t}\right) \end{aligned}$$

This shows that the continuity equation for the probability current is

$$\partial_{\mu} J^{\mu} = \frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{J} = 0$$

The probability current density

$$\mathbf{J} = \frac{1}{2im}\left(\psi^* \boldsymbol{\nabla}\psi - \psi \ \boldsymbol{\nabla}\psi^*\right)$$

of course, has the same form as in non-relativistic quantum mechanics. However, we note that the form of the probability density (which results from the requirement of covariance)

$$\rho = \frac{i}{2m}\left(\psi^* \frac{\partial \psi}{\partial t} - \psi \ \frac{\partial \psi^*}{\partial t}\right)$$

is quite different from that in non-relativistic quantum mechanics and it is here that the problem of the negative energy states shows up. For example, even for the simplest of solutions, namely, plane waves of the form

$$\phi(x) = e^{-ik\cdot x}$$

we obtain

$$\rho = \frac{i}{2m}(-ik^0 - ik^0) = \frac{k^0}{m} = \pm\frac{E}{m}$$

Since energy can take both positive and negative values, it follows that ρ cannot truly represent the probability density which, by definition, has to be positive semi-definite. Klein-Gordon equation is second order in time derivatives. This has the consequence that the probability involves a first order time derivative and that is how the problem of the negative energy states enters.

The positive energy solutions alone do not define a complete set of states (basis) in the Hilbert space and, consequently, even if we restrict the states to be of positive energy to begin with, negative energy states may be generated through quantum mechanical corrections.

It is for these reasons that the Klein-Gordon equation was abandoned as a quantum mechanical equation for a single relativistic particle.

Dirac equation

The origin of negative probability density is the second order derivative $\frac{\partial}{\partial t}$ in the Klein-Gordon equation. In order to avoid these problems, Dirac in the year 1927, derived a relativistic wave equation linear in $\frac{\partial}{\partial t}$ and ∇. He succeeded in overcoming the problem of the negative probability density, with the unexpected bonus that the equation described spin-1/2 particles.

Dirac approached the problem of finding a relativistic wave equation by starting from the Hamiltonian of the form

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = H\psi(\vec{r},t) \qquad or \qquad E\psi = H\psi$$

The simplest Hamiltonian that is linear in the momentum and mass term is

$$H = c\vec{\alpha}.\vec{p} + \beta mc^2$$

Substituting H, we have

$$\left(E - c\vec{\alpha}.\vec{p} - \beta mc^2\right)\psi = 0$$

or

$$\left(i\hbar\frac{\partial}{\partial t} + i\hbar c\vec{\alpha}.\vec{\nabla} - \beta mc^2\right)\psi = 0$$

where $\vec{\alpha}$ has three components α_x, α_y and α_z.

Multiplying by $\left[E + c\vec{\alpha}.\vec{p} + \beta mc^2\right]$ from left, we have

$$\left[E + \left(c\vec{\alpha}.\vec{p} + \beta mc^2\right)\right]\left[E - \left(c\vec{\alpha}.\vec{p} + \beta mc^2\right)\right]\psi = 0$$
$$\left[E^2 - \left(c\vec{\alpha}.\vec{p} + \beta mc^2\right)\left(c\vec{\alpha}.\vec{p} + \beta mc^2\right)\right]\psi = 0$$

Using $\vec{\alpha}.\vec{p} = \left(\hat{i}\alpha_x + \hat{j}\alpha_y + \hat{k}\alpha_z\right).\left(\hat{i}p_x + \hat{j}p_y + \hat{k}p_z\right) = \alpha_x p_x + \alpha_y p_y + \alpha_z p_z$

the term $\left(c\vec{\alpha}.\vec{p} + \beta mc^2\right)\left(c\vec{\alpha}.\vec{p} + \beta mc^2\right)$ can be simplified as follows:

$$\begin{aligned}
&\left(c\vec{\alpha}.\vec{p} + \beta mc^2\right)\left(c\vec{\alpha}.\vec{p} + \beta mc^2\right)\\
&= \left[c\left(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z\right) + \beta mc^2\right].\left[c\left(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z\right) + \beta mc^2\right]\\
&= c^2\left[\left(\alpha_x^2 p_x^2 + \alpha_y^2 p_y^2 + \alpha_z^2 p_z^2\right) + \alpha_x p_x\alpha_y p_y + \alpha_x p_x\alpha_z p_z + \alpha_y p_y\alpha_x p_x + \alpha_y p_y\alpha_z p_z + \right.\\
&\quad \left.\alpha_z p_z\alpha_x p_x + \alpha_z p_z\alpha_y p_y\right] + m^2c^4\beta^2 + mc^3\left(\alpha_x p_x\beta + \alpha_y p_y\beta + \alpha_z p_z\beta\right) +\\
&\quad mc^3\left(\beta\alpha_x p_x + \beta\alpha_y p_y + \beta\alpha_z p_z\right)\\
&= c^2\left[\alpha_x^2 p_x^2 + \alpha_y^2 p_y^2 + \alpha_z^2 p_z^2 + \left(\alpha_x\alpha_y + \alpha_y\alpha_x\right)p_x p_y + \left(\alpha_y\alpha_z + \alpha_z\alpha_y\right)p_y p_z + \right.\\
&\quad \left.\left(\alpha_z\alpha_x + \alpha_x\alpha_z\right)p_z p_x\right] + m^2c^4\beta^2 + mc^3\left[\left(\alpha_x\beta + \beta\alpha_x\right)p_x + \left(\alpha_y\beta + \beta\alpha_y\right)p_y + \left(\alpha_z\beta + \beta\alpha_z\right)p_z\right]
\end{aligned}$$

Using above relation, the above eq. becomes

$$\begin{aligned}
&\left\{E^2 - c^2\left[\alpha_x^2 p_x^2 + \alpha_y^2 p_y^2 + \alpha_z^2 p_z^2 + \left(\alpha_x\alpha_y + \alpha_y\alpha_x\right)p_x p_y + \left(\alpha_y\alpha_z + \alpha_z\alpha_y\right)p_y p_z + \right.\right.\\
&\left.\left.\left(\alpha_z\alpha_x + \alpha_x\alpha_z\right)p_z p_x\right] - mc^3\left[\left(\alpha_x\beta + \beta\alpha_x\right)p_x + \left(\alpha_y\beta + \beta\alpha_y\right)p_y + \left(\alpha_z\beta + \beta\alpha_z\right)p_z\right] - m^2c^4\beta^2\right\}\psi = 0
\end{aligned}$$

This equation agrees with free particle equation

$$-\hbar^2 \frac{\partial^2 \psi}{\partial t^2} = -\hbar^2 c^2 \nabla^2 \psi + m^2 c^4 \psi$$

when $\vec{\alpha}, \beta$ satisfy the relations

$$\left.\begin{array}{c} \alpha_x^2 = \alpha_y^2 = \alpha_z^2 = 1 \\ \beta^2 = 1 \\ \alpha_x\alpha_y + \alpha_y\alpha_x = \alpha_y\alpha_z + \alpha_z\alpha_y = \alpha_z\alpha_x + \alpha_x\alpha_z = 0 \\ \alpha_x\beta + \beta\alpha_x = \alpha_y\beta + \beta\alpha_y = \alpha_z\beta + \beta\alpha_z = 0 \end{array}\right\}$$

The four quantities α_x, α_y, α_z and β anticommute (anticommutator of two operators A and B is defined as {A,B}=AB+BA) in pairs, and their squares are unity. Further,

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

with $I \equiv \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ and $0 \equiv \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$

and $\vec{\sigma}$ are the Pauli spin matrices given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

More precisely

$$\alpha_x = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}; \qquad \alpha_y = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}$$

$$\alpha_z = \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}; \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

Covariant form of the Dirac equation

The relativistic Dirac equation is given as

$$i\hbar \frac{\partial \psi}{\partial t} = -i\hbar c\, \vec{\alpha}.\vec{\nabla}\psi + \beta mc^2 \psi$$

Multiplying by β from left, we have

$$i\hbar\beta \frac{\partial \psi}{\partial t} = -i\hbar c\, \beta\vec{\alpha}.\vec{\nabla}\psi + \beta^2 mc^2 \psi$$

$\beta^2 = 1$, therefore

$$i\hbar\beta \frac{\partial \psi}{\partial t} = -i\hbar c\, \beta\vec{\alpha}.\vec{\nabla}\psi + mc^2 \psi \qquad (1)$$

Now we introduce Dirac γ-matrices $\gamma^{\mu} \equiv (\beta, \beta\vec{\alpha})$ where μ=0, 1, 2, 3, i.e.

$$\gamma^0 = \beta$$
$$\gamma^i = \beta\alpha^k = \gamma^0\alpha^k \qquad k = 1,2,3$$

Using Dirac γ-matrices, eq. (1) may be written as

$$\left(i\hbar\gamma^{\mu}\frac{\partial}{\partial x^{\mu}} - mc\right)\psi = 0$$

$$or \qquad \left(i\hbar\gamma^{\mu}\partial_{\mu} - mc\right)\psi = 0$$

This eq. is the known as the covariant form of the Dirac equation.

Properties of Dirac matrices

The Dirac γ matrices satisfy the following anti commutation relations

$$\gamma^{\mu}\gamma^{\nu} + \gamma^{\nu}\gamma^{\mu} = 2g^{\mu\nu}$$

where $g^{\mu\nu}$ is metric tensor given by

$$g_{\mu\nu} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

Further, since $\gamma^0 = \beta$, we have

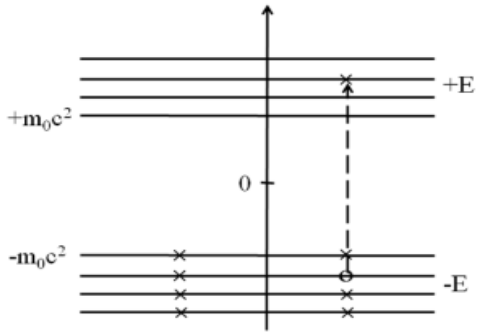
$$\gamma^{0\dagger} = \gamma^0, \quad \left(\gamma^0\right)^2 = I$$
$$\gamma^{k\dagger} = (\beta\alpha k)^{\dagger} = \alpha^k\beta = -\gamma^k$$
$$\left(\gamma^k\right)^2 = \beta\alpha^k\beta\alpha^k = -I$$

where k=1,2,3 and the superscript † denotes the Hermitian conjugate of a matrix which is obtained by interchanging the rows and columns and taking complex conjugate of each element. The Hermitian conjugation results can be summarized by

$$\gamma^{\mu\dagger} = \gamma^0\gamma^{\mu}\gamma^0$$

Positron theory

Dirac proposed that the negative energy states are occupied and the exclusion principle prevents transition into such occupied states. The normal states of the vacuum then consists of an infinite density of negative energy electrons called as negative energy sea. It is assumed that there are no electromagnetic or gravitational effects of these electrons but that deviations from the norm produced by emptying one or more of the negative energy states can be observed.



Schematic diagram showing transition from negative energy to positive energy.

The absence of a negatively charged electron that has negative mass and kinetic energy would then be expected to manifest itself as a positively charged particle that has an equal positive mass and kinetic energy. In this way, a "hole" theory or positrons can be developed without recourse to holes.

When an energy $E > 2m_0c^2$ is supplied to an electron of negative energy, it can be excited into a states of positive energy, as shown in figure . The absence of an electron of charge $-e$ and energy $-E$ is interpreted as the presence of an antiparticle (a positron) of charge $+e$ and energy $+E$. Thus the net effect of this excitation is the production of pair e^--e^+.

Dirac's equation with electromagnetic potentials

Terms involving electromagnetic potentials can be added to the Dirac's relativistic in a relativistic way by making the replacements

$$c\vec{p} \rightarrow c\vec{p} - e\vec{A}$$
$$E \rightarrow E - e\phi$$

where $\vec{A}$ and ϕ are the vector and scalar potentials, respectively. Substituting in eq. Dirac equation, we get

$$\left[E - e\phi - \vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right) - \beta mc^2\right]\psi = 0$$

Multiplying above equation by $\left[E - e\phi + \vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right) + \beta mc^2\right]$ from the left, we get

$$\left\{(E - e\phi)^2 - \left[\vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right)\right]^2 - m^2c^4 - (E - e\phi)\vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right) + \vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right)(E - e\phi)\right\}\psi = 0$$

Consider the identity

$$\left(\vec{\alpha}\cdot\vec{\beta}\right)\left(\vec{\alpha}\cdot\vec{C}\right) = \vec{B}\cdot\vec{C} + i\vec{\sigma}'\cdot\left(\vec{B}\times\vec{C}\right)$$

Replacing $\vec{B}$ and $\vec{C}$ with $\left(c\vec{p} - e\vec{A}\right)$, we get

$$\left[\vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right)\right]^2 = \left(c\vec{p} - e\vec{A}\right)^2 + i\vec{\sigma}'\cdot\left(c\vec{p} - e\vec{A}\right)\times\left(c\vec{p} - e\vec{A}\right)$$

Now $$\left(c\vec{p} - e\vec{A}\right)\times\left(c\vec{p} - e\vec{A}\right) = -ce\left(\vec{A}\times\vec{p} + \vec{p}\times\vec{A}\right)$$

The term $\vec{A}\times\vec{p} + \vec{p}\times\vec{A}$ can be evaluated as follows

$$\begin{aligned}
\left(\vec{A}\times\vec{p} + \vec{p}\times\vec{A}\right)\psi &= \vec{A}\times\vec{p}\psi + \vec{p}\times\left(\vec{A}\psi\right) \\
&= -i\hbar\left[\vec{A}\times\vec{\nabla}\psi + \vec{\nabla}\times\left(\vec{A}\psi\right)\right] \\
&= -i\hbar\left[\vec{A}\times\vec{\nabla}\psi + \vec{\nabla}\times\left(\psi\vec{A}\right)\right] \\
&= -i\hbar\left[\vec{A}\times\vec{\nabla}\psi + \psi\vec{\nabla}\times\vec{A} + \vec{\nabla}\psi\times\vec{A}\right] \\
&= -i\hbar\left(\vec{\nabla}\times\vec{A}\right)\psi \\
\left(\vec{A}\times\vec{p} + \vec{p}\times\vec{A}\right) &= -i\hbar\left(\vec{\nabla}\times\vec{A}\right)
\end{aligned}$$

Substituting, we have $$\left(c\vec{p} - e\vec{A}\right)\times\left(c\vec{p} - e\vec{A}\right) = ie\hbar c\vec{\nabla}\times\vec{A} = ie\hbar c\vec{B}$$

where $\vec{B}$ is the magnetic field.

$$\begin{aligned}
\left[\vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right)\right]^2 &= \left(c\vec{p} - e\vec{A}\right)^2 + i\vec{\sigma}'\cdot\left(ie\hbar c\vec{B}\right) \\
&= \left(c\vec{p} - e\vec{A}\right)^2 - e\hbar c\vec{\sigma}'.\vec{B}
\end{aligned}$$

Now we consider the last two terms

$$\begin{aligned}
&\left[-(E - e\phi)\vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right) + \vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right)(E - e\phi)\right]\psi \\
&= \left[-E\vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right) + e\phi\vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right) + \vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right)E - \vec{\alpha}\cdot\left(c\vec{p} - e\vec{A}\right)e\phi\right]\psi \\
&= \left[-E\vec{\alpha}\cdot c\vec{p} + E\vec{\alpha}\cdot e\vec{A} + e\phi\vec{\alpha}\cdot c\vec{p} - e\phi\vec{\alpha}\cdot e\vec{A} + \vec{\alpha}\cdot c\vec{p}E - \vec{\alpha}\cdot e\vec{A}E - \vec{\alpha}\cdot c\vec{p}e\phi + \vec{\alpha}\cdot e\vec{A}e\phi\right]\psi \\
&= \left[e\vec{\alpha}\cdot\left(E\vec{A} - \vec{A}E\right) + ce\vec{\alpha}\cdot\left(\phi\vec{p} - \vec{p}\phi\right)\right]\psi
\end{aligned}$$

Now $$\begin{aligned}(E\vec{A}-\vec{A}E)\psi &= E\vec{A}\psi-\vec{A}E\psi \\ &= i\hbar\frac{\partial}{\partial t}(\vec{A}\psi)-\vec{A}i\hbar\frac{\partial\psi}{\partial t} \\ &= \vec{A}i\hbar\frac{\partial\psi}{\partial t}+\left(i\hbar\frac{\partial\vec{A}}{\partial t}\right)\psi-\vec{A}i\hbar\frac{\partial\psi}{\partial t} \\ &= \left(i\hbar\frac{\partial\vec{A}}{\partial t}\right)\psi\end{aligned}$$

Further, $$\begin{aligned}(\phi\vec{p}-\vec{p}\phi)\psi &= -\phi i\hbar\vec{\nabla}\psi+i\hbar\vec{\nabla}(\phi\psi) \\ &= -i\hbar\phi\vec{\nabla}\psi+i\hbar(\vec{\nabla}\phi)\psi+i\hbar\phi\vec{\nabla}\psi = (i\hbar\vec{\nabla}\phi)\psi\end{aligned}$$

eq. takes the form

$$\begin{aligned}-(E-e\phi)\vec{\alpha}\cdot(c\vec{p}-e\vec{A})+\vec{\alpha}\cdot(c\vec{p}-e\vec{A})(E-e\phi) &= e\vec{\alpha}\cdot\left(i\hbar\frac{\partial\vec{A}}{\partial t}\right)+ce\vec{\alpha}\cdot(i\hbar\vec{\nabla}\phi) \\ &= ie\hbar c\vec{\alpha}\cdot\left(\frac{1}{c}\frac{\partial\vec{A}}{\partial t}+\vec{\nabla}\phi\right) \\ &= -ie\hbar c\vec{\alpha}\cdot\vec{E}\end{aligned}$$

where $\vec{E}=-\frac{1}{c}\frac{\partial\vec{A}}{\partial t}-\vec{\nabla}\phi$.

Finally, substituting , we get

$$\left[(E-e\phi)^2-(c\vec{p}-e\vec{A})^2-m^2c^4+e\hbar c\vec{\sigma}'\cdot\vec{B}-ie\hbar c\vec{\alpha}\cdot\vec{E}\right]\psi=0$$

Non relativistic limit

In order to obtain the non-relativistic limit we substitute

$$E\rightarrow E'+mc^2$$

Further, we assume $E'<<mc^2$ and $e\phi<<mc^2$. Now

$$\begin{aligned}(E-e\phi)^2 &= (E'+mc^2-e\phi)^2 \\ &= m^2c^4\left[1+\frac{E'-e\phi}{mc^2}\right]^2 \\ &= m^2c^4\left[1+\frac{2(E'-e\phi)}{mc^2}+\text{higher order terms}\right]\end{aligned}$$

Neglecting higher order terms, we get

$$(E-e\phi)^2\approx m^2c^4+2(E'-e\phi)mc^2$$

Substituting , we get

$$\left[2(E'-e\phi)mc^2-(c\vec{p}-e\vec{A})^2+e\hbar c\vec{\sigma}'\cdot\vec{B}-ie\hbar c\vec{\alpha}\cdot\vec{E}\right]\psi=0$$

or $$E'\psi=\left[\frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}\right)^2+e\phi-\frac{e\hbar}{2mc}\vec{\sigma}'\cdot\vec{B}+\frac{ie\hbar}{2mc}\vec{\alpha}\cdot\vec{E}\right]\psi$$

Here E' is equivalent to the time derivative operator $i\hbar\frac{\partial}{\partial t}$ if a factor $\exp(-imc^2t/\hbar)$ is taken out of ψ. The term containing $\vec{B}$ has the form associated with the energy of a magnetic dipole of moment $\vec{\mu}=\frac{e\hbar}{2mc}\vec{\sigma}'$. In practical cases the term containing $\vec{E}$ is of order of $(v/c)^2$ times the $e\phi$ term and hence may be neglected in the non relativistic limit.

Dirac's equation in a central field

The electron spin carries no energy in itself. Therefore, it can be observed only through its coupling with the orbital motion of the electron. This coupling can be made visible either *through conservation of total angular momentum* or t*hrough the spin-orbit energy*. In both cases we work with such potentials $\vec{A}, \phi$ that there is no transfer of angular momentum to the electron. This implies that we have a central field ($\vec{A} = 0$ and ϕ spherically symmetric).

Spin angular momentum

Dirac's equation with electromagnetic potentials is given as

$$\left[E - e\phi - \vec{\alpha}.\left(c\vec{p} - e\vec{A}\right) - \beta mc^2\right]\psi = 0$$

With $\vec{A}(\vec{r},t) = 0$ and $\phi(\vec{r},t) = \phi(r)$, we have

$$\left(E - V - c\vec{\alpha}\cdot\vec{p} - \beta mc^2\right)\psi = 0$$

$$E\psi = \left(c\vec{\alpha}\cdot\vec{p} + \beta mc^2 + V\right)\psi$$

where $V = e\phi$.

It might be expected that the orbital angular momentum $\vec{L} = \vec{r}\times\vec{p}$ is a constant of motion in such a central field. Let us investigate this point by calculating the time rate of change of $\vec{L}$ in the Heisenberg picture.

$$i\hbar\frac{dL_x}{dt} = [L_x, H] = \left[L_x, \left\{c\vec{\alpha}.\vec{p} + \beta mc^2 + V\right\}\right]$$
$$= \left[L_x, \left\{c\left(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z\right) + \beta mc^2 + V\right\}\right]$$

Using commutation relations

$$[L_x, c\alpha_x p_x] = \left[L_x, \beta mc^2\right] = [L_x, V(r)] = 0$$

the above eq. becomes

$$i\hbar\frac{dL_x}{dt} = [L_x, c\alpha_y p_y] + [L_x, c\alpha_z p_z]$$

Now

$$\begin{aligned}
[L_x, c\alpha_y p_y] &= c\alpha_y [L_x, p_y] \\
&= c\alpha_y \left[yp_z - zp_y, p_y\right] \\
&= c\alpha_y \left\{\left[yp_z, p_y\right] - \left[zp_y, p_y\right]\right\} \\
&= c\alpha_y \left\{[y, p_y]p_z + y\left[p_z, p_y\right] - [z, p_y]p_y - z\left[p_y, p_y\right]\right\} \\
&= i\hbar c\alpha_y p_z
\end{aligned}$$

Similarly

$$\begin{aligned}
[L_x, c\alpha_z p_z] &= c\alpha_z [L_x, p_z] \\
&= c\alpha_z \left[yp_z - zp_y, p_z\right] \\
&= c\alpha_z \left\{-[z, p_z]p_y\right\}
\end{aligned}$$

$$i\hbar\frac{dL_x}{dt} = [L_x, H] = \left[L_x, \{c\vec{\alpha}.\vec{p} + \beta mc^2 + V\}\right]$$
$$= \left[L_x, \{c(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z) + \beta mc^2 + V\}\right]$$

Using commutation relations $[L_x, c\alpha_x p_x] = [L_x, \beta mc^2] = [L_x, V(r)] = 0$

$$i\hbar\frac{dL_x}{dt} = [L_x, c\alpha_y p_y] + [L_x, c\alpha_z p_z]$$

Now
$$\begin{aligned}[L_x, c\alpha_y p_y] &= c\alpha_y [L_x, p_y] \\ &= c\alpha_y [yp_z - zp_y, p_y] \\ &= c\alpha_y \{[yp_z, p_y] - [zp_y, p_y]\} \\ &= c\alpha_y \{[y, p_y]p_z + y[p_z, p_y] - [z, p_y]p_y - z[p_y, p_y]\} \\ &= i\hbar c\alpha_y p_z\end{aligned}$$

Similarly
$$\begin{aligned}[L_x, c\alpha_z p_z] &= c\alpha_z [L_x, p_z] \\ &= c\alpha_z [yp_z - zp_y, p_z] \\ &= c\alpha_z \{-[z, p_z]p_y\} \\ &= -i\hbar c\alpha_z p_y\end{aligned}$$

$$i\hbar\frac{dL_x}{dt} = -i\hbar c(\alpha_z p_y - \alpha_y p_z)$$

Thus, L_x is not constant of motion.

However, on physical grounds it is possible to define total angular momentum that it is constant in a central field of force.

$$\begin{aligned}i\hbar\frac{d\sigma'_x}{dt} &= [\sigma'_x H] \\ &= \left[\sigma'_x, \{c\vec{\alpha}.\vec{p} + \beta mc^2 + V(r)\}\right] \\ &= \left[\sigma'_x, \{c(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z) + \beta mc^2 + V(r)\}\right]\end{aligned}$$

Using commutation relations $[\vec{\sigma}'_x, \alpha_y] = 2i\alpha_z; [\vec{\sigma}'_x, \alpha_z] = -2i\alpha_y; [\sigma'_x, \beta] = 0; [\sigma'_x, \alpha_x] = 0$

and the fact that σ'_x commutes with p_x, p_y and p_z as $\vec{p}$ is differential operator and $\vec{\sigma}'$ are numbers, the above eq. becomes

$$\begin{aligned}i\hbar\frac{d\sigma'_x}{dt} &= [\sigma'_x, c\alpha_y p_y + c\alpha_z p_z] \\ &= c[\vec{\sigma}'_x, \alpha_y]p_y + c[\vec{\sigma}'_x, \alpha_z]p_z \\ &= 2ic(\alpha_z p_y - \alpha_y p_z)\end{aligned}$$

Multiplying by $\hbar/2$ and adding to $i\hbar\frac{d\sigma'_x}{dt}$, we have

$$i\hbar\frac{d}{dt}\left(L_x + \frac{1}{2}\hbar\sigma'_x\right) = 0$$

Defining $\vec{J} = \vec{L} + \frac{1}{2}\hbar\vec{\sigma}'$ and $\vec{S} = \frac{1}{2}\hbar\vec{\sigma}'$ we have $\vec{J} = \text{constant}$ or $[\vec{J}, H] = 0$

where $\vec{J}$ can be taken as total angular momentum and $\vec{S}$ is the spin angular momentum of electron.

References used :

1. Relativistic Quantum Mechanics by J. D. Bjorken and S. D. Drell, Mc-Graw Hill, New York,
2. Advanced Quantum Mechanics by J. J. Sakurai, Addison-Wesley New York , &
3. Quantum Mechanics by L. I. Schiff, Mc-Graw Hill, Kogakusha.

Questions

1. Obtain the Klein-Gordon equation. What were its limitations?
2. Derive the Dirac equation for a free particle and obtain its solutions.
3. Develop the Dirac equation with the inclusion of electromagnetic vector and scalar potentials and obtain its non-relativistic limit.
4. Deduce the covariant form of Dirac equation and discuss the properties of Dirac γ-matrices.
5. Derive the Dirac equation under influence of a central potential and show that spin-orbit energy appears as an automatic consequence of the Dirac equation.
6. Apply Dirac equation for a central field to study the hydrogen atom and obtain the relation for energy along with total spread in energy of fine-structure levels for a given quantum number n.
7. Discuss the positron theory and its limitations.
8. What are the identical particles and particle exchange operator? Obtain the eigenvalues of particle exchange operator.

E-Content

DEPARTMENT OF PHYSICS

GOVT. V.Y.T.PG AUTONOMOUS COLLEGE DURG 491001 CHHATTISGARH

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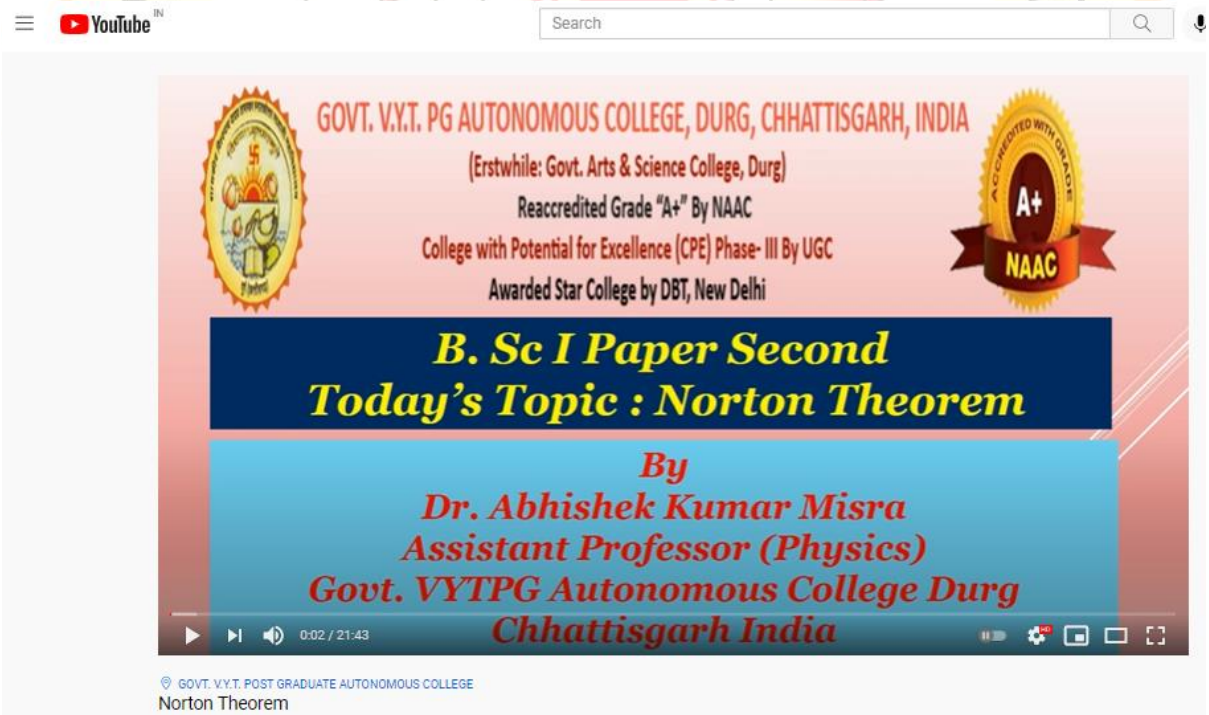
Module: Norton Theorem and its circuit diagram

Module is divided in four sections:

1. **VIDEO CONTENT**
2. **(a) NOTES**
   (b) SUPPLEMENTARY MATERIAL
3. **SUBJECTIVE ASSIGNMENT BASED ON MODULE**
4. **OBJECTIVE QUESTION BASED ON MODULE**
5. **FEEDBACK SECTION**

Video Content: https://youtu.be/LEgoTndSUSA

In this video I explained Statement and derivation of Norton theorem. The two terminal linear networks can be converted into Norton equivalent circuit.



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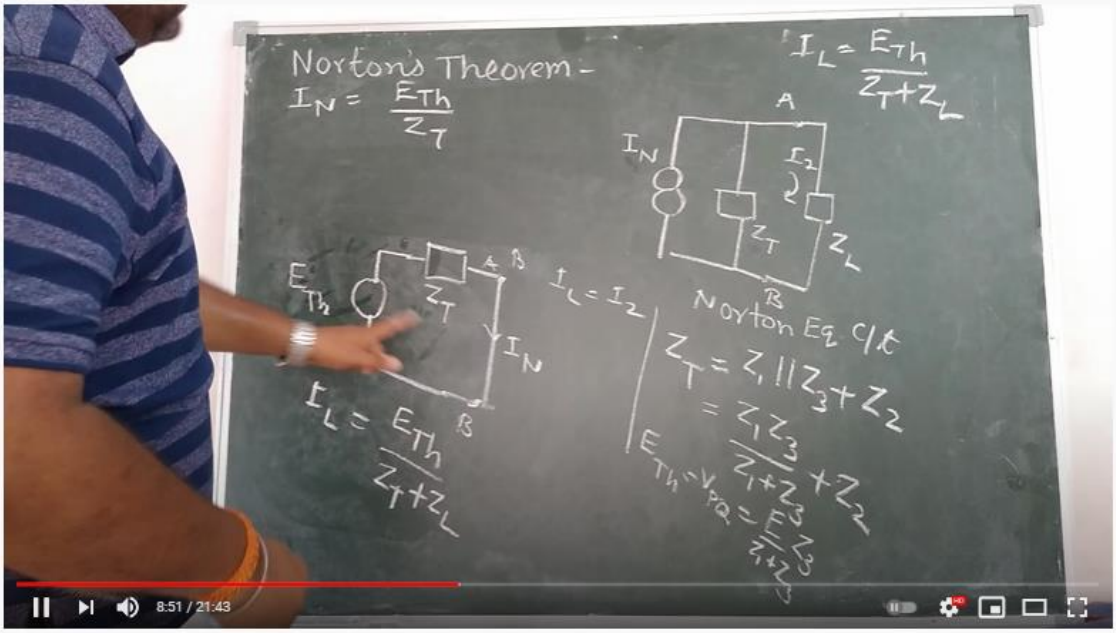

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Norton Theorem

793 views • May 28, 2020

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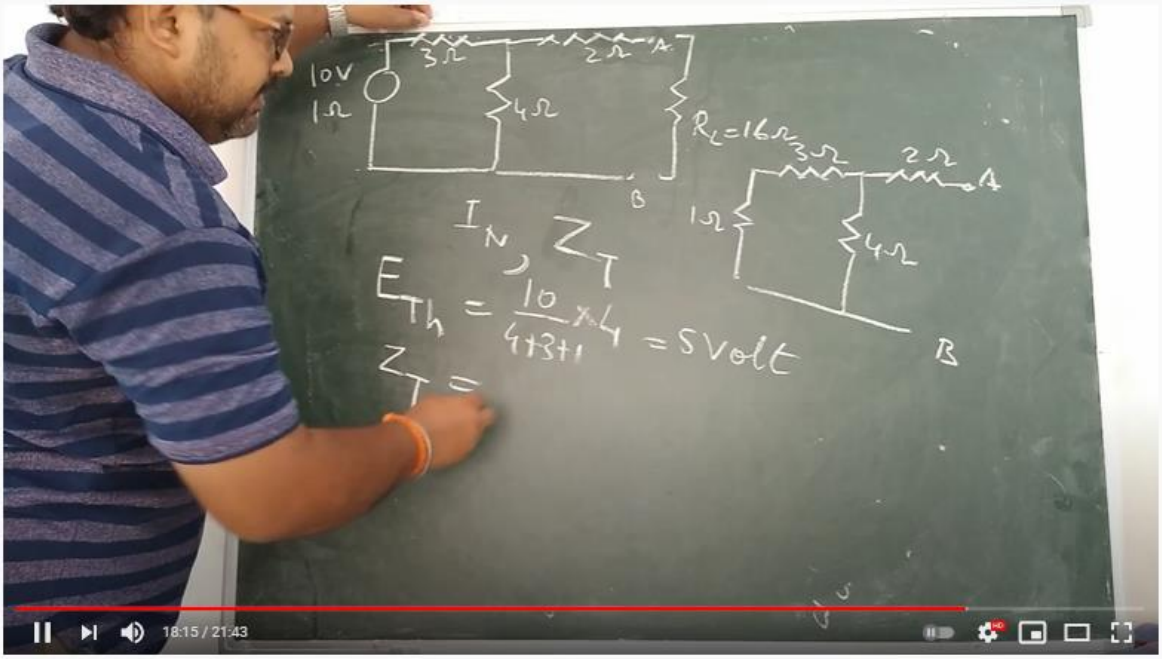

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Norton Theorem

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2(a) NOTES

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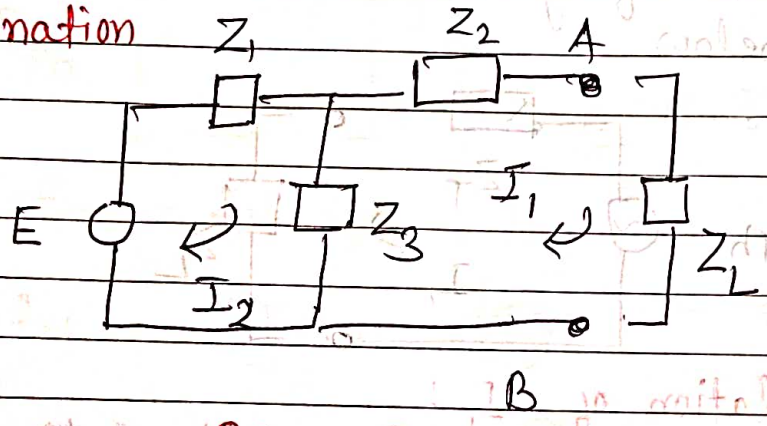
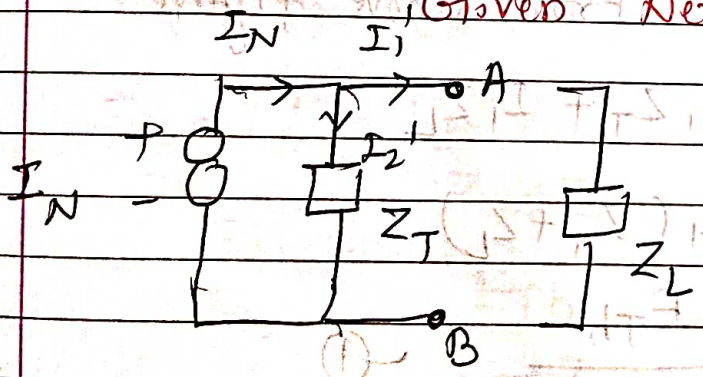
Norton Theorem:-

Statement:- According to this theorem any two terminal linear network containing energy source can be replaced by its equivalent circuit consisting of a current source I_N and impedance Z_T acting parallel to each other. Here I_N is short circuit current across the terminals of given network and Z_T is equivalent impedance across the terminals of given network when energy source is replaced by its internal impedance.

Explanation



Given Network



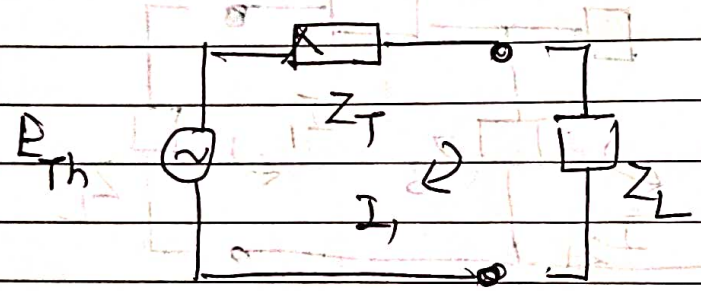
Norton equivalent circuit

Consider a two terminal linear network consisting of three impedances Z_1, Z_2, Z_3 and energy source E is shown in figure. Let I_1 is current through the load impedance Z_L across its output

Second figure represents the equivalent Circuit of given network which consists of current source I_N and an equivalent impedance Z_T acting parallel to each other. Let I_1' is the current through load Impedance Z_L then according to Norton theorem

$$I_1 = I_1'$$

Proof:- To prove Norton theorem, first of all we made Thevenin equivalent Circuit of given network which is shown below



Calculation of I_1:- From above figure

$$E_{Th} = I_1 Z_T + I_1 Z_L$$

$$E_{Th} = I_1 (Z_T + Z_L)$$

$$I_1 = \frac{E_{Th}}{Z_T + Z_L} \quad \text{---(1)}$$

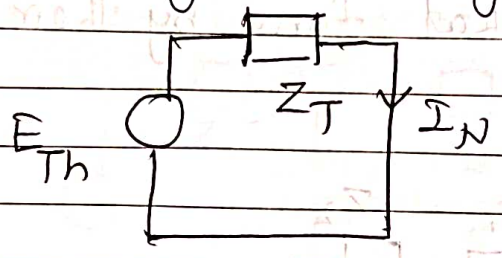
Calculation of I_1':- From Norton equivalent Circuit

$$I_N = I_1' + I_2'$$

$$I_1' = \frac{Z_T}{Z_T + Z_L} \cdot I_N \quad \text{— (2)}$$

$$I_2' = \frac{Z_L}{Z_T + Z_L} \cdot I_N \quad \text{— (3)}$$

Calculation of I_N :- Here I_N is short circuit current across the terminal of given network. To calculate I_N from Thevenin circuit by following method



$$E_{Th} = I_N \cdot Z_T$$

$$I_N = \frac{E_{Th}}{Z_T} \quad \text{— (4)}$$

From eqn (2) and (4)

$$I_1' = \frac{Z_T}{Z_T + Z_L} \cdot \frac{E_{Th}}{Z_T}$$

$$I_1' = \frac{E_{Th}}{Z_T + Z_L} \quad \text{— (5)}$$

From eqn (1) and (5)

$$I_1 = I_1'$$

This is statement of Norton theorem.

2 . (b) SUPPLEMENTARY MATERIAL

Norton's Theorem

Norton's Theorem states that – A linear active network consisting of the independent or dependent voltage source and current sources and the various circuit elements can be substituted by an equivalent circuit consisting of a current source in parallel with a resistance. The current source being the short-circuited current across the load terminal and the resistance being the internal resistance of the source network.

The Norton's theorems reduce the networks equivalent to the circuit having one current source, parallel resistance and load. Norton's theorem is the converse of Thevenin's Theorem. It consists of the equivalent current source instead of an equivalent voltage source as in Thevenin's theorem.

The determination of internal resistance of the source network is identical in both the theorems.

In the final stage that is in the equivalent circuit, the current is placed in parallel to the internal resistance in Norton's Theorem whereas in Thevenin's Theorem the equivalent voltage source is placed in series with the internal resistance.

Explanation of Norton's Theorem

To understand Norton's Theorem in detail, let us consider a circuit diagram given below

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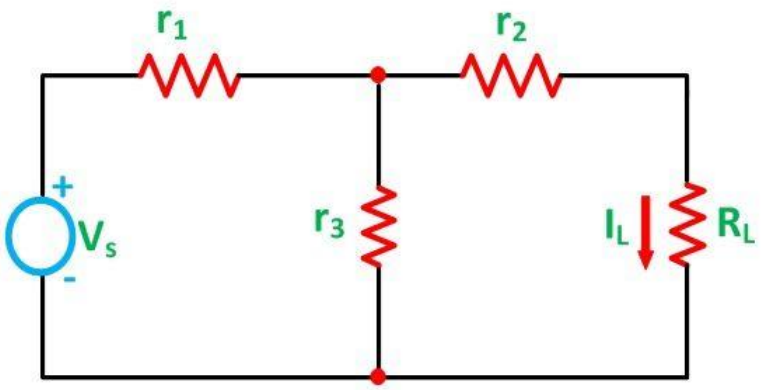
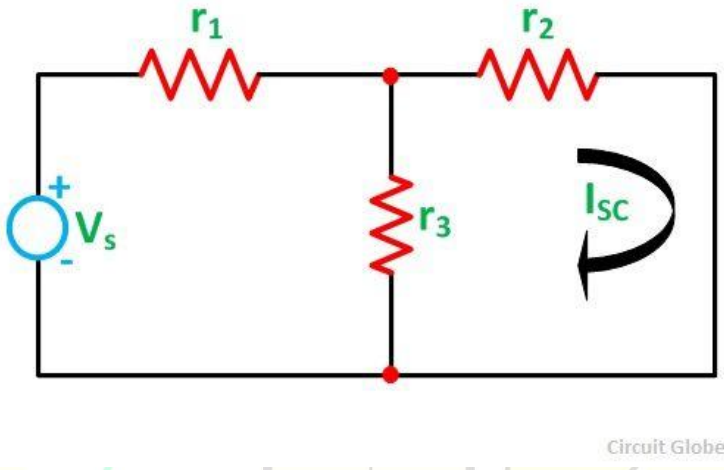


To find the current through the load resistance IL as shown in the circuit diagram above, the load resistance has to be short-circuited as shown in the diagram below:



Now, the value of current I flowing in the circuit is found out by the equation

$$I = \frac{V_S}{r_1 + \frac{r_2 r_3}{r_2 + r_3}}$$

And the short-circuit current I_{SC} is given by the equation shown below:

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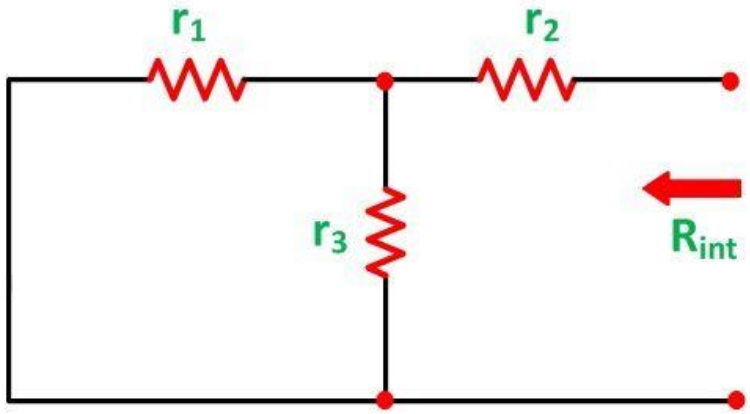
$$I_{sc} = I \frac{r_3}{r_3 + r_2}$$

Now the short circuit is removed, and the independent source is deactivated as shown in the circuit diagram below and the value of the internal resistance is calculated by:



So,

$$R_{int} = r_2 + \frac{r_1 r_3}{r_1 + r_3}$$

As per Norton's Theorem, the equivalent source circuit would contain a current source in parallel to the internal resistance, the current source being the short-circuited current across the shorted terminals of the load resistor. The Norton's Equivalent circuit is represented as

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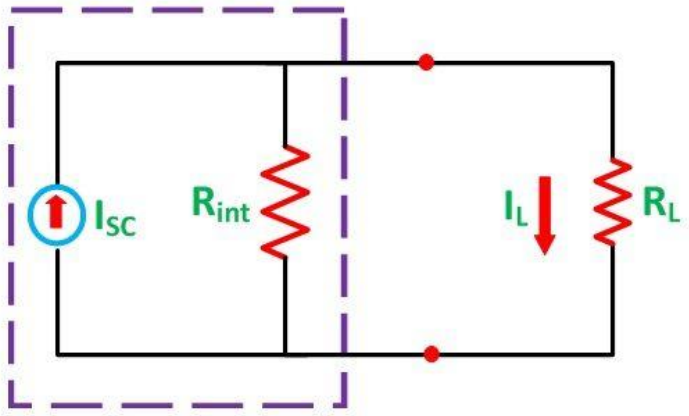

Circuit Globe

Finally, the load current I_L calculated by the equation shown below

$$I_L = I_{sc} \frac{R_{int}}{R_{int} + R_L}$$

here,

- I_L is the load current
- I_{sc} is the short circuit current
- R_{int} is the internal resistance of the circuit
- R_L is the load resistance of the circuit

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Steps for Solving a Network Utilizing Norton's Theorem

Step 1 – Remove the load resistance of the circuit.

Step 2 – Find the internal resistance R_{int} of the source network by deactivating the constant sources.

Step 3 – Now short the load terminals and find the short circuit current I_{SC} flowing through the shorted load terminals using conventional network analysis methods.

Step 4 – Norton's equivalent circuit is drawn by keeping the internal resistance R_{int} in parallel with the short circuit current I_{SC}.

Step 5 – Reconnect the load resistance R_L of the circuit across the load terminals and find the current through it known as load current I_L.

Reference:

https://circuitglobe.com/what-is-nortons-theorem.html

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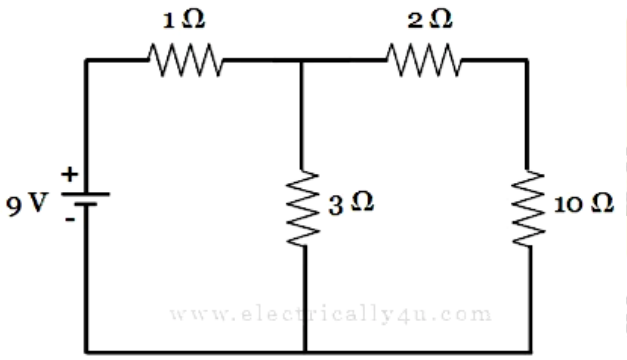
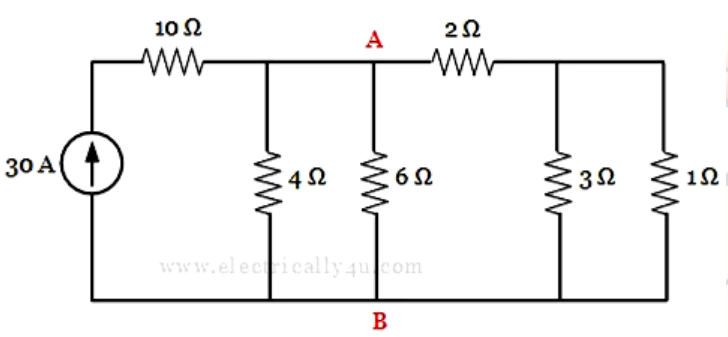
3. ASSIGNMENT

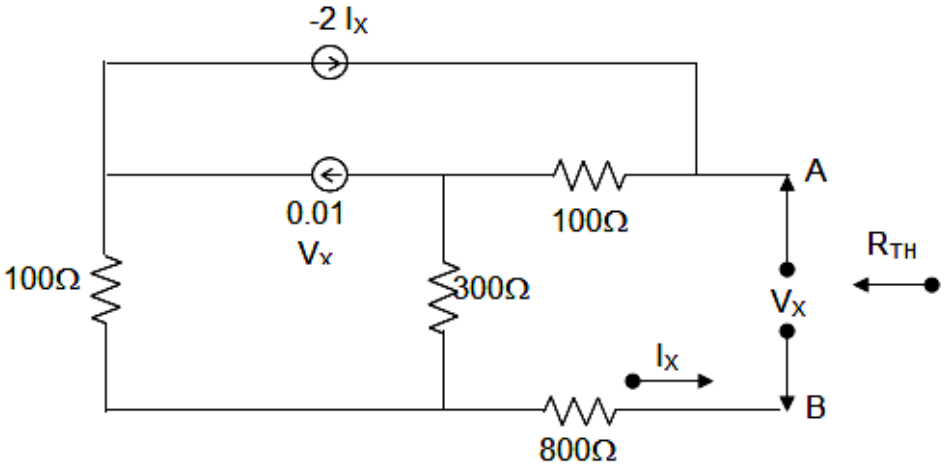
1. **For the given circuit, determine the current flowing through 10 Ω resistor using Norton's theorem.**



2. **Determine the current through AB in the given circuit using Norton's theorem.**



3. **In the following circuit, the value of Norton's resistance between terminals a and b are?**



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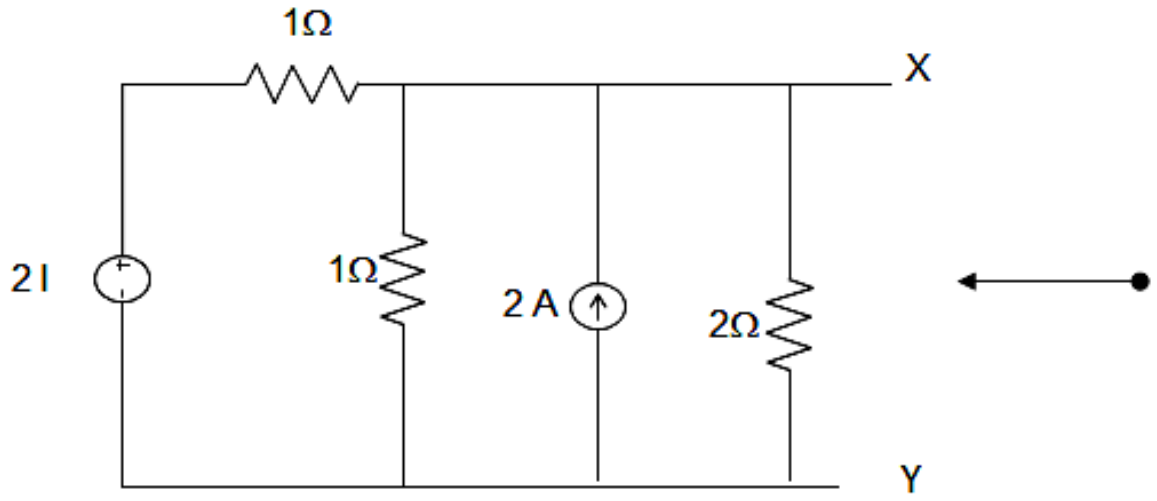
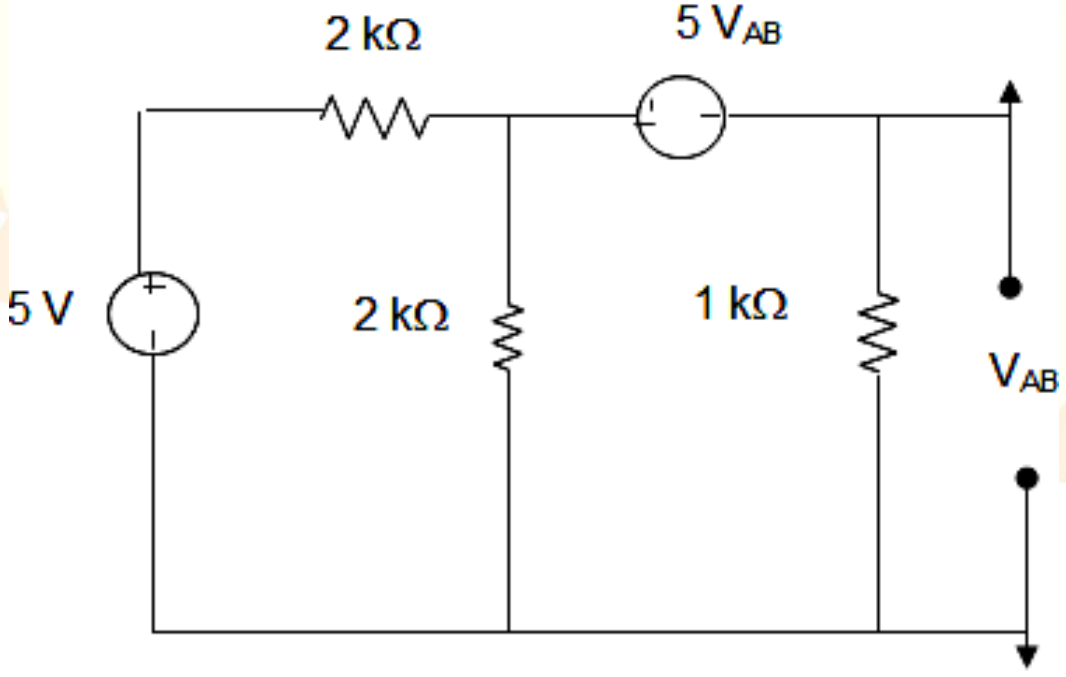
4. **For the circuit shown in the figure below, the Norton Resistance looking into X-Y is**



5. **For the circuit given below, the Norton's resistance across the terminals A and B is**



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4. MULTIPLE CHOICE QUESTIONS

1. The Norton current is the_____

a) Short circuit current

b) Open circuit current

c) Open circuit and short circuit current

d) Neither open circuit nor short circuit current

2. Norton resistance is found by?

a) Shorting all voltage sources

b) Opening all current sources

c) Shorting all voltage sources and opening all current sources

d) Opening all voltage sources and shorting all current sources

3. Isc is found across the _____ terminals of the network.

a) Input b) Output

c) Neither input nor output d) Either input or output

4. Can we use Norton's theorem on a circuit containing a BJT?

a) Yes b) No

c) Depends on the BJT d) Insufficient data provided

5. In Norton's theorem Isc is_____

a) Sum of two current sources b) A single current source

c) Infinite current sources d) 0

Ans: 1 (a), 2. (c), 3. (b), 4. (b), 5. (b)

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5. FEEDBACK QUESTIONS

1. Did the lecture cover what you were expecting?
2. What is your opinion about the video lecture?
3. How much this session was useful from the knowledge and information point of view
4. Are you satisfied with the content of the video lecture and given questions?
5. If you could change one specific thing what would that be?

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Identical Particles in Quantum Mechanics

by

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Identical Particles

In quantum mechanics, a (quantum) particle is described by a wave packet of finite size. The simultaneous exact specification of position (spread of wave packet) and momentum of the particle is restricted by the Heisenberg's uncertainty principle.

Therefore, there is no way to keep track of individual particles separately, especially if they interact with each-other to an appreciable extent.

In quantum mechanics, the wave functions of the particles overlap considerably and hence the quantum particles are indistinguishable.

Physical Meaning of Identity

Identical particles in a system remain unaltered by interchanging them.

In quantum mechanics, identical particles can be substituted for each-other with no change in physical situation of the system.

However, with the spin consideration, identical particles can be distinguished, if they have different spin components along some particular axis e.g. z-axis, which remain unchanged during elastic collisions.

Symmetric and Antisymmetric Wave Functions

Schrodinger equation for n identical particles is

$$H(1,2,---n)\,\psi(1,2,---n,t) = i\hbar\,\partial/\partial t\,\psi(1,2,---n,t) \qquad \text{------} \quad (1)$$

where each number represents all coordinates (position and spin) of one of the particles.

Hamiltonian H is symmetrical in its arguments due to identity of particles, which means the particles can be substituted for each-other without changing the Hamiltonian H or any other observable.

There are two kinds of solutions of wave function ψ of eq. (1) that have symmetric properties of particular interest.

(i) **Symmetric wave function ψ_S** : A wave function is symmetric, if the interchange of any pair of particles among its arguments leave the wave function unchanged.

(ii) **Antisymmetric wave function ψ_A** : A wave function is antisymmetric, if the interchange of any pair of particles among its arguments changes the sign of the wave function.

Symmetric character of a wave function does not change with time i.e. if ψ_S (*or* ψ_A) is symmetric (*or antisymmetric*) at a particular time t, then $H\psi_S$ (*or* $H\psi_A$) and hence $\partial\psi_S/\partial t$ (*or* $\partial\psi_A/\partial t$) and the integration of wave function ψ_S (*or* ψ_A) are always symmetric (*or antisymmetric*).

If P is an exchange operator, then

$$P\,\psi_S(1,2) = \psi_S(2,1)$$

$$P\,\psi_A(1,2) = -\psi_A(2,1)$$

Construction of symmetric and antisymmetric wave functions from unsymmetrized functions : Exchange Degeneracy

If the arguments of wave function ψ are permuted in any way, then the resulting wave function is also a solution of equation (1). n! Solutions can be obtained from any one solution, each of which corresponds to one of the n! permutation of the n arguments of ψ. Any linear combination of these functions is also a solution of the wave equation (1). The sum of all these functions is symmetric (unnormalized) wave function ψ_S ,since interchange of any pair of particles changes any one of the component function into another of them and the latter into the former, leaving the entire wave function unchanged.

An antisymmetric unnormalized wave function can be constructed by adding all the permuted wave functions that arise from original solution by means of an even number of interchanges of pairs of particles (cyclic ones) and subtracting the sum of all the permuted wave functions that arise by means of an odd number of interchanges of pairs of particles in the original solution.

In cases where Hamiltonian does not depend on time, stationary state solutions

$$\psi(1,2,\text{---}n,t) = \phi(1,2,\text{---}n)\, e^{-iEnt/\hbar} \qquad \text{-----} \qquad (2)$$

can be found and the time independent Schrodinger's eqn. can be written as

$$H(1,2,\text{---}n)\ \phi(1,2,\text{---}n) = E\,\phi(1,2,\text{---}n) \qquad \text{-----} \qquad (3)$$

There are n! solutions of this equation (eigen functions) derived from ϕ (1,2,---n) by means of permutations of its arguments belonging to the same eigen value E. Any linear combination of these eigen functions is also an eigen function [solution of eq.(3)] belonging to eigen value E. Hence, the system is degenerate and this type of degeneracy is called exchange degeneracy.

For a system of two particles, Schrodinger time independent wave equation is

$$H(1,2)\,\psi(1,2) = E\,\psi(1,2) \qquad \text{-----} \qquad (4)$$

2! = 2 solutions of this equation are ψ (1,2) and ψ (2,1) and correspond to a single energy state E.

Symmetric wave function can be written as

$$\psi_S = \psi(1,2) + \psi(2,1)$$

and antisymmetric wave function can be written as

$$\psi_A = \psi(1,2) - \psi(2,1)$$

For a system of three particles, Schrodinger time independent wave equation is

$$H(1,2,3)\,\psi(1,2,3) = E\,\psi(1,2,3)$$

This equation has following 3! = 6 solutions corresponding to the same eigen value E :

$$\psi(1,2,3),\ \psi(2,3,1),\ \psi(3,1,2),\ \psi(1,3,2),\ \psi(2,1,3),\ \psi(3,2,1)$$

Out of these six functions, those arising by an even number of interchanges of the pairs of particles in original wave function ψ (1,2,3) are :

$$\psi(1,2,3),\ \psi(2,3,1),\ \psi(3,1,2)$$

and the functions arising by an odd number of interchanges of pair of particles in original wave function $\psi(1,2,3)$ are :

$$\psi(1,3,2),\ \psi(2,1,3),\ \psi(3,2,1)$$

Therefore, symmetric (unnormalized) wave function can be written as :

$$\psi_S = \{\psi(1,2,3) + \psi(2,3,1) + \psi(3,1,2)\} + \{\psi(1,3,2) + \psi(2,1,3) + \psi(3,2,1)\}$$

and antisymmetric (unnormalized) wave function as :

$$\psi_A = \{\psi(1,2,3) + \psi(2,3,1) + \psi(3,1,2)\} - \{\psi(1,3,2) + \psi(2,1,3) + \psi(3,2,1)\}$$

Particle Exchange Operator

Particle exchange operator $P_{1,2}$ is defined as :

$$P_{1,2}\ \psi(r_1 s_1; r_2 s_2) = \psi(r_2 s_2; r_1 s_1)$$

If the two particles are identical, then the Hamiltonian must be invariant under interchange of particles i.e. energy of the system remains the same, if we merely relabel the particles.

Eigen values and Eigen functions of Particle Exchange Operator

The eigen value equation for the particle exchange operator is :

$$P_{12}\ \psi(1,2) = \alpha\ \psi(1,2)$$

where α is the eigen value of operator $P_{1,2}$ in state $\psi(1,2)$.

Operating again,

$$P_{12}^2\ \psi(1,2) = P_{12}\ P_{12}\ \psi(1,2) = P_{12}\ \alpha\ \psi(1,2) = \alpha\ P_{12}\ \psi(1,2) = \alpha^2\ \psi(1,2)$$

From the definition of particle exchange operator, we have

$$P_{12}\ \psi(1,2) = \psi(2,1)$$

Operating again,

$$P_{12}^2\ \psi(1,2) = P_{12}\ \psi(2,1)$$

i.e. $$P_{12}^2\ \psi(1,2) = \psi(1,2)$$

Therefore,

$$\alpha^2 = 1 \quad \text{or} \quad \alpha = \pm 1$$

i.e. eigen value of particle exchange operator are ± 1.

Eigen functions of particle exchange operator corresponding to eigen values +1 and -1 are symmetric and antisymmetric.

$$P_{12}\,\psi_S = \psi_S \quad \text{and} \quad P_{12}\,\psi_A = -\psi_A$$

This may be seen as follows :

$$\psi_S = \psi(1,2) + \psi(2,1)$$

$$P_{12}\psi_S = P_{12}[\psi(1,2) + \psi(2,1)] = \psi(2,1) + \psi(1,2) = \psi_S$$

Also, $$\psi_A = \psi(1,2) - \psi(2,1)$$

$$P_{12}\,\psi_A = P_{12}[\psi(1,2) - \psi(2,1)] = \psi(2,1) - \psi(1,2) = -\psi_A$$

Thus, particle exchange operator applied twice brings the particles back to their original configuration and hence produces no change in the wave function.

Commutation relation of Particle Exchange Operator with Hamiltonian

We have,

$$P_{12}\,\psi(1,2) = \psi(2,1)$$

$$P_{12}\,H(1,2)\,\psi(1,2) = H(2,1)\,\psi(2,1) = H(1,2)\,\psi(2,1) = H(1,2)\,P_{12}\psi(1,2)$$

[since Hamiltonian H is symmetric i.e. H(1,2) = H(2,1)]

$$[P_{12}\,H(1,2) - H(1,2)\,P_{12}]\,\psi(1,2) = 0$$

As $\psi(1,2)$ is non-zero,

$$P_{12}\,H(1,2) - H(1,2)\,P_{12} = 0$$

$$[P_{12}, H] = 0$$

Thus, particle exchange operator commutes with Hamiltonian.

Distinguishablility of Identical Particles

Two identical particles are distinguishable if the sum of probability density of individual wave functions of the two states is equal to the probability density associated with the symmetrised wave functions i.e.

$$|\psi(1,2)|^2 + |\psi(2,1)|^2 = |\{\psi(1,2) \pm \psi(2,1)\}|^2 = |\psi(1,2)|^2 + |\psi(2,1)|^2 \pm 2\,\mathrm{Re}\,[\psi(1,2)\,\psi^*(2,1)]$$

Thus, if the space and spin co-ordinates of the exchange degenarate functions (of the two particles) are different, the interference term i.e. 2 Re $[\psi(1,2)\,\psi^*(2,1)] = 0$ and particle wave functions do not overlap, *making the particles distinguishable*.

Pauli's Exclusion Principle

For a system of non-interacting n identical particles, the approximate (unperturbed) Hamiltonian of the system is equal to the sum of Hamiltonian function for the separate particles i.e.

$$H_0(1,2,\text{------}n) = H_0(1) + H_0(2) + \text{------} + H_0(n)$$

and the approximate energy eigen function is a product of one particle eigen function of H_0.

$$\psi(1,2,\text{---}n) = \phi_a(1)\,\phi_b(2)\text{-----}\,\phi_k(n)$$

with $E = E_a + E_b + \text{-------} + E_k$.

$$H_0(1)\,\phi_a(1) = E_a\,\phi_a(1)\text{ , etc.}$$

If the particles are Fermions (electrons), then for a system of two non-interacting particles, an antisymmetric wave function can be written as a determinant

$$\Phi_A(1,2) = \frac{1}{\sqrt{2}}\,[\phi_a(1)\,\phi_b(2) - \phi_b(1)\,\phi_a(2)]$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi a(1) & \varphi a(2) \\ \varphi b(1) & \varphi b(2) \end{vmatrix}$$

For a system of n non-interacting Fermi particles, the antisymmetric energy wave function can be written as

$$\Phi_A(1,2,\text{-----}n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \Phi_a(1) & \Phi_a(2) & \text{---} & \Phi_a(n) \\ \Phi_b(1) & \Phi_b(2) & \text{---} & \Phi_b(n) \\ \text{---} & \text{---} & \text{---} & \text{---} \\ \Phi_k(1) & \Phi_k(2) & \text{---} & \Phi_k(n) \end{vmatrix}$$

This is called 'Slater determinant'.

Since a determinant vanishes if any two rows are identical, it is obvious that ϕ_A will vanish if more than one particle is in the same state i.e. if a = b.

This is Pauli's exclusion principle which states that no two particles described by antisymmetric wave functions can exist in the same quantum state.

Connection between Spin and Statistics

The symmetry property of wave function has close relationship with spin of the particle.

(i) The identical particles having integral spin quantum numbers are described by symmetric wave functions i.e.

$$P\,\psi_S(1,2,3,\text{----}r,\text{----}s,\text{----}n) = +\,\psi_S(1,2,3,\text{----}s,\text{----}r,\text{----}n)$$

Such particles obey Bose-Einstein statistics and are called Bosons e.g. photons (spin 1) and neutral He-atoms in normal state (spin 0).

(ii) The identical particles having half odd integral spin quantum numbers are described by antisymmetric wave functions i.e.

$$P\,\psi_A(1,2,3,\text{----}r,\text{----}s,\text{----}n) = -\,\psi_A(1,2,3,\text{----}s,\text{----}r,\text{----}n)$$

Such particles obey Fermi-Dirac statistics and are called Fermions e.g. electrons, protons, neutron, muons (spin 1/2).

Spin Angular Momentum

Spin is intrinsic angular momentum (a quantum concept with no classical analogue).

It is independent of r, θ and ϕ.

It has two intrinsic states i.e. two z-components of spin momentum.

Electron has intrinsic angular momentum characterized by quantum number ½.

Intrinsic electron spin is a vector **S** (spin quantum number = ½) with s_z = +1/2 and -1/2 and the respective spin wave functions are α and β (α and β are orthogonal).

Spin angular momentum of electron :

$$S\,\alpha = \sqrt{s(s+1)}\hbar\,\alpha = \sqrt{3}/2\,\hbar\,\alpha \qquad s_z\,\alpha = m_s\,\hbar\,\alpha = ½\,\hbar\,\alpha$$

$$S\,\beta = \sqrt{s(s+1)}\hbar\,\beta = \sqrt{3}/2\,\hbar\,\beta \qquad s_z\,\beta = m_s\,\hbar\,\beta = -½\,\hbar\,\beta$$

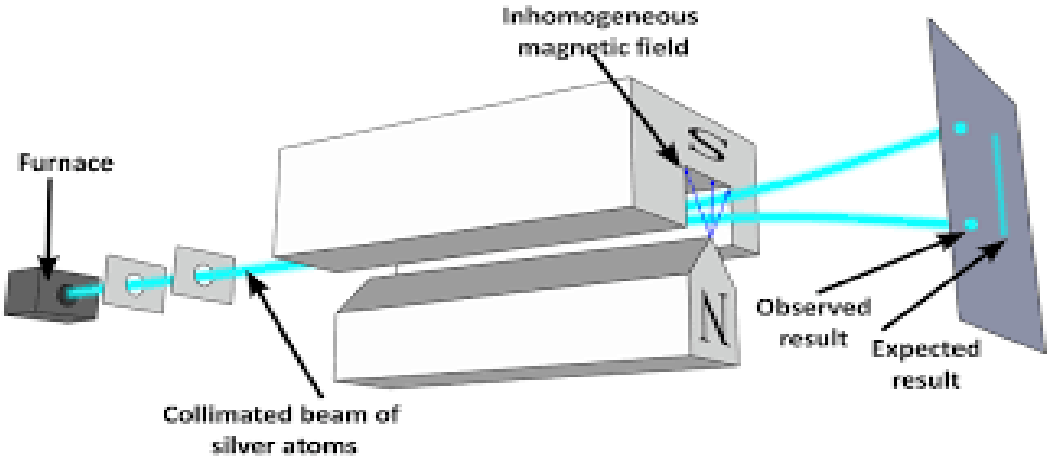
$$\int\alpha^*\beta\,d\sigma = \int\beta^*\alpha\,d\sigma = 0 \qquad \int\alpha^*\alpha\,d\sigma = \int\beta^*\beta\,d\sigma = 1$$

[σ is spin variable.]

Stern-Gerlach Experiment

In 1922, at the University of Frankfurt (Germany), Otto Stern and Walther Gerlach, did fundamental experiments in which beams of silver atoms were sent through inhomogeneous magnetic fields to observe their deflection. These experiments demonstrated that these atoms have quantized magnetic moments that can take two values.

Inhomogeneous magnetic field was generated with –ve field gradient in z-direction i.e. $\partial B/\partial z < 0$. The magnetic field is strong near N-pole and weak near S-pole, as in fig. When vapour of silver-beam was passed through this inhomogeneous B-field, it was observed to split into two traces, which were attributed to the two spin state of m_z.



Explanation :

Force acting on Ag-atom is

$$\mathbf{F} = -\,\text{grad}\, U = \text{grad}\, \mathbf{m.B} \qquad (U = -\,\mathbf{m.B})$$

$$F = m\cos\theta\, \partial B/\partial z \qquad a_z = F/M_0 = m/M_0 \cos\theta\, \partial B/\partial z\,, \quad t = L/v$$

$$z = \tfrac{1}{2}\, a_z t^2 = \tfrac{1}{2}\, m \cos\theta\, (L^2/M_0 v^2)\, \partial B/\partial z$$

Classically, cos θ can have all possible values from -1 to +1, giving smear of Ag-beam after passing through B-field (not observed in this experiment).

But quantum mechanically, due to space quantization, cos θ = ± 1. So,

$$z = \pm\tfrac{1}{2}\, m\, (L^2/M_0 v^2)\, \partial B/\partial z$$

Goudsmit and Uhlenbeck hypothesis

(i) Each electron has spin angular momentum **S**, whose component in z-direction can have values $s_z = \pm \tfrac{1}{2}$.

(ii) Each electron has spin magnetic moment $\boldsymbol{\mu_s} = -\,(e/m_0 c)\, \mathbf{S}$.

Spin obeys commutation relations :

$$[S_x, S_y] = i\hbar\varepsilon_{jkl}\, S_l$$

where ε_{jkl} is Levi-Civita symbol. It follows that S^2 and S_z are :

$$S^2 |s,m_s\rangle = \hbar^2 s(s+1) |s,m_s\rangle$$

$$S_z |s,m_s\rangle = \hbar m_s |s,m_s\rangle$$

Spin raising and lowering operators acting on these eigen vectors give :

$$S_{\pm}|s,m_s\rangle = \hbar \sqrt{[s(s+1) - m_s(m_s \pm 1)]}\ |s,m_s\rangle$$

where $S_{\pm} = S_x \pm iS_y$

All quantum mechanical particles possess an intrinsic spin, which is quantized (though this value may be zero, too), such that the state function of the particle is $\psi(\mathbf{r},\boldsymbol{\sigma})$; where σ is out of the following discrete set of values

$$\sigma \in \{-s\hbar, -(s-1)\hbar, \text{---0--} +(s+1)\hbar, +s\hbar\}$$

Bosons have integer spin and fermions have half-integer spin. Total angular momentum is the sum of orbital angular momentum and the spin.

Pauli matrices

Quantum mechanical operators associated with spin ½ observables are :

$$\hat{S} = (\hbar/2)\,\sigma$$

where in Cartesian components :

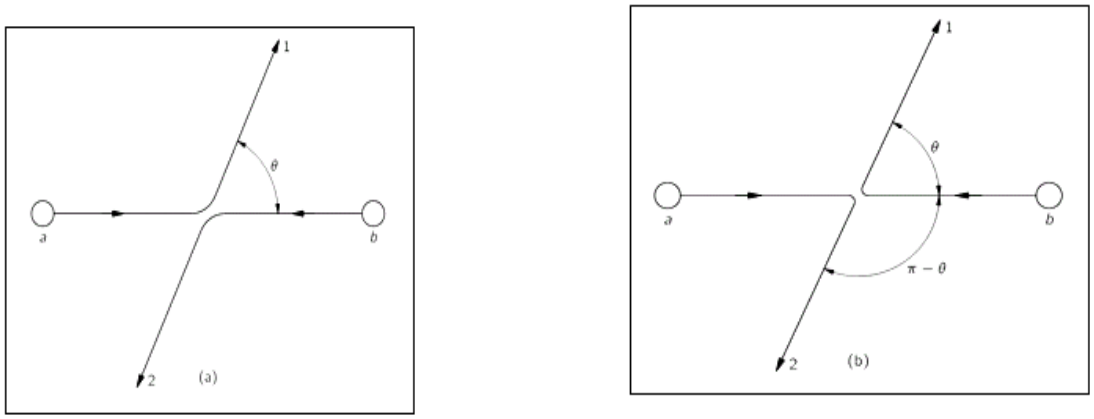
$$S_x = (\hbar/2)\,\sigma_x\,,\ S_y = (\hbar/2)\,\sigma_y\,,\ S_z = (\hbar/2)\,\sigma_z\,;$$

σ_x , σ_y and σ_z are Pauli's spin matrices.

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Collision of Identical Particles

Let us consider the collision of two particles a and b, in which particle 'a' scatters in direction 1 and b in direction 2, as shown in fig-(a). If f(θ) be the amplitude for this process, then the probability P_1 of observing such an event is proportional to $|f(\theta)|^2$.



(Scattering of identical particles in CM system)

If, as a result of collision, particle 'a' enters into counter 2 and 'b' into counter 1, then the probability P_2 for this process is proportional to $|f(\pi-\theta)|^2$.

If 'a' and 'b' are identical particles, then the two processes shown in fig-a and b cannot be distinguished. The amplitude that either 'a' or 'b' goes into counter 1, while the other goes into counter 2, is the sum of the amplitudes for the two processes.

An interchange of two identical particles [1⇆2 i.e. $\mathbf{r} \to (-\mathbf{r})$ in CM frame] does not affect the position vector of centre of mass, which is ½ ($\mathbf{r}_1 + \mathbf{r}_2$), but changes the sign of relative position vector $\mathbf{r}$ (= $\mathbf{r}_1 - \mathbf{r}_2$).

The asymptotic form of unsymmetrized scattering wave function in the centre of mass co-ordinate system is given by

$$u(\mathbf{r}) \xrightarrow[r \to \infty]{} e^{ikz} + r^{-1} f(\theta, \phi) e^{ikr}$$

where r, θ, ϕ are the polar co-ordinates of the relative position vector $\mathbf{r}$.

Since the polar co-ordinate of the vector $-\mathbf{r}$ are r, π - θ, ϕ + π, we have

$$u(-\mathbf{r}) \to e^{-ikz} + r^{-1} f(\pi - \theta, \phi + \pi)\, e^{ikr}$$

The asymptotic forms of the symmetric and antisymmetric wave functions are given by

$$(e^{ikz} \pm e^{-ikz}) + [f(\theta, \phi) \pm f(\pi - \theta, \phi + \pi)] r^{-1} e^{ikr}$$

with upper and lower signs respectively.

Hence, differential cross section in the centre of mass co-ordinate system is the square of the magnitude of the bracket term

$$\sigma(\theta, \phi) = |f(\theta, \phi)|^2 + |f(\pi - \theta, \phi + \pi)|^2 \pm 2\, \mathrm{Re}\, [f(\theta, \phi) f^*(\pi - \theta, \phi + \pi)]$$

Taking into account the effect of spin on the collision of two identical particles, we have for bosons, which have symmetric wave functions :

$$\psi_{sym} = \phi_s \chi_s \quad \text{or} \quad \psi_{sym} = \phi_A \chi_A$$

[here ϕ is space wave function & χ is spin wave function.]

Fermions have anti symmetric wave functions : $\psi_{antisym} = \phi_s \chi_A$ or $\psi_{antisym} = \phi_A \chi_s$

If spin wave function $\chi_s = |sm\rangle$ is symmetric, then space wave function ϕ is anti-symmetric (so that ψ is anti-symmetric) and

$$d\sigma_A/d\Omega = |f(\theta) - f(\pi-\theta)|^2$$

and if spin wave function $\chi_A = |sm\rangle$ is anti-symmetric, then space wave function ϕ is symmetric (so that ψ is anti-symmetric) and

$$d\sigma_s/d\Omega = |f(\theta) + f(\pi-\theta)|^2$$

Since symmetric spin wave function $\chi_s \Rightarrow |sm\rangle = |1,0\rangle, |1, \pm 1\rangle \to 3$

and anti-symmetric spin wave function $\chi_A \Rightarrow |sm\rangle = |0,0\rangle \to 1$

$$(d\sigma/d\Omega)_{fermions} = \tfrac{3}{4}\, d\sigma_A/d\Omega + \tfrac{1}{4}\, d\sigma_s/d\Omega$$

$$= \tfrac{3}{4} |f(\theta) - f(\pi-\theta)|^2 + \tfrac{1}{4} |f(\theta) + f(\pi-\theta)|^2$$

$$= \tfrac{3}{4} [f(\theta) - f(\pi-\theta)] [f(\theta) - f(\pi-\theta)]^* + \tfrac{1}{4} [f(\theta) + f(\pi-\theta)] [f(\theta) + f(\pi-\theta)]^*$$

$= \frac{3}{4} [|f(\theta)|^2 + |f(\pi-\theta)|^2 - 2\text{Re}\{f(\theta) f^*(\pi-\theta)\}] + \frac{1}{4} [|f(\theta)|^2 + |f(\pi-\theta)|^2 + 2\text{Re}\{f(\theta) f^*(\pi-\theta)\}]$

$= |f(\theta)|^2 + |f(\pi-\theta)|^2 + [-\frac{3}{4} \times 2\text{Re}\{f(\theta) f^*(\pi-\theta)\}] + \frac{1}{4} \times 2\text{Re}\{f(\theta) f^*(\pi-\theta)\}]$

$= |f(\theta)|^2 + |f(\pi-\theta)|^2 - \text{Re}\{f(\theta) f^*(\pi-\theta)\}$

The result for 2s = odd (for fermions) or even (for bosons) can be summarized by writing the scattering cross-section σ (θ) as

$$\sigma(\theta) = |f(\theta)|^2 + |f(\pi - \theta)|^2 + \frac{(-1)^{2s}}{2s+1} 2\,\text{Re}[f(\theta) f^*(\pi - \theta)]$$

At $\theta = \pi/2$:

$$(d\sigma/d\Omega)_{\text{fermions}} = |f(\pi/2)|^2 + |f(\pi/2)|^2 - \text{Re}\{f^*(\pi/2) f(\pi/2)\} = 2|f(\pi/2)|^2 - |f(\pi/2)|^2$$

$$= |f(\pi/2)|^2$$

But $(d\sigma/d\Omega)_{\text{classical}} = |f(\theta)|^2 + |f(\pi-\theta)|^2$

(In classical mechanics, there is no interference term "Re $f(\theta) f^*(\pi-\theta)$".)

At $\theta = \pi/2$:

$$(d\sigma/d\Omega)_{\text{classical}} = 2|f(\pi/2)|^2$$

Therefore, at $\theta = \pi/2$: $(d\sigma/d\Omega)_{\text{classical}} = 2(d\sigma/d\Omega)_{\text{fermions}}$

i.e. quantum differential scattering cross-section is half of classical differential scattering cross-section.

If the space wave function is symmetric, then differential scattering cross-section

$$d\sigma_s/d\Omega = |f(\theta) + f(\pi-\theta)|^2$$

If the space wave function is anti-symmetric, then differential scattering cross-section

$$d\sigma_A/d\Omega = |f(\theta) - f(\pi-\theta)|^2$$

Electron Spin Functions

In Pauli's theory, eigen values of the operator σ_x is

$$\sigma_x \Psi = \alpha \Psi \qquad \text{----------} \quad (1)$$

where α is the eigen value of σ_x in state Ψ.

Since, $\Psi = \begin{bmatrix} \Psi 1 \\ \Psi 2 \end{bmatrix}$ and $\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$; equation (1) takes the form

$$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \Psi 1 \\ \Psi 2 \end{bmatrix} = \alpha \begin{bmatrix} \Psi 1 \\ \Psi 2 \end{bmatrix}$$

$$\begin{bmatrix} \Psi 2 \\ \Psi 1 \end{bmatrix} = \begin{bmatrix} \alpha \Psi 1 \\ \alpha \Psi 2 \end{bmatrix}$$

$$\Psi_2 = \alpha \Psi_1 \qquad \text{and} \qquad \Psi_1 = \alpha \Psi_2$$

Therefore, we have,

$$\alpha^2 = 1 \qquad \text{or} \quad \alpha = \pm 1$$

A convenient set of orthonormal one particle spin function is provided by the normalized eigen functions of L^2 and L_x matrices. In this case, the eigen functions are (2S+1) row and one column matrices.

For electron S =1/2, so eigen function matrices for electron have (2x1/2 +1) = 2-rows and 1-column.

The respective normalized wave functions for x-component of the wave function are

$$\Psi_x(1/2) = 1/\sqrt{2}\begin{bmatrix}1\\1\end{bmatrix} \quad \text{and} \quad \Psi_x(-1/2) = 1/\sqrt{2}\begin{bmatrix}1\\-1\end{bmatrix}$$

In a similar way,

$$\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}\begin{bmatrix}\Psi 1\\ \Psi 2\end{bmatrix} = \beta\begin{bmatrix}\Psi 1\\ \Psi 2\end{bmatrix}$$

$$\begin{bmatrix}-i\Psi 2\\ i\Psi 1\end{bmatrix} = \begin{bmatrix}\beta\Psi 1\\ \beta\Psi 2\end{bmatrix}$$

$-i\Psi_2 = \beta\Psi_1$ and $i\Psi_1 = \beta\Psi_2$

Therefore, we have,

$\beta^2 = 1$ or $\beta = \pm 1$

So, the normalized wave functions for y-component of the wave function are

$$\Psi_y(1/2) = 1/\sqrt{2}\begin{bmatrix}1\\i\end{bmatrix} \quad \text{and} \quad \Psi_y(-1/2) = 1/\sqrt{2}\begin{bmatrix}1\\-i\end{bmatrix}$$

Similarly, the normalized wave functions for z-component of the wave function are

$$\Psi_z(1/2) = 1/\sqrt{2}\begin{bmatrix}1\\0\end{bmatrix} \quad \text{and} \quad \Psi_z(-1/2) = 1/\sqrt{2}\begin{bmatrix}0\\1\end{bmatrix}$$

Spin Functions for n-particle system / Electron spin function for many electron systems

Let us consider n identical particles 1,2,----,n. The spin wave function of a single particle is completely determined by the specification of (2s+1) numbers, whereas the space wave function involves the specification of a continuously infinite set of numbers (which is equivalent to a continuous function of the space co-ordinates).

A convenient set of orthonormal one-particle spin functions is given by the normalized eigen functions of total angular momentum J^2 and its component J_z matrices. Then eigen functions are (2s+1)-row, one-column matrices that have zeros in all positions except one. For example, if s = 3/2, the four spin eigen functions are :

$$\Psi(3/2) = \begin{bmatrix}1\\0\\0\\0\end{bmatrix}, \Psi(1/2) = \begin{bmatrix}0\\1\\0\\0\end{bmatrix}, \Psi(-1/2) = \begin{bmatrix}0\\0\\1\\0\end{bmatrix}, \Psi(-3/2) = \begin{bmatrix}0\\0\\0\\1\end{bmatrix}$$

and correspond to S_z eigen values 3/2 ħ, ½ ħ, -1/2 ħ, -3/2 ħ.

The orthonormality is demonstrated by multiplying the Hermitian adjoint of one spin function into itself or another function

$$[0 \quad 1 \quad 0 \quad 0]\begin{bmatrix}0\\1\\0\\0\end{bmatrix} = 1, \qquad [0 \quad 1 \quad 0 \quad 0]\begin{bmatrix}0\\0\\1\\0\end{bmatrix} = 0, \text{ ----- etc.}$$

Hermitian adjoint of Ψ(1/2) and Ψ(1/2) **Hermitian adjoint of Ψ(1/2) and Ψ(-1/2)**

Symmetric or antisymmetric many-particle wave functions can be constructed from unsymmetrized solutions that include the spin.

It is sometimes convenient to choose the unsymmetrized solutions to eigen functions of the square of the magnitude of the total spin of the identical particles $(\mathbf{S_1} + \mathbf{S_2} + \text{------} + \mathbf{S_n})^2$ and of the z-component of this total spin $(S_{1z} + S_{2z} + \text{------} + S_{nz})$.

These quantities are constants of motion, if the Hamiltonian does not contain interaction terms between the spins and other angular momenta.

In addition, such functions are often useful as zero-order wave functions when the spin interactions are weak enough to be regarded as a perturbation.

There is no loss of generality in choosing the unsymmetrized solutions in this way, since any solutions can be expressed as a linear combination of total spin eigen functions.

Effect of identity and spin

The interaction between identical particles does not depend on spin. In order to take into account the identity and spin of the two electrons, we need form an antisymmetric wave function from the products of $\chi_i^+(\mathbf{r_1}, \mathbf{r_2})$ and appropriate spin functions. The spin functions can be taken to be the set of the following four symmetrised combinations :

(+ +)

(1)

$$1/\sqrt{2}\,[(+\,-) + (-\,+)]$$

$$(-\,-)$$

$$1/\sqrt{2}\,[(+\,-) - (-\,+)]$$

where $(+) = \sigma_x(-)$ and $(-) = \sigma_x(+)$.

In the elastic scattering of an electron from a hydrogen atom (which may be considered as core of infinite mass, as compared to electron), the spin of incident electron does not have any definite relation to the spin of atomic electrons.

We can use either of these sets of spin functions, calculate the scattering with each of the four spin states of a set and then average the results with equal weights for each state.

The first three of the spin functions (1) are symmetric and must be multiplied by the antisymmetric space function $\chi_i^+(\mathbf{r_1}, \mathbf{r_2}) - \chi_i^+(\mathbf{r_2}, \mathbf{r_1})$; the fourth spin function is antisymmetric and must be multiplied by $\chi_i^+(\mathbf{r_1}, \mathbf{r_2}) + \chi_i^+(\mathbf{r_2}, \mathbf{r_1})$.

The asymptotic forms of the symmetrised space functions for large values of one of the electron co-ordinates, say $\mathbf{r_1}$ are

$$\chi_i^+(\mathbf{r_1}, \mathbf{r_2}) \pm \chi_i^+(\mathbf{r_2}, \mathbf{r_1}) \rightarrow C\,[\exp(i\mathbf{k_\alpha}.\mathbf{r_1}) + r^{-1}\, e^{ik\alpha r}\,[f_D(\theta) \pm f_E(\theta)]\,\omega_\alpha(r_2) \qquad \text{--- (2)}$$

where ω_α = core bound initial wave function, f_D = direct or non-exchange elastic scattering amplitude for which incident electron is scattered and atomic electron is left in its original state; f_E = exchange elastic scattering amplitude.

The dots represent atomic excitation and θ is the angle between $\mathbf{r_1}$ and $\mathbf{k_\alpha}$.

The differential cross-section is computed with the upper sign in one quarter of the collisions and with lower sign in three quarters of the cases.

Thus, we obtain

$$\sigma(\theta) = \tfrac{1}{4}\,|f_D(\theta) + f_E(\theta)|^2 + \tfrac{3}{4}\,|f_D(\theta) - f_E(\theta)|^2 \qquad \text{--- (3)}$$

Equation (3) may also be derived without explicit reference to spin wave functions by making use of the fact that the particles having different spin components are distinguishable.

If in half the collisions, the electrons have different sum of direct and exchange cross-sections i.e. $|f_D(\theta)|^2 + |f_E(\theta)|^2$ and in the other half where the electrons are indistinguishable, the antisymmetric space function is used.

Thus, we obtain

$$\sigma(\theta) = \tfrac{1}{2}\,\{|f_D(\theta)|^2 + |f_E(\theta)|^2\} + \tfrac{1}{2}\,|f_D(\theta) - f_E(\theta)|^2 \qquad \text{--- (4)}$$

Obviously, equation (4) is same as equation (3).

Thus, in the classical limit, where the identical particles are distinguishable, the interference term $2\mathrm{Re}[f(\theta,\phi)f^*(\pi - \theta, \phi + \pi)] = 0$ and the scattering cross-section $\sigma(\theta, \phi)$ becomes just the sum of differential cross-section for observation of the incident particle $(|f(\theta, \phi)|^2$ and $(|f(\pi - \theta, \phi + \pi)|^2$.

$$\sigma(\theta,\phi) = |f(\theta,\phi)|^2 + |f(\pi - \theta, \phi + \pi)|^2$$

If f is independent of ϕ, then the scattering per unit solid angle will be symmetric about $\theta = 90^0$ in the centre of mass co-ordinate system.

References used :

1. *Quantum Mechanics by **L. I. Schiff**,*
2. *Quantum Mechanics – Concepts & Applications by **Nouredine Zettili** &*
3. *Quantum Mechanics by **V. K. Thankappan**.*

Assignments

1. What is the physical meaning of identity ?

2. How symmetric and antisymmetric wave functions can be constructed from unsymmetrized functions ?

3. Discuss distinguishability of identical particles. Explain Pauli's exclusion principle with the help of Slater determinant.

4. What is spin angular momentum ? Describe Stern-Gerlac experiment. Write Goudsmit and Uhlenbech hypothesis.

5. Obtain expression for scattering cross-section for the collision of two identical particles.

Numerical Solution of ordinary differential equations

by

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Numerical solution of first order ordinary differential equations

A first order **Initial Value Problem** (IVP) is defined as a first order differential equation together with specified initial condition at $x = x_0$:

$$\frac{dy}{dx} = f(x, y) \qquad \text{with} \quad y(x_0) = y_0$$

There exist several methods for finding solutions of differential equations.
The classical methods for approximate solution of an IVP are:

i) Picard Iteration method

ii) Taylor Series method

Picard Iteration Method:

Picard method is an iterative method. An iterative method gives a sequence of approximations $y_1(x)$, $y_2(x)$, …,$y_k(x)$,…to the solution of differential equations such that the nth approximation is obtained from one or more prevoius approximations.

PICARD'S METHOD

Consider the first order equation

$$dy/dx = f(x, y) \qquad \ldots(1)$$

It is required to find that particular solution of (1) which assumes the value y_0 when $x = x_0$. Integrating (1) between limits, we get

$$\int_{y_0}^{y} dy = \int_{x_0}^{x} f(x, y)\, dx \quad \text{or} \quad y = y_0 + \int_{x_0}^{x} f(x, y)\, dx \qquad \ldots(2)$$

This is an integral equation equivalent to (1), for it contains the unknown y under the integral sign.

As a first approximation y_1 to the solution, we put $y = y_0$ in $f(x, y)$ and integrate (2), giving

$$y_1 = y_0 + \int_{x_0}^{x} f(x, y_0)\, dx$$

For a second approximation y_2, we put $y = y_1$ in $f(x, y)$ and integrate (2), giving

$$y_2 = y_0 + \int_{x_0}^{x} f(x, y_1)\, dx.$$

Similarly, *a third approximation is* $y_3 = y_0 + \int_{x_0}^{x} f(x, y_2)\, dx.$

Continuing this process, a sequence of functions of x, *i.e.*, y_1, y_2, y_3 ... is obtained each giving a better approximation of the desired solution than the preceding one.

$$y_{k+1}(x) = y_0 + \int_{x_0}^{x} f(x, y_k)\, dx \; ; \qquad k = 0, 1, 2, \ldots$$

Assignments

Q . Using Picard's process of successive approximation, obtain a solution upto fifth approximation of the equation dy/dx = y + x, such that y = 1 when x = 0.

Solution. (*a*) We have $y = 1 + \int_0^x (y + x)\, dx$.

First approximation. Put $y = 1$, in $y + x$, giving

$$y_1 = 1 + \int_0^x (1 + x)\, dx = 1 + x + x^2/2.$$

Second approximation. Put $y = 1 + x + x^2/2$ in $y + x$, giving

$$y_2 = 1 + \int_0^x (1 + 2x + x^2/2)\, dx = 1 + x + x^2 + x^3/6.$$

Third approximation. Put $y = 1 + x + x^2 + x^3/6$ in $y + x$, giving

$$y_3 = 1 + \int_0^x (1 + 2x + x^2 + x^3/6)\, dx = 1 + x + x^2 + \frac{x^3}{3} + \frac{x^4}{24}.$$

Fourth approximation. Put $y = y_3$ in $y + x$, giving

$$y_4 = 1 + \int_0^x \left(1 + 2x + x^2 + \frac{x^3}{3} + \frac{x^4}{24}\right) dx = 1 + x + x^2 + \frac{x^3}{3} + \frac{x^4}{12} + \frac{x^5}{120}.$$

Fifth approximation. Put $y = y_4$ in $y + x$, giving

$$y_5 = 1 + \int_0^x \left(1 + 2x + x^2 + \frac{x^3}{3} + \frac{x^4}{12} + \frac{x^5}{120}\right) dx = 1 + x + x^2 + \frac{x^3}{3} + \frac{x^4}{12} + \frac{x^5}{60} + \frac{x^6}{720}$$

Q . Find the value of y for x = 0.1 by Picard's method, given that

$\frac{dy}{dx} = \frac{y-x}{y+x}$, y(0) = 1.

Solution. We have $y = 1 + \int_0^x \frac{y - x}{y + x}\, dx$

First approximation. Put $y = 1$ in the integrand, giving

$$y_1 = 1 + \int_0^x \frac{1 - x}{1 + x}\, dx = 1 + \int_0^x \left(-1 + \frac{2}{1 + x}\right) dx$$

$$= 1 + \left[-x + 2 \log (1 + x)\right]_0^x = 1 - x + 2 \log (1 + x)$$

Second approximation. Put $y = 1 - x + 2 \log (1 + x)$ in the integrand, giving

$$y_2 = 1 + \int_0^x \frac{1 - x + 2 \log (1 + x) - x}{1 - x + 2 \log (1 + x) + x}\, dx = 1 + \int_0^x \left[1 - \frac{2x}{1 + 2 \log (1 + x)}\right] dx$$

which is very difficult to integrate.

Hence we use the first approximation and taking $x = 0.1$ we obtain

$$y(0.1) = 1 - (.1) + 2 \log 1.1 = 0.9828.$$

Problems

1. Using Picard's method, solve $dy/dx = -xy$ with $x_0 = 0, y_0 = 1$ upto third approximation. *(Mumbai, 2005)*
2. Employ Picard's method to obtain, correct to four places of decimal, solution of the differential equation $dy/dx = x^2 + y^2$ for $x = 0.4$, given that $y = 0$ when $x = 0$. *(J.N.T.U., 2009)*
3. Obtain Picard's second approximate solution of the initial value problem : $y' = x^2/(y^2 + 1), y(0) = 0$. *(Marathwada, 2008)*
4. Find an approximate value of y when $x = 0.1$, if $dy/dx = x - y^2$ and $y = 1$ at $x = 0$, using Picard's method.

Semi-classical theory of radiation

by

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Semi-classical theory of radiation

In the semi-classical radiation theory, atoms of the material particles are treated quantum-mechanically. But the electromagnetic radiation, with which these atoms interact, is treated classically. *That is why, this is called a semi-classical radiation theory*.

The interactions between the particles and the radiation field correspond to interaction terms in the Hamiltonian, which are treated by time-dependent perturbation theory.

Semi-classical radiation theory describes absorption and induced emission, but is insufficient to describe the spontaneous emission of radiation.

The quantum theory of radiation is used to describe the spontaneous emission.

Hamiltonian of the atomic electron (for simplicity, one electron having mass 'm', charge 'e' and spin S), in the absence of external perturbation is given by :

$$H_0 = p^2/2m + V(r)$$

When the electromagnetic radiation having vector potential A(r,t) and scalar potential φ(r,t) is applied on the atom, then due to interaction of electron with the electromagnetic radiation, p and V are modified as :

$p \rightarrow (p - eA/c)$ and $V \rightarrow (V + e\varphi)$

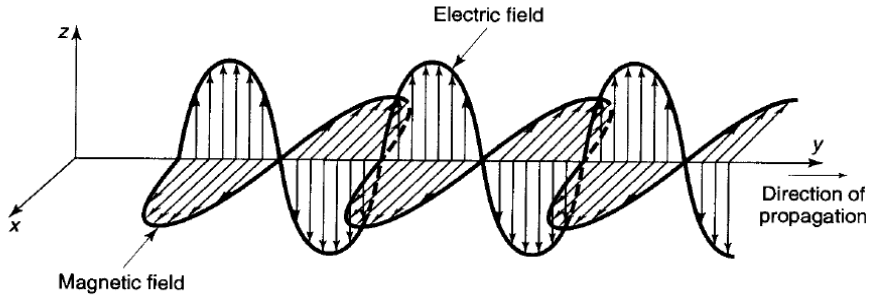
Magnetic field B and electric field E are related to the vector potential A and scalar potential φ by $B = \nabla \times A$ and $E = -\nabla\varphi - (1/c)\,\partial A/\partial t$, respectively.

Hence, the Hamiltonian of the atomic electron in an external electromagnetic field is given by :

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + V(\mathbf{r}) + e\phi - \frac{e}{mc}\mathbf{S}\cdot\mathbf{B}$$

(We have assumed that only one atomic electron is involved in interaction and the nucleus is infinitely large).

$$H = \frac{\mathbf{p}^2}{2m} - \frac{e}{2mc}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{e^2}{2mc^2}\mathbf{A}^2 + V(\mathbf{r}) + e\phi - \frac{e}{mc}\mathbf{S}\cdot\mathbf{B}$$



Operating **p**·**A** on an arbitrary function $\psi(\mathbf{r})$,

$$(\mathbf{p}\cdot\mathbf{A})\,\psi(\mathbf{r}) = -i\hbar\nabla\cdot\mathbf{A}\,\psi = -i\hbar\,[\mathbf{i}\,\partial/\partial x + \mathbf{j}\,\partial/\partial y + \mathbf{k}\,\partial/\partial z)\cdot\mathbf{A}\,\psi$$

$$= -i\hbar\,[(\partial Ax/\partial x + \partial Ay/\partial y + \partial Az/\partial z)\psi + \mathbf{A}\cdot(\mathbf{i}\,\partial\psi/\partial x + \mathbf{j}\,\partial\psi/\partial y + \mathbf{k}\,\partial\psi/\partial z)]$$

$$= -i\hbar\,[(\nabla\cdot\mathbf{A})\,\psi + \mathbf{A}\cdot\nabla\psi] = -i\hbar\,(\nabla\cdot\mathbf{A})\,\psi + \mathbf{A}\cdot(-i\hbar\nabla)\,\psi$$

$$= -i\hbar\,[(\nabla\cdot\mathbf{A}) + \mathbf{A}\cdot\mathbf{p}]\,\psi$$

Choosing the *Lorentz gauge* $\nabla\cdot\mathbf{A} = 0$ and $\varphi = 0$, we have

$$\mathbf{p}\cdot\mathbf{A} = \mathbf{A}\cdot\mathbf{p}$$

Therefore,

$$H = \mathbf{p}^2/2m - (e/mc)\,\mathbf{A}\cdot\mathbf{p} + (e/2mc^2)\,\mathbf{A}^2 + V(\mathbf{r}) - (e/mc)\,\mathbf{S}\cdot\mathbf{B}$$

$$= H_0 + H'(t)$$

where, $H_0 = \mathbf{p}^2/2m + V(r)$ *is the unperturbed 'atomic' Hamiltonian and*

$H'(t) = -(e/mc)\,\mathbf{A}\cdot\mathbf{p} + (e^2/2mc^2)\,\mathbf{A}^2 - (e/mc)\,\mathbf{B}\cdot\mathbf{S}$

is the time dependent perturbation term.

For a semi classical treatment of radiation, the term A^2 (being small) is ignored.

Hence, the small perturbation, in the low intensity limit, is

$H'(t) = -(e/mc)\,\mathbf{A}\cdot\mathbf{p} - (e/mc)\,\mathbf{B}\cdot\mathbf{S}$

For a plane electromagnetic wave of frequency $\omega = ck$, the time dependence of

A (**r**,t) is

$$\mathbf{A}\,(\mathbf{r},t) = 2\,|\mathbf{A_0}|\,\boldsymbol{\varepsilon}\cos(\mathbf{k}.\mathbf{r} - \omega t)$$

$$= A_0\,\boldsymbol{\varepsilon}\exp[(i\mathbf{k}.\mathbf{r} - i\omega t)] + A^*_0\,\boldsymbol{\varepsilon}\exp[-(i\mathbf{k}.\mathbf{r} - i\omega t)]$$

The Coulomb gauge condition $\nabla\cdot A = 0$ yields $k\cdot A_0 = 0$ i.e. A(r,t) lies in a plane perpendicular to the wave's direction of propagation.

The electric E(r,t) magnetic field B(r,t) associated with the vector potential A (r,t) are given by

$$\vec{E}(\vec{r},t) = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t} = \frac{i\omega}{c}A_0\vec{\varepsilon}\left[-e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right],$$

$$\vec{B}(\vec{r},t) = \vec{\nabla}\times\vec{A} = i(\vec{k}\times\vec{\varepsilon})A_0\left[-e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right] = \vec{n}\times\vec{E}$$

[since **k** = k **n** = (ω/c) **n**]

These two relations show that **E** and **B** have same magnitude |**E**| = |**B**|.

Energy density for a single photon of the incident radiation is given by

$$u = \frac{1}{8\pi}(|\vec{E}|^2 + |\vec{B}|^2) = \frac{1}{4\pi}|\vec{E}|^2 = \frac{\omega^2}{\pi c^2}|A_0|^2 \sin^2(\vec{k}\cdot\vec{r} - \omega t)$$

Averaging this expression over time, we see that the energy of a single photon per unit volume, $\hbar\omega/V$, is given by $(\omega^2/2\pi c^2)|A_0|^2 = \hbar\omega/V$ and hence $|A_0|^2 = 2\pi\hbar c^2/(\omega V)$, which, when put into the above equation for **A** (**r**,t) gives

$$\vec{A}(\vec{r}, t) = \sqrt{\frac{2\pi\hbar c^2}{\omega V}}\left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right]\vec{\varepsilon}$$

This gives

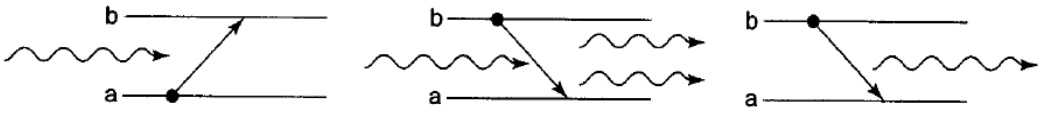
H′(t) = - (e/mc) **A**(**r,**t)·**p** – (e/mc) **B**·**S**

= - (e/mc) $(2\pi\hbar c^2/\omega V)^{1/2}$ **ε**·**p**[exp (i**k.r** - iωt) + exp (- i**k.r** + iωt)] – (e/mc) **B**·**S**

Thus, the interaction of an atomic electron with radiation has the structure of harmonic perturbation. The term exp (-iωt) gives rise to **absorption** of incident photon of energy ħω by the atom *i.e. absorption occurs when the atom receives a photon from radiation;* and exp (iωt) to **stimulated emission** of a photon of energy ħω by the atom, *which occurs when radiation gains a photon from decaying atom*.

In stimulated emission, one starts with one (incident) photon & ends up with two – incident photon plus the photon given up by the atom resulting from transition of atom from higher to lower energy level.

When there are large no. of atoms in the same excited state, a single external photon triggers an avalanche of photons (LASER).



(a) Absorption (b) Stimulated emission (c) Spontaneous emission

Classical treatment do not account for 'spontaneous emission', which occurs even in the absence of external perturbing field. Spontaneous emission *is a purely quantum effect.*

Considering the small time dependent perturbation H′, if the system is initially in state |i> and the perturbation is turned on at t = 0, the first order perturbation amplitude for finding the system in state |f> at t > 0 is given by

$$a_{fi}^{(1)}(t) = \frac{1}{i\hbar}\int_0^t e^{\omega_{fi}it'}\langle f|H'(t')|i\rangle\, dt' = \frac{ie}{mc\hbar}\int_0^t e^{i\omega_{fi}t'}\langle f|\mathbf{A}(\mathbf{r}, t)\cdot\mathbf{p} + \mathbf{S}\cdot[\nabla\times\mathbf{A}(\mathbf{r}, t)]|i\rangle\, dt'$$

with ħω = E_f – E_i. Integrating over dt′, we obtain

$$a_{fi}^{(1)}(t) = \frac{ie}{mc\hbar}\int_0^t \left\{ e^{i(\omega_{fi}-\omega)t'} \langle f | \mathbf{A}_0 e^{i\mathbf{k}\cdot\mathbf{r}} [\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p} + i\mathbf{S}\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})] | i \rangle \right.$$

$$\left. + e^{i(\omega_{fi}+\omega)t'} \langle f | \mathbf{A}_0^* e^{-i\mathbf{k}\cdot\mathbf{r}} [\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p} - i\mathbf{S}\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})] | i \rangle \right\} dt'$$

Therefore,

$$a_{fi}^{(1)}(t) = -\frac{e^{i(\omega_{fi}-\omega)t}-1}{\omega_{fi}-\omega}\frac{T_{fi}^{+}}{\hbar} - \frac{e^{i(\omega_{fi}+\omega)t}-1}{\omega_{fi}+\omega}\frac{T_{fi}^{-}}{\hbar}$$

where we define

$$\begin{cases} T_{fi}^{+} \equiv -\dfrac{e}{mc}\langle f | e^{i\mathbf{k}\cdot\mathbf{r}} A_0 [\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p} + i\mathbf{S}\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})] | i \rangle \\ T_{fi}^{-} \equiv -\dfrac{e}{mc}\langle f | e^{-i\mathbf{k}\cdot\mathbf{r}} A_0^* [\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p} - i\mathbf{S}\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})] | i \rangle \end{cases}$$

Here $T_{fi}^{\pm}$ are the transition matrices and have the matrix elements for a one-electron system in a linearly polarized radiation field as

$$T_{fi}^{\pm} \equiv -(e/mc) \langle f | e^{ik\cdot r} \mathbf{A_0}[\boldsymbol{\varepsilon}\cdot\mathbf{p} \pm i\mathbf{S}\cdot(\mathbf{k}\times\boldsymbol{\varepsilon})] | i \rangle$$

Since, $(e^{i\theta}-1)/\theta = (e^{i\theta/2}e^{i\theta/2} - e^{i\theta/2}e^{-i\theta/2})/\theta$

$$= 2i\, e^{i\theta/2} \sin(\theta/2)]/\theta$$

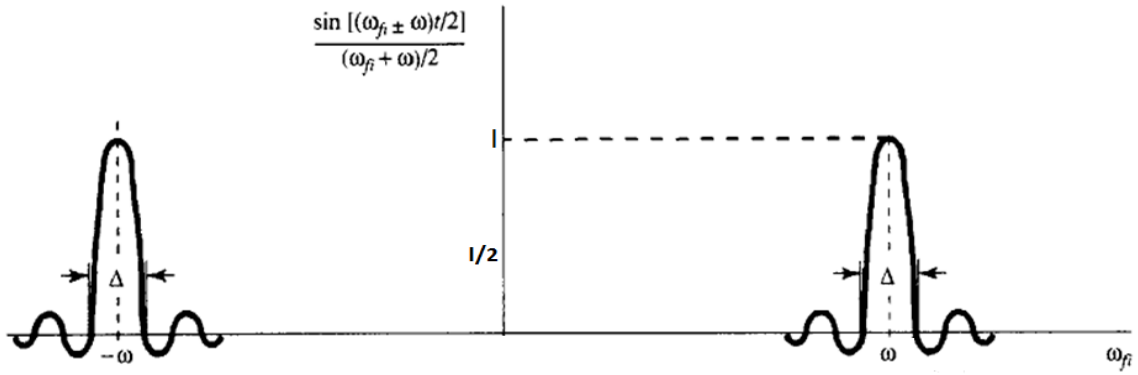
$$= [i\, e^{i\theta/2} \sin(\theta/2)] / (\theta/2)$$

we have

$$\frac{e^{i(\omega_{fi}\pm\omega)t}-1}{\omega_{fi}\pm\omega} = ie^{i(\omega_{fi}\pm\omega)/2}\frac{\sin[(\omega_{fi}\pm\omega)t/2]}{(\omega_{fi}\pm\omega)/2}$$

Therefore, the transition amplitude

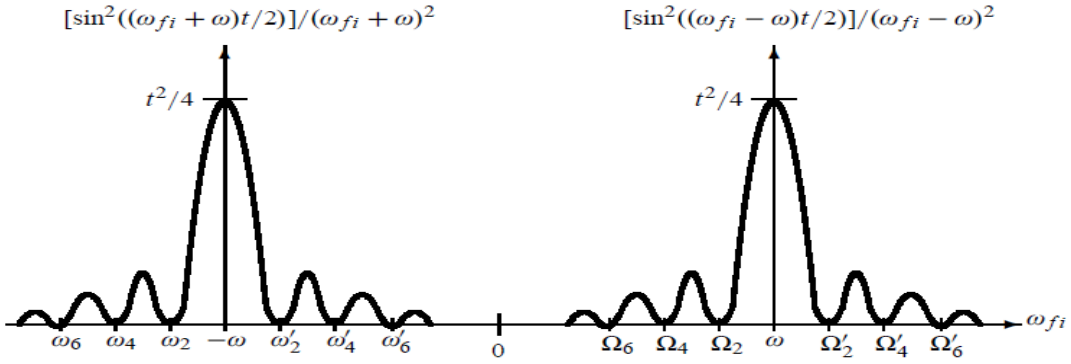
$$a_{fi}^{(1)}(t) = i\, e^{i(\omega fi \pm \omega)/2} \sin[\{(\omega_{fi} \pm \omega)t/2\}/(\omega_{fi} \pm \omega)/2]\, T_{fi}^{\pm}/\hbar$$



Transition probability $P_{fi}(t) = |a_{fi}^{(1)}(t)|^2$

At resonance *i.e. at* $\omega = \pm \omega_{fi}$:

$$P_{fi}^{\pm}(t) = |T_{fi}^{\pm}|^2/\hbar^2 \{\sin [\{(\omega_{fi} \pm \omega)t/2\}/(\omega_{fi} \pm \omega)/2]\}^2$$



Transition probability is an oscillating sinusoidal function with a period $2\pi/\omega_{fi}$. It has an interference pattern and decays rapidly as ω moves away from $\omega = \pm \omega_{fi}$. The height and width of the main peak are proportional to t^2 and $1/t$; *'t', being the interaction-time of electron with the radiation field i. e. time during which e.m. field is on*.

Transition peaks are maximum either at $\omega_{fi} = -\omega$ or at $\omega_{fi} = \omega$ i.e. probability of transition is maximum when the frequency of perturbing field $\omega = \pm \omega_{fi}$.

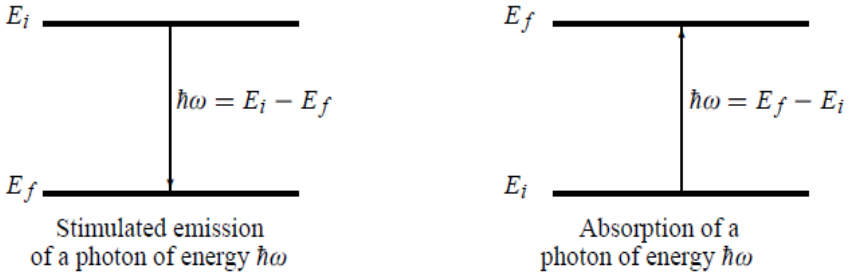
i. ***Absorption*** $(\omega_{fi} > 0)$:

$$P_{fi}(t) \cong \frac{|T_{fi}^{+}|^2}{\hbar^2} \left\{ \frac{\sin [(\omega_{fi} - \omega) t/2]}{(\omega_{fi} - \omega)/2} \right\}^2$$

ii. ***Induced emission*** $(\omega_{fi} < 0)$:

$$P_{fi}(t) \cong \frac{|T_{fi}^{-}|^2}{\hbar^2} \left\{ \frac{\sin [(\omega_{fi} + \omega) t/2]}{(\omega_{fi} + \omega)/2} \right\}^2$$

Line Width : It is the width of the main peak at half of the maximum intensity. *Its quantum analogue is initial transition probability per unit time for spontaneous emission.*



Thus, the effect of time dependent perturbation of the quantum system is to absorb *or emit* radiation quantum (photon) by *or from* the system as a result of electronic transition.

For a strictly monochromatic field, these transition probabilities depend strongly on the difference $\omega - |\omega_{fi}|$, and lead to a nonstationary transition rate. A transition probability that is linear in time (constant transition rate) is obtained if one considers the transition from an initial state $|i\rangle$ to a continuum of final states $|f\rangle$. In this case, the transition rate is obtained by using a *Fermi golden rule:*

$$W_{fi}^{\pm} = \frac{dP^{\pm}(t)}{dt} = \frac{2\pi}{\hbar}|\langle f|T^{\pm}|i\rangle|^2 \rho(E_f = E_i \pm \hbar\omega)$$

where $\rho(E_f)$ is the density of the final states. Similarly, when the radiation field is not monochromatic, but rather contains a spectrum of frequencies $u(\omega)$, the transition rate is

$$W_{fi} = \frac{4\pi^2 e^2}{m^2\hbar^2}\frac{u(\omega_{fi})}{\omega_{fi}^2}\langle f|e^{\pm i\mathbf{k}\cdot\mathbf{r}}[\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{p} \pm i\mathbf{S}\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})]|i\rangle|^2$$

where $|i\rangle$ and $|f\rangle$ are the initial and final (discrete) states, and the plus/minus signs correspond to absorption and induced emission, respectively.

MULTIPOLE TRANSITIONS

In the long wavelength approximation, $e^{\pm i\mathbf{k}\cdot\mathbf{r}} \approx 1 + i\mathbf{k}\cdot\mathbf{r}\cdots$ so $T_{fi}^{\pm}$ is given by the following multipole expansion:

$$T_{fi}^{\pm} \approx im\omega_{fi}\langle f|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}|i\rangle + \frac{i}{2}\langle f|(\mathbf{L}+2\mathbf{S})\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})|i\rangle - \frac{m\omega_{fi}}{2}\langle f|(\mathbf{k}\cdot\mathbf{r})(\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r})|i\rangle$$

The first term corresponds to an *electric-dipole transition.* The second term corresponds to a *magnetic-dipole transition,* and the third term corresponds to an *electric-quadrupole transition.* Usually, the transition rate is dominated by the electric-dipole term; in this case the transition rate is

$$W_{fi} = \frac{4\pi^2 e^2}{\hbar^2}u(\omega_{fi})|\langle f|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}|i\rangle|^2$$

However, for particular states $|i\rangle$ and $|f\rangle$, $\langle f|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}|i\rangle$ may vanish. This state is called the *forbidden transition.* Note that for an isotropic external radiation field, the polarization vector $\boldsymbol{\varepsilon}$ is randomly oriented. Averaging the components of the unit vector $\hat{\boldsymbol{\varepsilon}}$ over all angles gives

$$W_{fi} = \frac{4\pi^2 e^2}{3\hbar^2}u(\omega_{fi})|\langle f|\mathbf{r}|i\rangle|^2 \equiv B_{fi}u(u_{fi})$$

B_{fi} are known as the *Einstein coefficients* for absorption and induced emission.

SPONTANEOUS EMISSION

An excited atomic system can also emit radiation in the absence of an external radiation field. The transition rate for a spontaneous transition, in the dipole approximation, is given by

$$W_{fi}^{\text{spon}} = \frac{4}{3}\frac{e^2}{\hbar}\frac{\omega_{fi}^3}{c^3}|\langle f|r|i\rangle|^2 \equiv A_{fi}$$

where A_{fi} is the Einstein coefficient for spontaneous emission.

Electric-dipole transitions: To obtain the selection rules for electric-dipole transitions we consider matrix elements of the form $\langle f|x|i\rangle$, $\langle f|y|i\rangle$, and $\langle f|z|i\rangle$ where $|i\rangle$ and $|f\rangle$ are eigenstates of an electron moving in a central potential. The unperturbed wave function is then given by

$$\begin{cases} |i\rangle \equiv |n_i, l_i, m_i\rangle \rightarrow \psi_{n_i l_i m_i} = R_{n_i l_i}Y_{l_i}^{m_i}(\theta,\phi) \\ |f\rangle \equiv |n_f, l_f, m_f\rangle \rightarrow \psi_{n_f l_f m_f} = R_{n_f l_f}Y_{l_f}^{m_f}(\theta,\phi) \end{cases}$$

where $Y_l^m(\theta, \phi)$ are the spherical harmonic functions. In this representation,

$$\begin{cases} x \pm iy = r \sin\theta e^{\pm i\phi} = \mp\sqrt{\dfrac{8\pi}{3}} r Y_1^{\pm 1}(\theta, \phi) \\ z = r\cos\theta = \sqrt{\dfrac{4\pi}{3}} r Y_1^0(\theta) \end{cases}$$

Therefore, the matrix element $\langle f|z|i\rangle$ is proportional to the angular integral

$$\int \left(Y_{l_f}^{m_f}\right)^* (\theta, \phi)\, Y_1^0(\theta) Y_{l_i}^{m_i}(\theta, \phi)\, d\Omega$$

which is different from zero only if $\Delta l = l_f - l_i = \pm 1$ and $\Delta m = m_f - m_i = 0$. Similarly, the matrix elements $\langle f|x|i\rangle$ and $\langle f|y|i\rangle$ are proportional to linear combinations of the form

$$\int \left(Y_{l_f}^{m_f}\right)^* (\theta, \phi) Y_1^{\pm 1}(\theta) Y_{l_i}^{m_i}(\theta, \phi)\, d\Omega$$

which are different from zero only if $\Delta l = \pm 1$ and $\Delta m = \pm 1$. Grouping these results together we finally obtain

$$\begin{cases} \Delta l = l_f - l_i = \pm 1 \\ \Delta m = m_f - m_i = 0, \pm 1 \end{cases}$$

Einstein "*A* coefficient" – Spontaneous Emission

$B_{m\to n}$, $B_{n\to m}$ Einstein *B* Coefficients

induced emission

absorption

$A_{m\to n}$ spontaneous emission coefficient

N_m = number of systems (molecules) in state of energy E_m (upper state)

N_n = number of systems (molecules) in state of energy E_n (lower state)

At temp *T*, Boltzmann law gives:

$$\frac{N_m}{N_n} = \frac{e^{-E_m/k_BT}}{e^{-E_n/k_BT}} = e^{-h\nu_{mn}/k_BT}$$

At equilibrium :

rate of downward transitions = rate of upward transitions

$$N_m\left\{A_{m\to n} + B_{m\to n}\rho(\nu_{mn})\right\} = N_n B_{n\to m}\rho(\nu_{mn})$$

spontaneous emission stimulated emission absorption

Using $\frac{N_m}{N_n} = \frac{e^{-E_m/k_BT}}{e^{-E_n/k_BT}} = e^{-h\nu_{mn}/k_BT}$

$$e^{-h\nu_{mn}/k_BT} = \frac{B_{n\to m}\rho(\nu_{mn})}{A_{m\to n} + B_{m\to n}\rho(\nu_{mn})}$$

Solving for $\rho(\nu_{mn})$

$$\rho(\nu_{mn}) = \frac{A_{m\to n}e^{-h\nu_{mn}/k_BT}}{-B_{m\to n}e^{-h\nu_{mn}/k_BT} + B_{n\to m}}$$

$$B_{n\to m} = B_{m\to n}$$

Then:

$$\rho(\nu_{mn}) = \frac{\frac{A_{m\to n}}{B_{m\to n}}}{e^{h\nu_{mn}/k_BT} - 1}$$

Take "sample" to be black body, reasonable approximation.

Planck's distribution formula

$$\rho(\nu_{mn}) = \frac{8\pi h\nu_{mn}^3}{c^3}\frac{1}{e^{h\nu_{mn}/k_BT} - 1}$$

Gives

$$A_{m\to n} = \frac{8\pi h\nu_{mn}^3}{c^3} B_{m\to n}$$

$$A_{m\to n} = \frac{32\pi^3\nu_{mn}^3}{3c^3\hbar}\left|\mu_{mn}\right|^2$$

Spontaneous emission – light not necessary,
$I = 0$, ν^3 dependence.

Spontaneous Emission

ν^3 dependence

No spontaneous emission - NMR

$\nu \cong 10^8$ Hz

Optical spontaneous emission

$\nu \cong 10^{15}$ Hz

Typical optical spontaneous emission time, 10 ns (10^{-8} s).

$$\left(\frac{\nu_{NMR}}{\nu_{optical}}\right)^3 = \left(\frac{10^8}{10^{15}}\right)^3 = 10^{-21}$$

NMR spontaneous emission time – 10^{13} s (>10^5 years).

Longer magnetic dipole transition is much weaker than optical electric dipole transition.

References used :

1. *Quantum Mechanics by L. I. Schiff, Mc-Graw Hill, Kogakusha,*

2. *Quantum Mechanics – Concepts & Applications by Nouredine Zettili &*
3. *Quantum Mechanics by V. K. Thankappan.*

Assignments

1. What is semi-classical theory or radiation ?
2. Write expression for Hamiltonian of the atomic electron in the external electromagnetic field.
3. Obtain expression for the transition probability at resonance in the stimulated emission of radiation.
4. What is line width?
5. What are multipole transitions ? Write the selection rules for electric-dipole transitions.

E-Content

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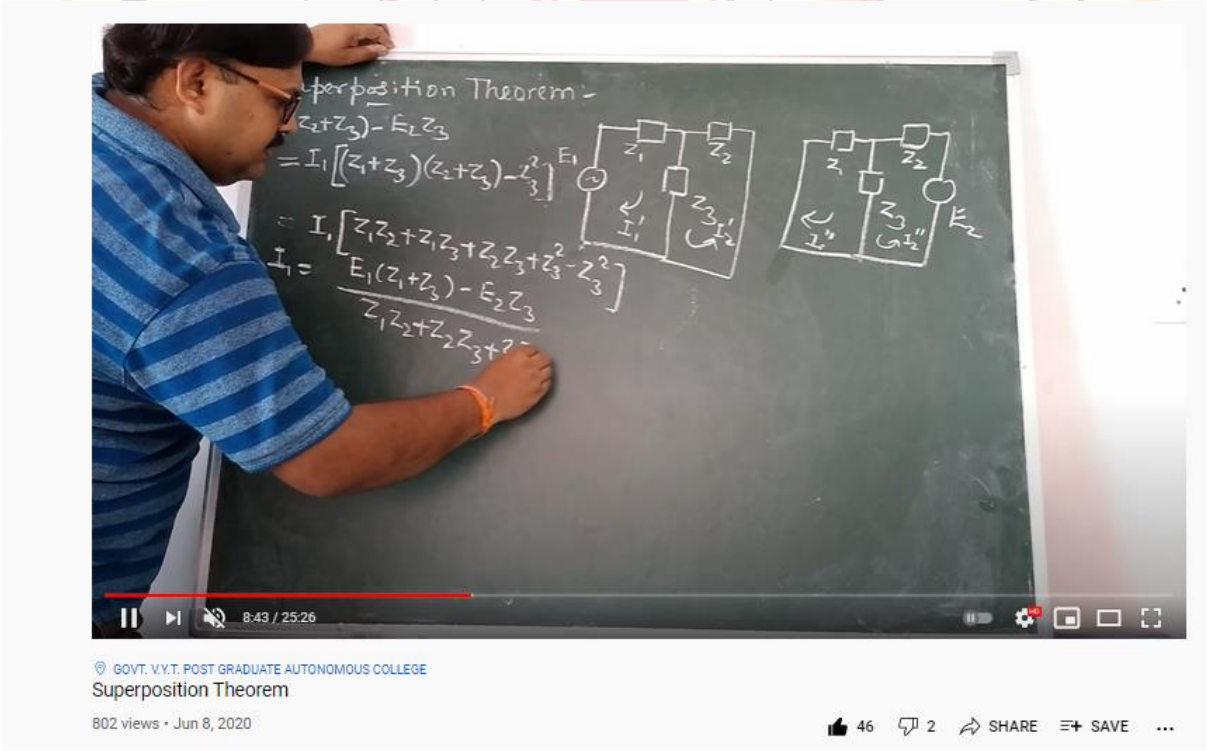
Module: Superposition Theorem and its circuit diagram

Module is divided in four sections:

1. **VIDEO CONTENT**
2. **(a) NOTES**
   (b) SUPPLEMENTARY MATERIAL
3. **SUBJECTIVE ASSIGNMENT BASED ON MODULE**
4. **OBJECTIVE QUESTION BASED ON MODULE**
5. **FEEDBACK SECTION**

Video Content: https://youtu.be/AfDpqpVETB4

In this video I explained Statement and derivation of Superposition theorem.



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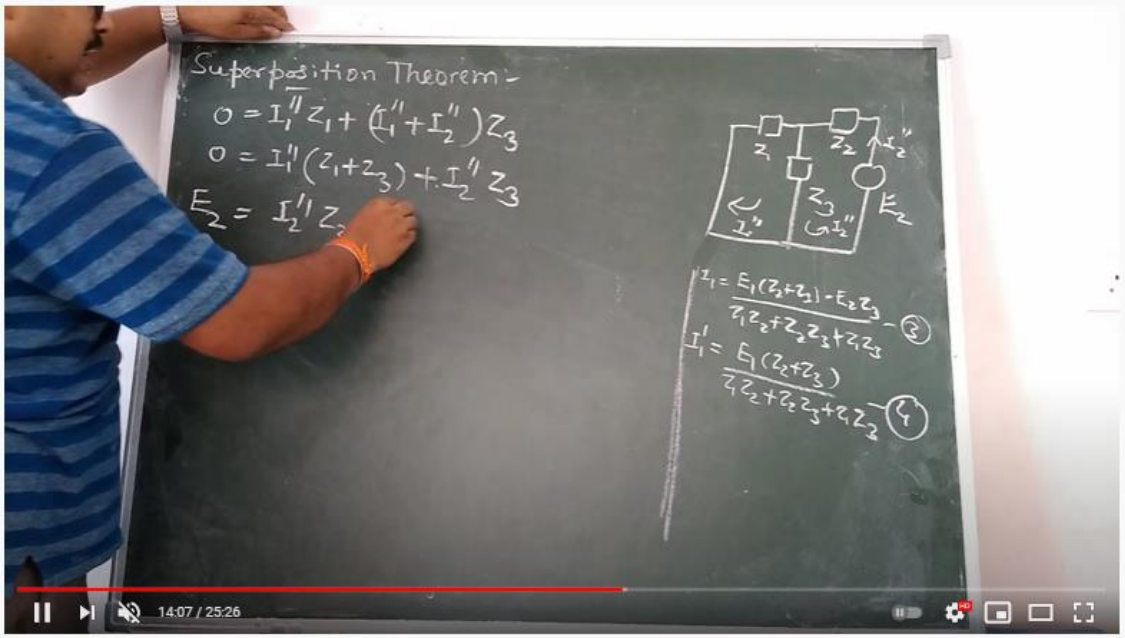

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Superposition Theorem

802 views • Jun 8, 2020

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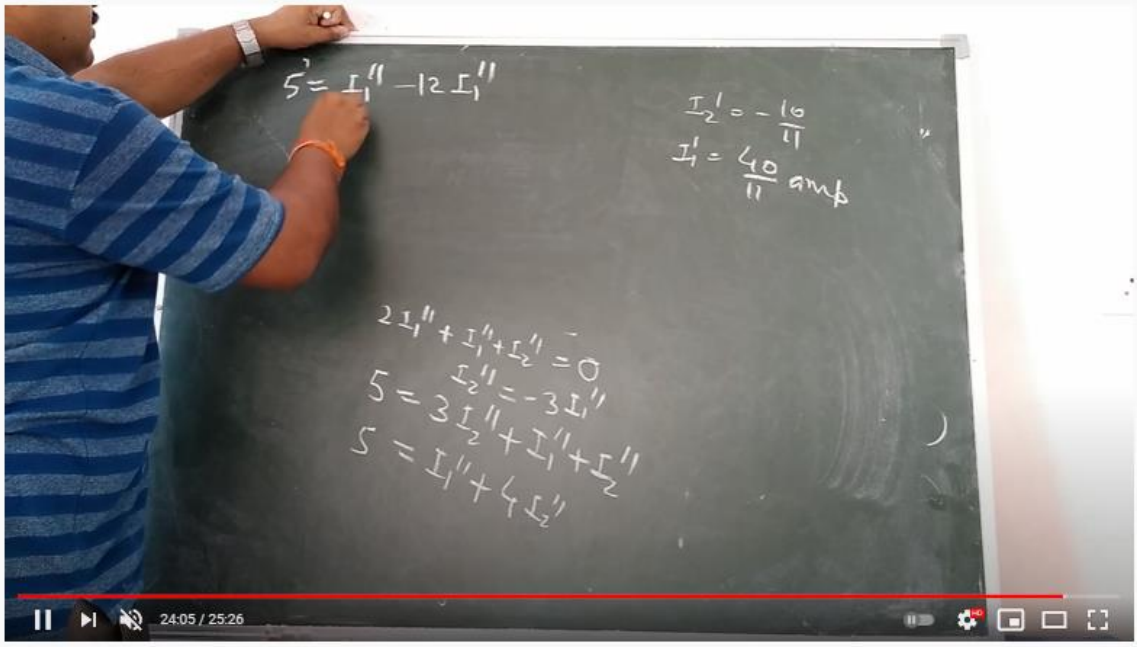

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Superposition Theorem

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2(a) NOTES

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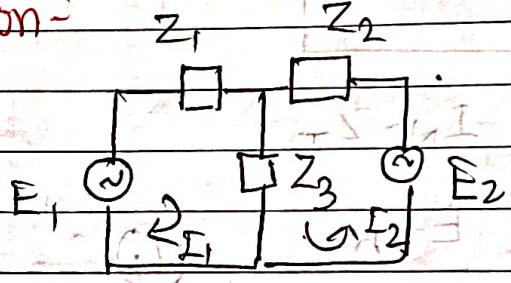
Superposition Theorem:

Statement: According to this theorem, in any linear network containing impedances and more than one source of emf, the current flowing in any branch is equal to vector sum of currents that would separately flow in that branch. If each source of emf were considered separately of course all the other sources being replaced at that time by their internal impedances.

Explanation:



Consider a network consists of two source E_1 and E_2 and impedances Z_1, Z_2 Z_3 shown in figure.

Let I_1 and I_2 are currents in mesh one and mesh (2) respectively due to source E_1 and E_2. Then

$$E_1 = I_1 Z_1 + (I_1 + I_2) Z_3$$

$$E_1 = I_1 (Z_1 + Z_3) + I_2 Z_3 \quad -(1)$$

$$E_2 = I_2 Z_2 + (I_1 + I_2) Z_3$$

$$E_2 = I_1 Z_3 + I_2 (Z_2 + Z_3) \quad -(2)$$

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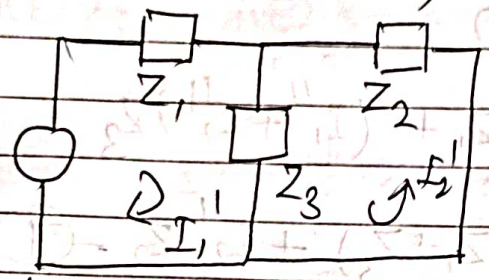
Multiply eq^n ① by (Z_2+Z_3) and eq^n (2) by Z_3 and then subtract we get

$$E_1(Z_2+Z_3) - E_2 Z_3 = I_1\left[(Z_1+Z_3)(Z_2+Z_3) - Z_3^2\right]$$

$$I_1 = \frac{E_1(Z_2+Z_3) - E_2 Z_3}{Z_1Z_2 + Z_1Z_3 + Z_2Z_3} \quad \text{— (3)}$$

Now consider the circuit in which source of emf E_2 is absent, then figure is



Let I_1' and I_2' are currents in mesh ① and mesh ②. Applying Kirchoff's law

$$E_1 = I_1' Z_1 + (I_1' + I_2') Z_3$$

$$E_1 = I_1'(Z_1+Z_3) + I_2' Z_3 \quad \text{— (4)} \times (Z_2+Z_3)$$

$$0 = I_2' Z_2 + (I_1' + I_2') Z_3$$

$$0 = I_1' Z_3 + I_2'(Z_2+Z_3) \quad \text{— (5)} \times Z_3$$

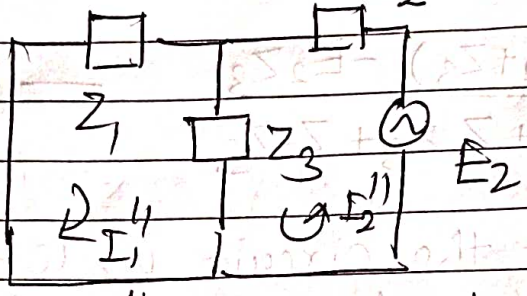
Subtracting

$$E_1(Z_2+Z_3) = I_1'\left[(Z_1+Z_3)(Z_2+Z_3) - Z_3^2\right]$$

$$E_1(Z_2+Z_3) = I_1'\left[Z_1Z_2 + Z_1Z_3 + Z_2Z_3\right]$$

$$I_1' = \frac{E_1 (Z_2 + Z_3)}{(Z_1Z_2 + Z_1Z_3 + Z_2Z_3)} \quad -(6)$$

Further we consider another circuit in which source of emf E_1 is removed Then circuit is



Let I_1'', I_2'' are currents in mesh ① and mesh ②

$$0 = I_1'' Z_1 + (I_1'' + I_2'') Z_3$$

$$0 = I_1'' (Z_1 + Z_3) + I_2'' Z_3 \quad -(7) \times (Z_2 + Z_3)$$

$$E_2 = I_2'' Z_2 + (I_1'' + I_2'') Z_3$$

$$E_2 = I_1'' Z_3 + I_2'' (Z_2 + Z_3) \quad -(8) \times Z_3$$

Subtracting

$$-E_2 Z_3 = I_1'' \left[(Z_1 + Z_3)(Z_2 + Z_3) - Z_3^2 \right]$$

$$I_1'' = \frac{-E_2 Z_3}{(Z_1Z_2 + Z_2Z_3 + Z_3Z_1)} \quad -(9)$$

From eqn ⑤, ⑥ and ⑨ we get

$$I_1 = I_1' + I_1''$$

Similarly we can prove

$$I_2 = I_2' + I_2''$$

Thus superposition theorem is proved.

2. (b) SUPPLEMENTARY MATERIAL

Superposition Theorem

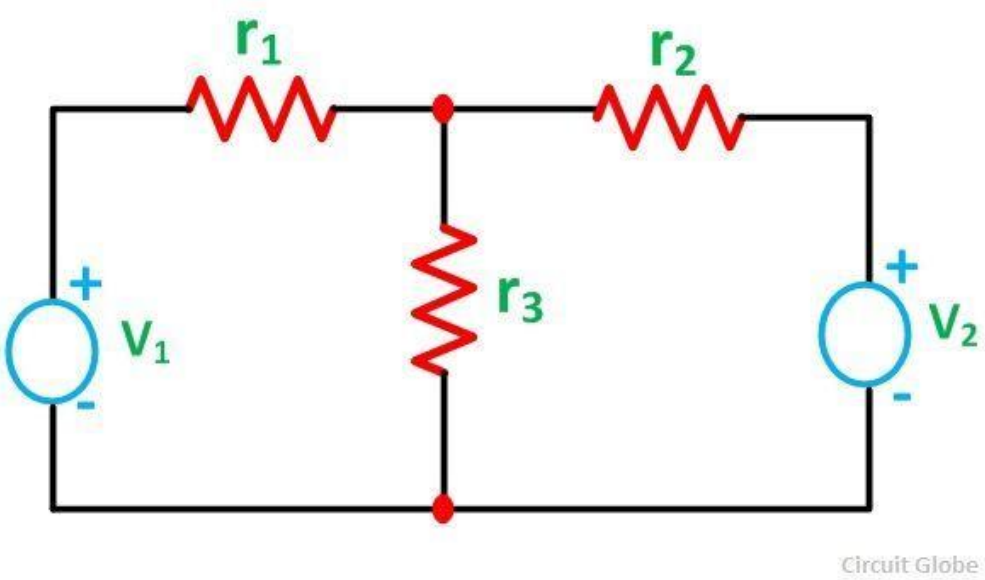
Superposition theorem states that in any linear, active, bilateral network having more than one source, the response across any element is the sum of the responses obtained from each source considered separately and all other sources are replaced by their internal resistance. The superposition theorem is used to solve the network where two or more sources are present and connected.

In other words, it can be stated as if a number of voltage or current sources are acting in a linear network, the resulting current in any branch is the algebraic sum of all the currents that would be produced in it when each source acts alone while all the other independent sources are replaced by their internal resistances.

It is only applicable to the circuit which is valid for the ohm's law (i.e., for the linear circuit).

Explanation of Superposition Theorem

Let us understand the superposition theorem with the help of an example. The circuit diagram is shown below consists of two voltage sources V_1 and V_2.



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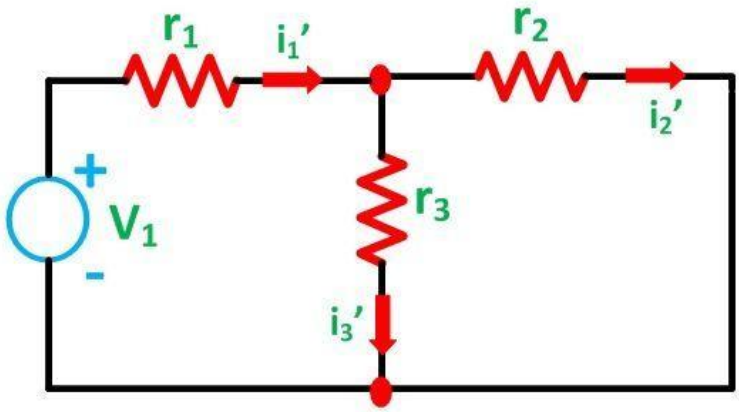
First, take the source V1 alone and short circuit the V2 source as shown in the circuit diagram below:



Here, the value of current flowing in each branch, i.e. i1', i2' and i3' is calculated by the following equations.

$$i_1' = \frac{V_1}{\frac{r_2 r_3}{r_2 + r_3} + r_1} \quad \ldots\ldots\ldots\ldots (1)$$

$$i_2' = i_1' \frac{r_3}{r_2 + r_3} \quad \ldots\ldots\ldots\ldots (2)$$

The difference between the above two equations gives the value of the current i3'

$$i_3' = i_1' - i_2'$$

Now, activating the voltage source V_2 and deactivating the voltage source V_1 by short-circuiting it, find the various currents, i.e. i_1'', i_2'', i_3'' flowing in the circuit diagram shown below:

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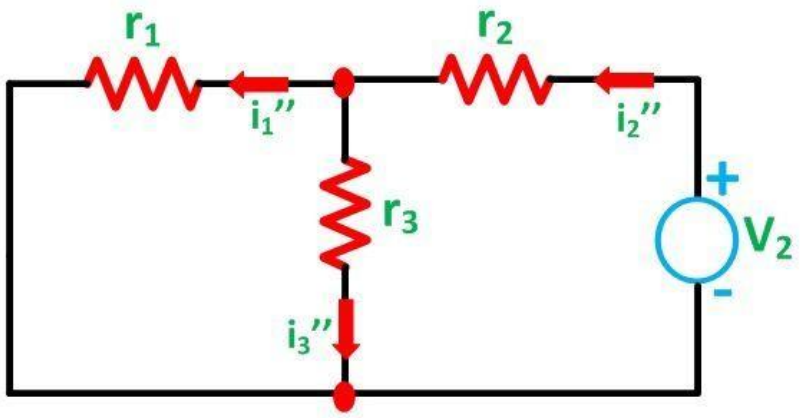

Here,

$$i_2'' = \frac{V_2}{\frac{r_1 r_3}{r_1 + r_3} + r_2} \quad \text{and} \quad i_1'' = i_2'' \frac{r_3}{r_1 + r_3}$$

And the value of the current i_3'' will be calculated by the equation shown below:

$$i_3'' = i_2'' - i_1''$$

As per the superposition theorem, the value of current i_1, i_2, i_3 is now calculated as:

$$i_3 = i_3' + i_3''$$

$$i_2 = i_2' - i_2''$$

$$i_1 = i_1' - i_1''$$

the various branches.

Steps for Solving network by Superposition Theorem

Considering the circuit diagram A, let us see the various steps to solve the superposition theorem:

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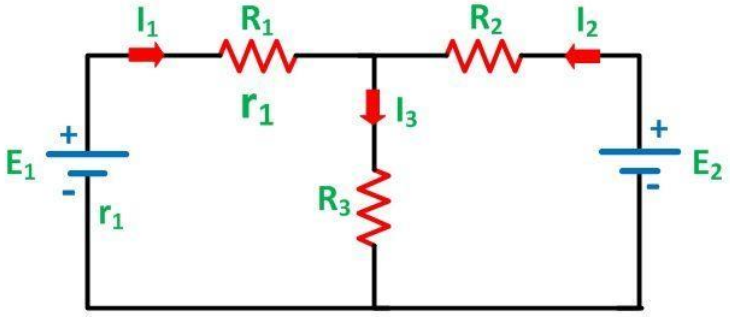
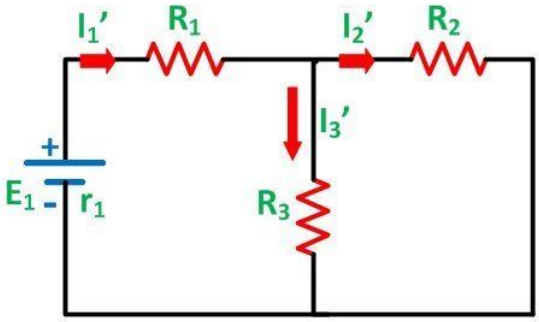
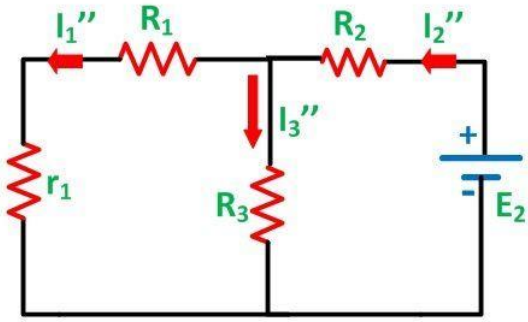


Circuit Diagram A



Circuit Diagram B



Circuit Diagram C

Step 1 – Take only one independent source of voltage or current and deactivate the other sources.

Step 2 – In the circuit diagram B shown above, consider the source E_1 and replace the other source E_2 by its internal resistance. If its internal resistance is not given, then it is taken as zero and the source is short-circuited.

Step 3 – If there is a voltage source than short circuit it and if there is a current source then just open circuit it.

Step 4 – Thus, by activating one source and deactivating the other source find the current in each branch of the network. Taking the above example find the current I_1', I_2'and I_3'.

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Step 5 – Now consider the other source E_2 and replace the source E_1 by its internal resistance r_1 as shown in the circuit diagram C.

Step 6 – Determine the current in various sections, I_1'', I_2'' and I_3''.

Step 7 – Now to determine the net branch current utilizing the superposition theorem, add the currents obtained from each individual source for each branch.

Step 8 – If the current obtained by each branch is in the same direction then add them and if it is in the opposite direction, subtract them to obtain the net current in each branch.

The actual flow of current in the circuit C will be given by the equations shown below:

$$I_1 = I_1' - I_1''$$

$$I_2 = I_2' - I_2''$$

$$I_3 = I_3' - I_3''$$

Thus, in this way, we can solve the superposition theorem.

Reference:

https://circuitglobe.com/what-is-superposition-theorem.html

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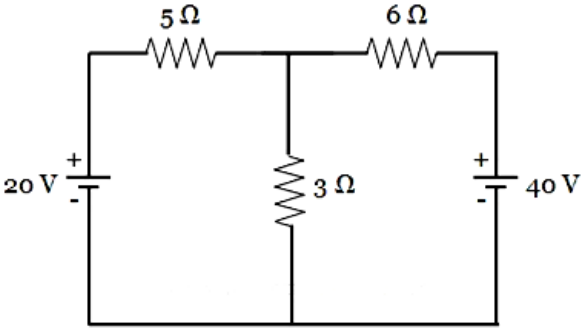
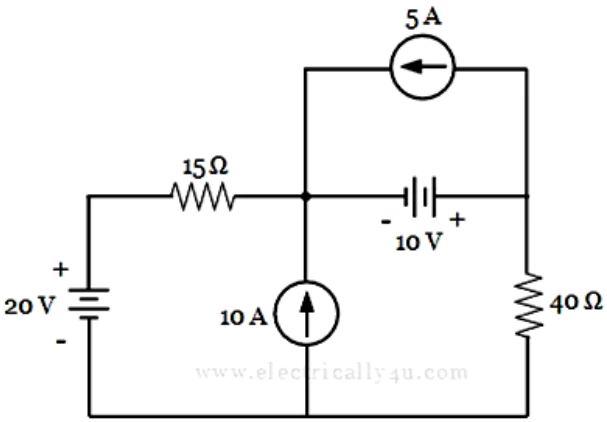
3. ASSIGNMENT

1. **Find the current through 3 Ω resistor using superposition theorem.**



2. **Find the voltage across through 15 Ω resistor using superposition theorem.**



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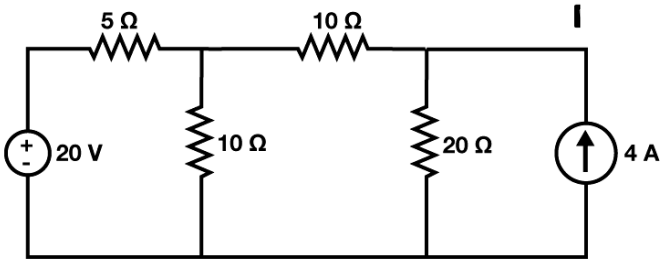
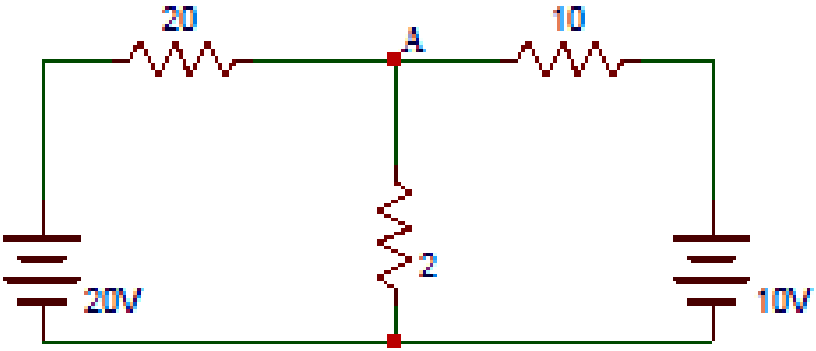
3. **Find the current flowing through 20 Ω using the superposition theorem.**



4. **Find the voltage across 2Ω resistor due to 20V source in the circuit shown below.**



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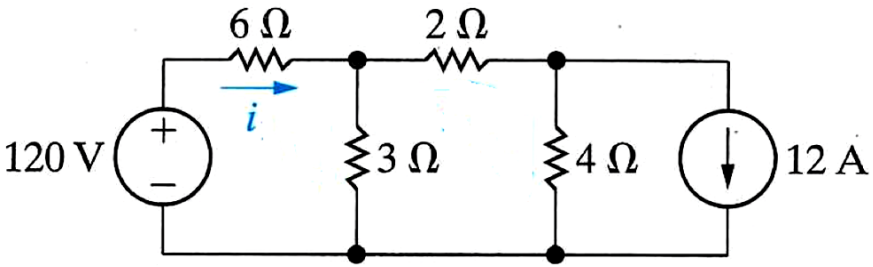
5. **Use superposition theorem to determine the current delivered by the voltage source in the circuit of figure both source are DC**



4. MULTIPLE CHOICE QUESTIONS

1. In superposition theorem, when we consider the effect of one voltage source, all the other voltage sources are _____

a) Shorted b) Opened

c) Removed d) Undisturbed

2. In superposition theorem, when we consider the effect of one current source, all the other voltage sources are _____

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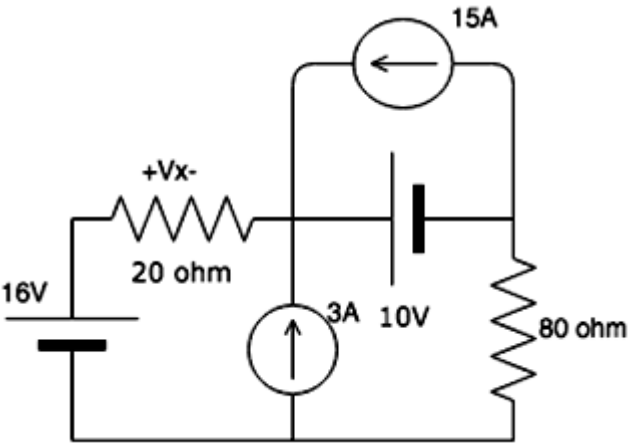
a) Shorted b) Opened

c) Removed d) Undisturbed

3. Find the value of Vx due to the 16V source.



a) 4.2V b) 3.2V c) 2.3V d) 6.3V

4. Superposition theorem is valid for _____

a) Linear systems

b) Non-linear systems

c) Both linear and non-linear systems

d) Neither linear nor non-linear systems

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5. Superposition theorem does not work for _____

a) Current

b) Voltage

c) Power

d) Works for all: current, voltage and power

Ans: 1 (a), 2.(a), 3.(b), 4.(a), 5.(c)

5. FEEDBACK QUESTIONS

1. Did the lecture cover what you were expecting?
2. What is your opinion about the video lecture?
3. How much this session was useful from the knowledge and information point of view?
4. Are you satisfied with the content of the video lecture and given questions?
5. If you could change one specific thing what would that be?

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Module: Thevenin Theorem and its circuit diagram

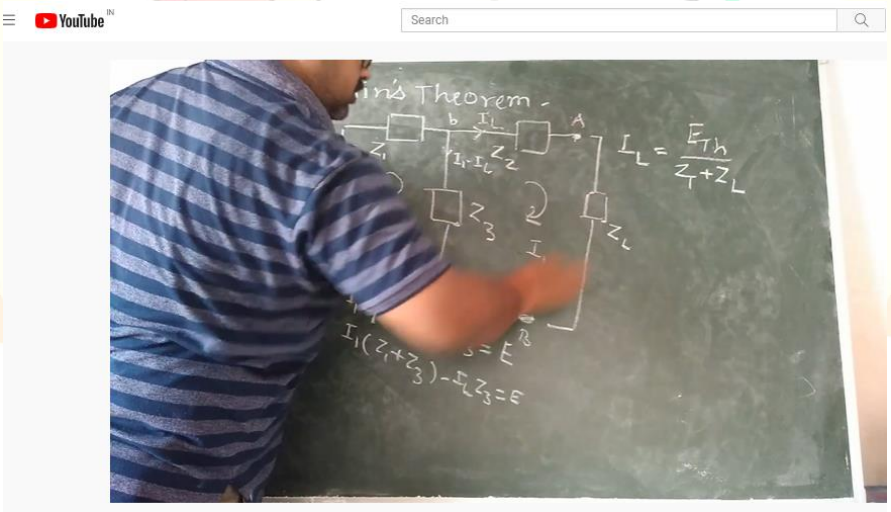
Module is divided in four sections:

1. **VIDEO CONTENT**
2. **(a) NOTES**
   (b) SUPPLEMENTARY MATERIAL
3. **SUBJECTIVE ASSIGNMENT BASED ON MODULE**
4. **OBJECTIVE QUESTION BASED ON MODULE**
5. **FEEDBACK SECTION**

Video Content:

https://youtu.be/IBphnGWAaT8

In this video I explained Statement and derivation of Thevenin theorem. The two terminal linear networks can be converted into Thevenin equivalent circuit.



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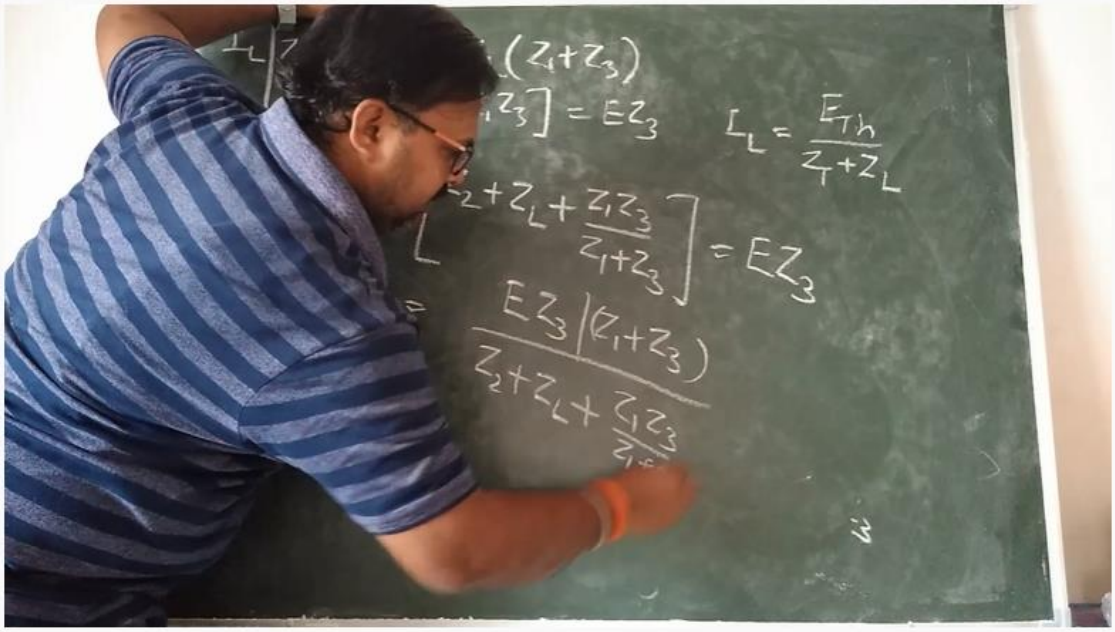

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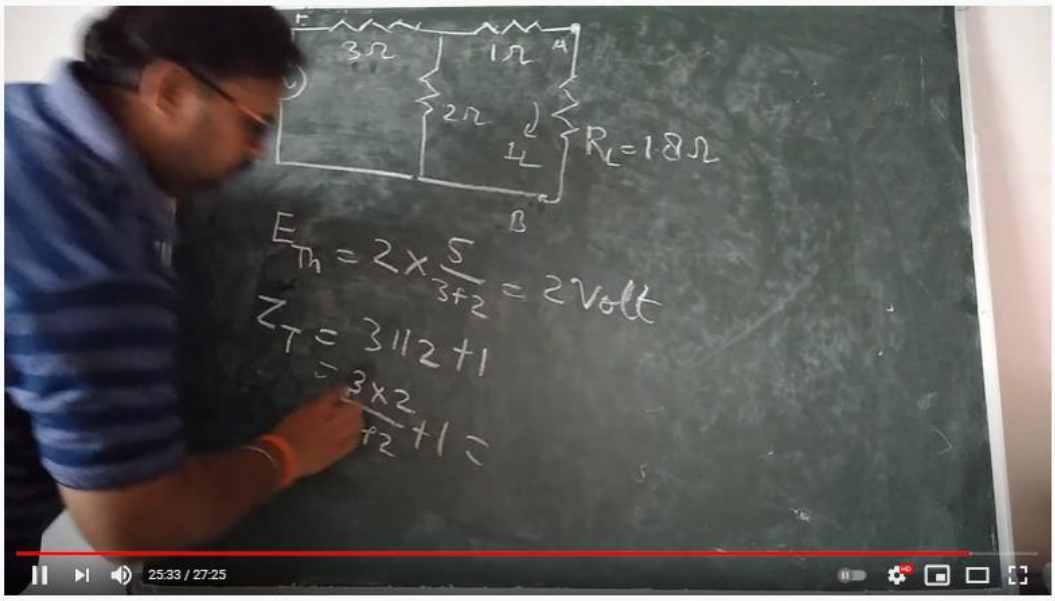
Thevenin's Theorem



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Thevenin's Theorem
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2(a) NOTES

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Circuit elements:- The individual circuit component as Inductor, resistor Capacitor with two terminals by which it may be connected to other electric component.

Network:- Any electrical circuit containing resistance, capacitance inductance and generators is known as electrical network. The circuit which contains no source of electromotive force (emf) is known as Passive network and the circuit which contains source of emf is called Active network. When current in network is directly proportional to driving voltage, then network is called linear network.

Branch:- A branch of network is defined as group of elements in series (group of elements along which current remains constant).

Mesh or loop:- A closed path in network is called Loop or Mesh.

Node or Junction:- A node is point where two or more branches meet and are connected electrically.

Network Theorems:- The simple networks can be solved by series parallel circuit or by using Kirchhoff's law, but some networks are not solvable by using series parallel circuit theory. These can be solved easily by applying some theorems. These theorems are called Network Theorems.

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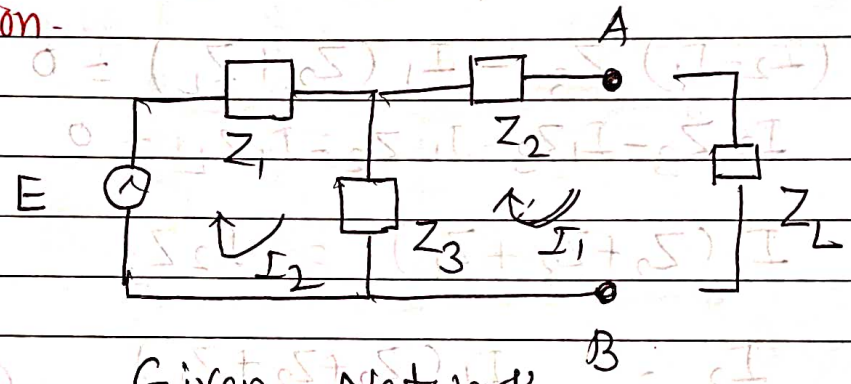
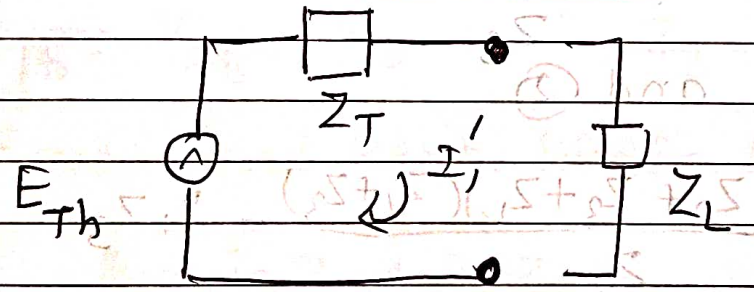
Thevenin Theorem:-

Statement:- Any two terminal linear network containing impedance and energy source can be replaced by its equivalent circuit containing an energy source E_{Th} and Impedance Z_T acting in series. Here E_{Th} is open circuit voltage across the terminals of given network and Z_T is impedance across the terminal when energy sources are replaced by its internal impedance if any.

Explanation-



Given Network



Thevenin equivalent circuit

Consider a linear network consisting of impedance Z_1, Z_2, Z_3 and energy source E_1. Let I_1 is current across its output through the load impedance Z_L when connected across its output.

In second figure E_{Th} is Thevenin voltage and Z_T impedance are acting in

in series. Let I_1' is the current across its output. Then according to Thevenin theorem

$$I_1 = I_1'$$

Proof:

Calculation of I_1 :

From figure (1), applying Kirchoff's law

$$E = I_2 Z_1 + (I_2 - I_1) Z_3$$

$$= I_2 Z_1 + I_2 Z_3 - I_1 Z_3$$

$$E = I_2 (Z_1 + Z_3) - I_1 Z_3 \quad \text{--- (1)}$$

$$(I_2 - I_1) Z_3 - I_1 (Z_2 + Z_L) = 0$$

$$I_2 Z_3 - I_1 Z_3 - I_1 Z_2 - I_1 Z_L = 0$$

$$I_1 (Z_2 + Z_3 + Z_L) = I_2 Z_3$$

$$I_2 = \frac{I_1 (Z_2 + Z_3 + Z_L)}{Z_3} \quad \text{--- (2)}$$

From (1) and (2)

$$E = \frac{I_1 (Z_2 + Z_3 + Z_L)(Z_1 + Z_3)}{Z_3} - I_1 Z_3$$

$$E Z_3 = I_1 \left[(Z_2 + Z_3 + Z_L)(Z_1 + Z_3) - Z_3^2 \right]$$

$$= I_1 \left[Z_1 Z_2 + Z_2 Z_3 + Z_1 Z_3 + Z_3^2 + Z_1 Z_L + Z_3 Z_L - Z_3^2 \right]$$

$$= I_1 \left[Z_1 Z_2 + Z_2 Z_3 + Z_1 Z_3 + Z_1 Z_L + Z_3 Z_L \right]$$

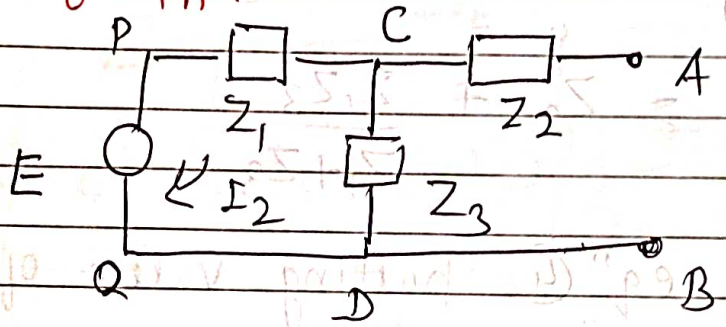
$$EZ_3 = I_1\left[Z_2(Z_1+Z_3) + Z_L(Z_1+Z_3) + Z_1Z_3\right]$$

$$I_1 = \frac{EZ_3}{(Z_1+Z_3)\left[Z_2+Z_L+\frac{Z_1Z_3}{Z_1+Z_3}\right]} \quad -③$$

Calculation of I_1':- From second figure

$$I_1' = \frac{E_{Th}}{Z_1+Z_L} \quad -④$$

Calculation of E_{Th} :-



$$E_{Th} = V_{AB} = V_{CD} = I_2Z_3$$

From closed Mesh ~~RQDC~~ PCDQP

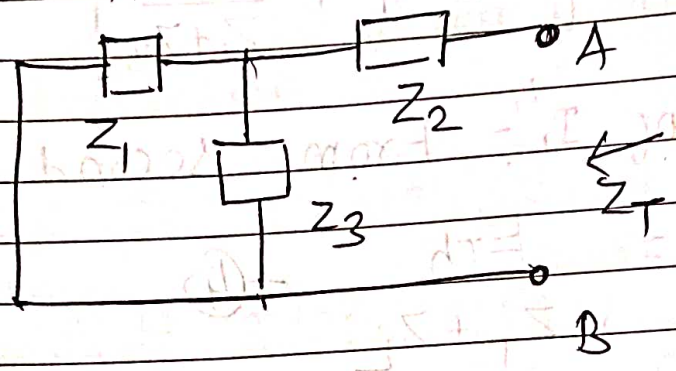
$$E = I_2Z_1 + I_2Z_3$$

$$I_2 = \frac{E}{Z_1+Z_3}$$

Therefore $E_{Th} = I_2Z_3$

$$= \frac{EZ_3}{Z_1+Z_3}$$

Calculation of Z_T: Z_T is equivalent impedance across the terminals of given network when energy source has been replaced by its internal impedance.



$$Z_T = Z_2 + Z_1 \| Z_3$$

$$= Z_2 + \frac{Z_1 Z_3}{Z_1 + Z_3}$$

In eqⁿ (4) putting value of E_{Th} and Z_T

$$I_1' = \frac{E Z_3}{(Z_1 + Z_3)\left[Z_2 + \frac{Z_1 Z_3}{Z_1 + Z_3} + Z_L\right]} \quad \text{---(5)}$$

From eqⁿ (3) and (5)

$$\boxed{I_1 = I_1'}$$

2.(b) SUPPLEMENTARY MATERIAL

Thevenin's Theorem

Thevenin's Theorem states that any complicated network across its load terminals can be substituted by a voltage source with one resistance in series. This theorem helps in the study of the variation of current in a particular branch when the resistance of the branch is varied while the remaining network remains the same.

For example, in designing electrical and electronics circuits.

A more general statement of Thevenin's Theorem is that any linear active network consisting of independent or dependent voltage and current source and the network elements can be replaced by an equivalent circuit having a voltage source in series with a resistance.

Where the voltage source being the open-circuited voltage across the open-circuited load terminals and the resistance being the internal resistance of the source.

In other words, the current flowing through a resistor connected across any two terminals of a network by an equivalent circuit having a voltage source Eth in series with a resistor Rth. Where Eth is the open-circuit voltage between the required two terminals called the Thevenin voltage and the Rth is the equivalent resistance of the network as seen from the two-terminal with all other sources replaced by their internal resistances called Thevenin resistance.

Explanation of Thevenin's Theorem

The Thevenin's statement is explained with the help of a circuit shown below:

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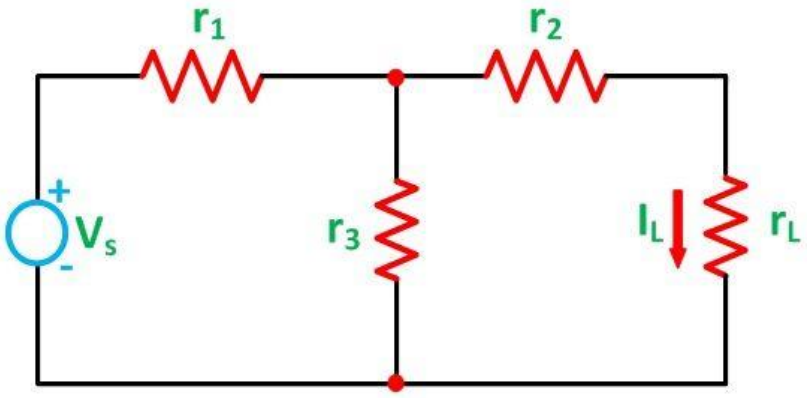
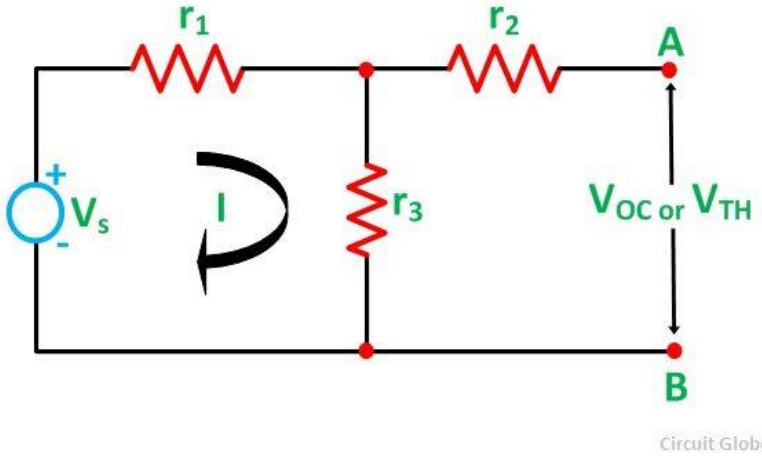


Let us consider a simple DC circuit as shown in the figure above, where we must find the load current IL by the Thevenin's theorem.

To find the equivalent voltage source, r_L is removed from the circuit as shown in the figure below and V_{oc} or V_{TH} is calculated.



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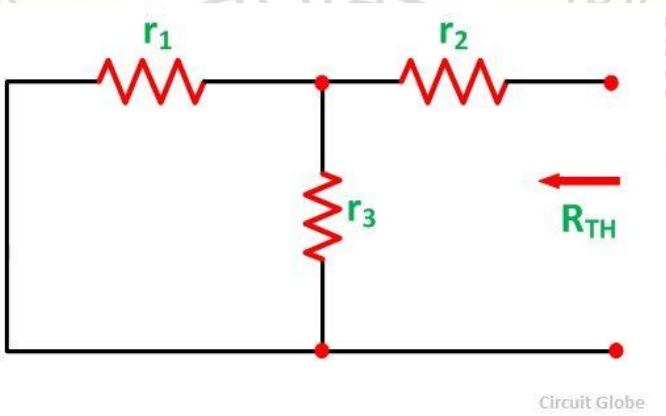
So,

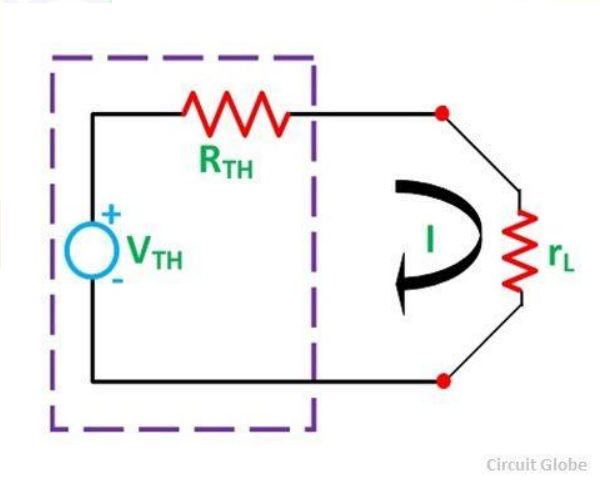
$$V_{OC} = I\, r_3 = \frac{V_S}{r_1 + r_3}\, r_3$$

Now, to find the internal resistance of the network (Thevenin's resistance or equivalent resistance) in series with the open-circuit voltage V_{OC} , also known as Thevenin's voltage V_{TH}, the voltage source is removed or we can say it is deactivated by a short circuit (as the source does not have any internal resistance) as shown in the figure below:



Therefore,

$$R_{TH} = r_2 + \frac{r_1 r_3}{r_1 + r_3}$$



Equivalent Circuit of Thevenin's Theorem

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As per Thevenin's Statement, the load current is determined by the circuit shown above and the equivalent Thevenin's circuit is obtained. The load current $\mathbf{I_L}$ is given as:

$$I_L = \frac{V_{TH}}{R_{TH} + r_L}$$

Where,

V_{TH} is the Thevenin's equivalent voltage. It is an open circuit voltage across the terminal AB known as load terminal

R_{TH} is the Thevenin's equivalent resistance, as seen from the load terminals where all the sources are replaced by their internal impedance

r_L is the load resistance

STEPS FOR SOLVING THEVENIN'S THEOREM

Step 1 – First of all remove the load resistance r_L of the given circuit.
Step 2 – Replace all the sources by their internal resistance.
Step 3 – If sources are ideal then short circuit the voltage source and open circuit the current source.
Step 4 – Now find the equivalent resistance at the load terminals, known as Thevenin's Resistance (R_{TH}).
Step 5 – Draw the Thevenin's equivalent circuit by connecting the load resistance and after that determine the desired response.
This theorem is possibly the most extensively used networks theorem. It is applicable where it is desired to determine the current through or voltage across any one element in a network. Thevenin's Theorem is an easy way to solve a complicated network

Reference:

https://circuitglobe.com/what-is-thevenins-theorem.html

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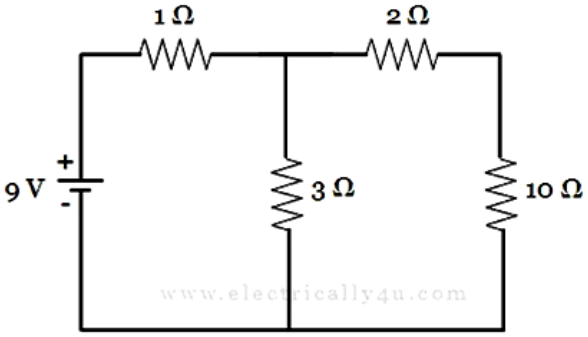
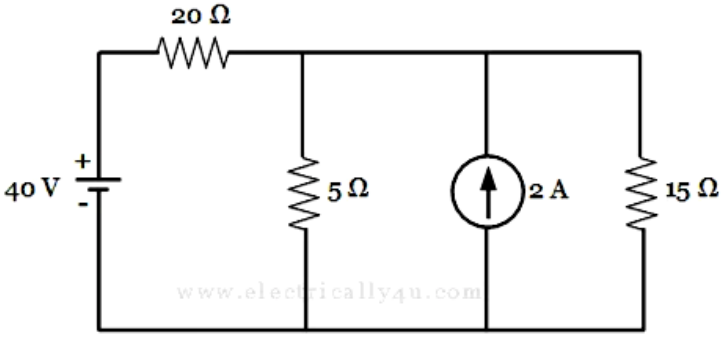
3. ASSIGNMENT

1. **Solve the given circuit to find the current through 10 Ω using Thevenin's Theorem.**



2. **Solve the given circuit to find the current through 15 Ω using Thevenin's Theorem.**



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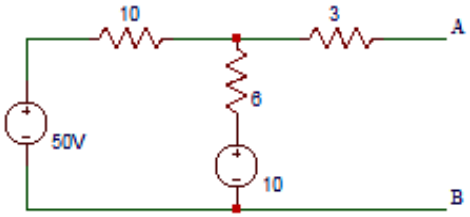
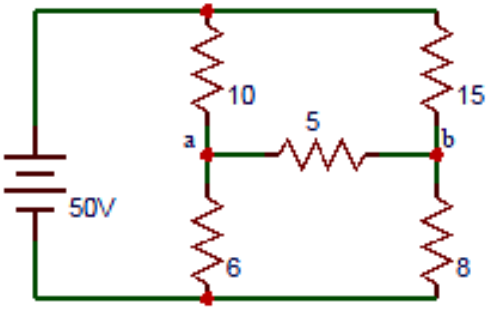
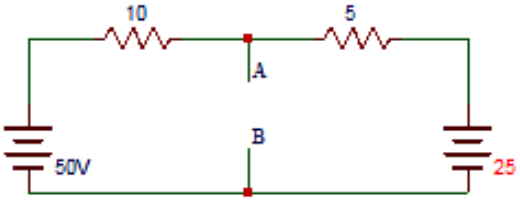
3. **Find the equivalent Thevenin's resistance between terminals A and B in the following circuit.**



4. **Determine the equivalent Thevenin's voltage between terminals 'a' and 'b' in the circuit shown below.**



5. **Find the equivalent Thevenin's resistance between terminals A and B in the circuit shown below.**



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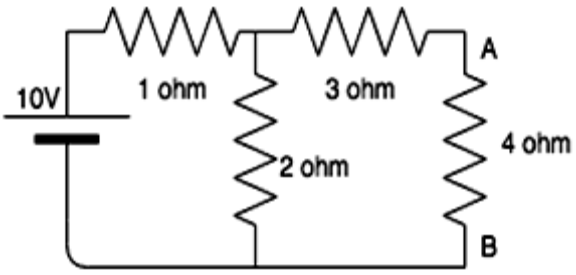
4. MULTIPLE CHOICE QUESTIONS

1. Calculate the Thevenin resistance across the terminal AB for the following circuit.

a) 4.34 ohm b) 3.67 ohm c) 3.43 ohm d) 2.32 ohm



2. The Thevenin voltage is the_____

a) Open circuit voltage

b) Short circuit voltage

c) Open circuit and short circuit voltage

d) Neither open circuit nor short circuit voltage

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3. Thevenin resistance is found by _____

a) Shorting all voltage sources

b) Opening all current sources

c) Shorting all voltage sources and opening all current sources

d) Opening all voltage sources and shorting all current sources

4. Which of the following is also known as the dual of Thevenin's theorem?

a) Norton's theorem

b) Superposition theorem

c) Maximum power transfer theorem

d) Millman's theorem

5. Thevenin's theorem is true for _____

a) Linear networks

b) Non-Linear networks

c) Both linear networks and nonlinear networks

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d) Neither linear networks nor non-linear networks

Ans: 1. (b), 2. (a), 3. (c), 4. (a), 5. (a)

5. FEEDBACK QUESTIONS

1. Did the lecture cover what you were expecting?
2. What is your opinion about the video lecture?
3. How much this session was useful from the knowledge and information point of view?
4. Are you satisfied with the content of the video lecture and given questions?
5. If you could change one specific thing what would that be?

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E-Content

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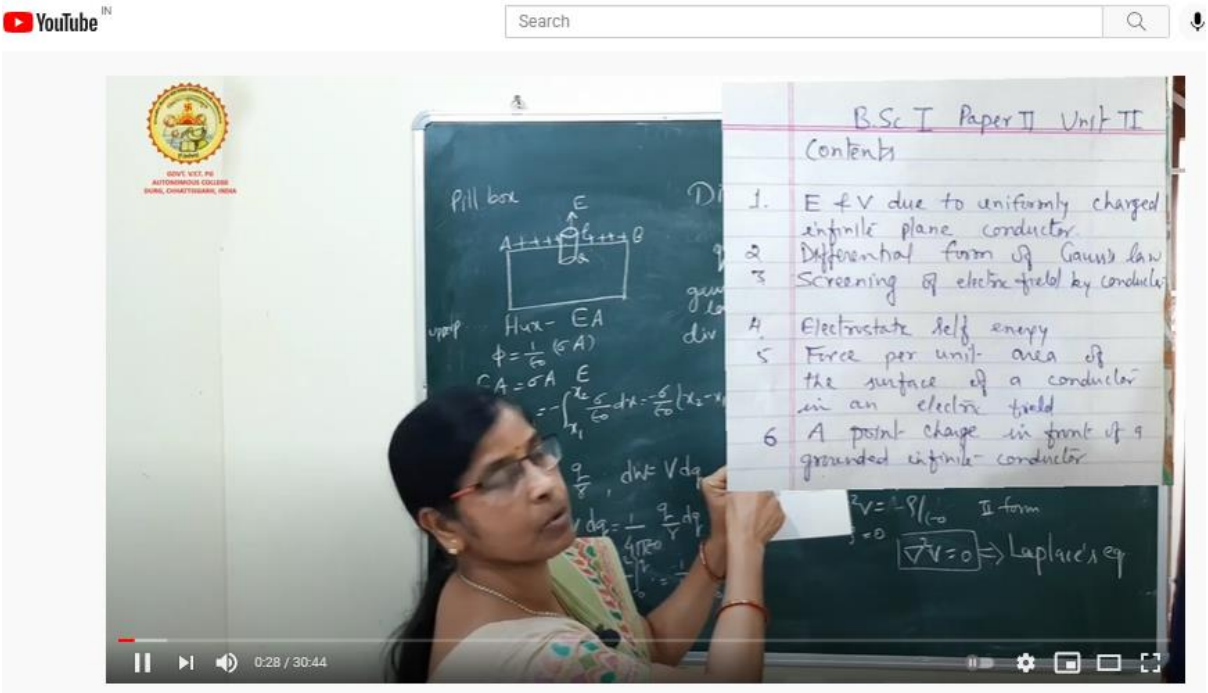
Module: Differential form of Gauss Law

Module is divided in four sections:

1. **VIDEO CONTENT**
2. **MATERIAL**
3. **OBJECTIVE QUESTION BASED ON MODULE**
4. **SUBJECTIVE ASSIGNMENT BASED ON MODULE**
5. **FEEDBACK SECTION**

Video Content: https://youtu.be/wV-DfrHoJO4

In this video I explained Gauss law and its differential form



13/4/2020

Gauss's Law

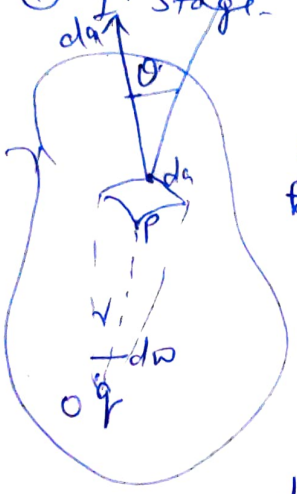
किसी विद्युत क्षेत्र में स्थित किसी भी आकार के बंद पृष्ठ से होकर अभिलंबवत गुजरने वाला विद्युत फलक्स, पृष्ठ के भीतर उपस्थित कुल आवेश का $1/\epsilon_0$ गुना होता है

$$\phi = \iint \vec{E} \cdot \vec{da} = \frac{1}{\epsilon_0} \Sigma q$$

$\Sigma q \rightarrow$ पृष्ठ के अंदर उपस्थित समस्त आवेशों का योग

$q = 0 \quad , \quad \phi = 0$

Proof - ① 1st stage - जबकि आवेश पृष्ठ के अंदर उपस्थित है



बंद पृष्ठ S के भीतर बिंदु O पर आवेश q स्थित है इस पृष्ठ पर कोई बिंदु P है जिस पर एक क्षेत्रफल da लिया जाता है da की दिशा पृष्ठ के $\perp$ है बिंदु O पर स्थित आवेश q के कारण P पर वि॰ क्षेत्र की तीव्रता -

$$\vec{E} = \frac{1}{4\pi\epsilon_0} \frac{q}{r^2} \quad \text{—①}$$

da तथा E के बीच θ कोण है, da से गुजरने वाला

flux $d\phi = E \cdot da = E\, da \cos\theta$ — ②

$$d\phi = \frac{1}{4\pi\epsilon_0} \frac{q}{r^2} da \cos\theta$$

$$= \frac{1}{4\pi\epsilon_0} q \frac{da'}{r^2} \qquad \text{where } da' = da\cos\theta$$

$$= \frac{1}{4\pi\epsilon_0} q\, dw \qquad \frac{da'}{r^2} = dw$$

$dw \rightarrow$ क्षेत्रफल da द्वारा बिंदु O पर बनने वाला घनकोण

इस प्रकार S से होकर गुजरने वाला कुल फलक्स

$$\phi = \Sigma d\phi = \frac{\Sigma q\, dw}{4\pi\epsilon_0} = \frac{q}{4\pi\epsilon_0} \Sigma dw$$

$$= \frac{q}{4\pi\epsilon_0} \cdot 4\pi = \frac{q}{\epsilon_0}$$

क्योंकि किसी भी बंद पृष्ठ द्वारा अपने अंदर स्थित किसी बिंदु पर

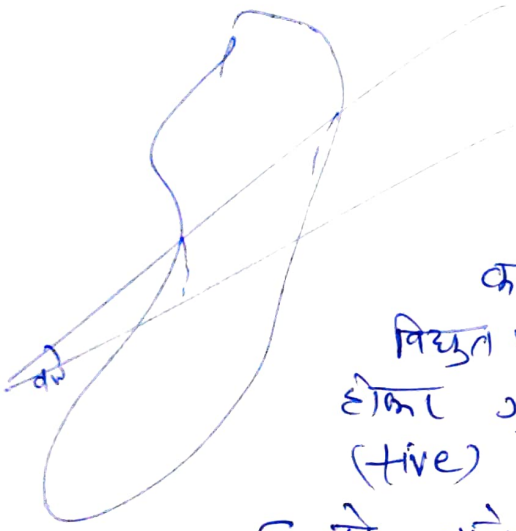
अंतरित कुल घन कोण $360^\circ = 4\pi$ होता है

यदि पृष्ठ S पर अनेक आवेश $q_1, q_2 \ldots$

... कुल फलक्स $\phi = \frac{1}{\epsilon_0}[q_1 + q_2 + q_3 + \ldots$

$= \frac{1}{\epsilon_0} \Sigma q$

② II Stage - आवेश पृष्ठ के बाहर है



माना कि आवेश q पृष्ठ के बाहर स्थित बिंदु O पर स्थित है बिंदु O पर घनकोण dw बनाते हुए एक शंकु खींचा जाय जो प्रथम सतह को S_1 तथा द्वितीय सतह को S_2 पर काटता है तो क्षेत्रफल S_1 से होकर जाने वाला विद्युत फलक्स Incident flux (-ve) तथा S_2 से होकर गुजरने वाला फलक्स (पृष्ठ से बाहर) outgoing flux (+ive) sign द्वारा प्रदर्शित किया जाता है

S_1 से जाने वाला incident flux $= -\frac{q\,dw}{4\pi\epsilon_0}$

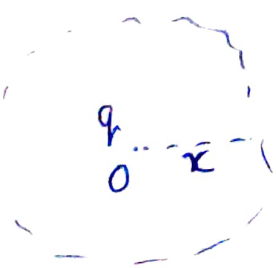
S_2 " " outgoing flux $= +\frac{q\,dw}{4\pi\epsilon_0}$

Total flux $= 0$

Applications of Gauss's law

Gaussian surface

किसी बिंदु आवेश के कारण विद्युत क्षेत्र की तीव्रता तथा विभव



बिंदु O पर रखे आवेश q के कारण बिंदु P पर E, V ज्ञात करना है

O को केन्द्र मानकर x त्रिज्या लेकर एक गोला खींचते हैं, यह गोला ही गाउसियन पृष्ठ होगा

$\phi = \iint E \cdot dq = E \cdot 4\pi x^2$

लेकिन गॉस के नियम से

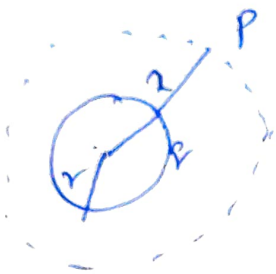
$\phi = \frac{1}{\epsilon_0} q$

बिंदु P पर विभव

$$V = -\int_{\infty}^{x} E\,dx = -\int_{\infty}^{r} \frac{q}{4\pi\epsilon_0 x^2}\,dx$$

$$= \frac{q}{4\pi\epsilon_0 r}$$

(2) किसी एकसमान आवेशित चालक गोले के कारण विद्युत क्षेत्र की तीव्रता तथा विद्युत विभव Spherical Shell



r त्रिज्या का चालक गोला q आवेश से आवेशित है. गोले के केन्द्र से x दूरी पर स्थित किसी बिंदु पर E, V की गणना करनी है

(1) जबकि बिंदु गोले के बाहर है

$x > r$

OP = x त्रिज्या का गोला Gaussian surface

इस पृष्ठ से संबद्ध विद्युत फलक्स $\phi = \iint E.dA$

$$= E.4\pi x^2$$

but $\phi = \frac{1}{4\pi\epsilon_0}\frac{1}{\epsilon_0}\Sigma q$

$$E.4\pi x^2 = \frac{1}{\epsilon_0} q$$

$$E = \frac{1}{4\pi\epsilon_0}\frac{q}{x^2}$$

बिंदु P पर विभव $V = -\int_{\infty}^{x} E\,dx = -\int_{\infty}^{x} \frac{q}{4\pi\epsilon_0}\frac{q}{x^2}$

$$= \frac{q}{4\pi\epsilon_0 x}$$

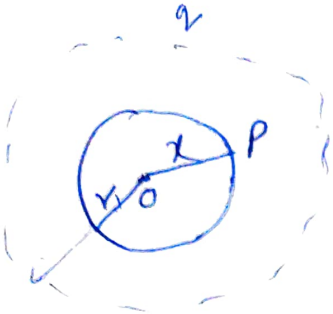
(2) जबकि बिंदु गोले के पृष्ठ पर स्थित है

$x = r$

$$E = \frac{1}{4\pi\epsilon_0}\frac{q}{r^2}$$

$$V = \frac{q}{}$$

(3) जबकि बिंदु गोले के अंदर स्थित है



$x < r$

छोटा गोला Gaussian surface

$$\phi = \iint E \cdot dq = E \cdot 4\pi x^2$$

चूंकि आंतरिक गोले के अंदर $q = 0$

$$\therefore \phi = 0$$
$$E = 0$$

बिंदु P पर विभव $V_{x<r}$

$$= -\int_{\infty}^{x} E\,dx = -\left[\int_{\infty}^{r} E_{x>r}\,dx + \int_{r}^{x} E_{x<r}\,dx\right]$$

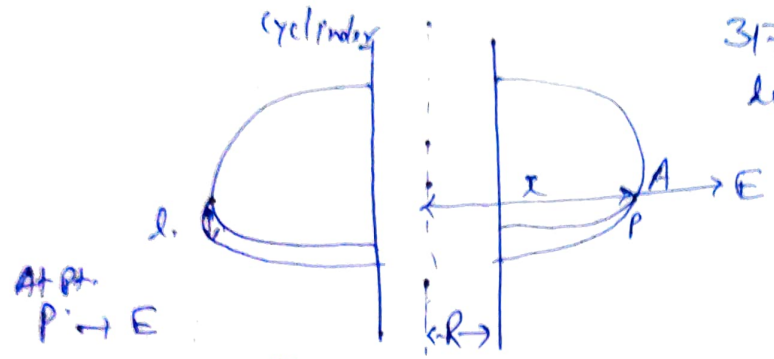
$$= -\left[\int_{\infty}^{r} \frac{1}{4\pi\varepsilon_0}\frac{q}{x^2}\,dx + 0\right]$$

$$= \frac{1}{4\pi\varepsilon_0}\frac{q}{r}$$

अर्थात् एक समान आवेशित चालक गोले या गोलीय खोल के अंदर प्रत्येक बिंदु पर विद्युत विभव ठीक उतना ही होता है जितना कि उसके पृष्ठ पर होता है

Applications of Gauss's law

An infinite line of charge & charged cyclindrical conductor



अनंत लंबाई, R → त्रिज्या
linear charge density λ

① P बेलन के बाहर
ले. l, x त्रिज्या Gaussian surface - P समाक्षीय
E की दिशा P → बाहर ⊥
∴ पृष्ठ के समतल तल से गुजरने वाला फलक्स = 0
वक्रपृष्ठ से जाने वाला flux

$$\phi = \iint E.da = \iint E \cdot 2\pi x l$$

∵ $x > R$ Gauss's law $\phi = \frac{1}{\epsilon_0}(q) = \frac{1}{\epsilon_0}\lambda l$.

$$E \cdot 2\pi x l = \frac{1}{\epsilon_0}\lambda l$$

$$E = \frac{1}{2\pi\epsilon_0}\lambda/x$$

② P बेलन के पृष्ठ पर $x = R$.

$$\therefore E = \frac{1}{2\pi\epsilon_0}\frac{\lambda}{R}$$

③ P बेलन के अंदर है $x < R$
बेलन के चारों $\phi = 0$ $\therefore E = 0$

Electrostatic field energy

विद्युत क्षेत्र में संचित ऊर्जा
charged spherical surface - σ
⇒ Force outward $\sigma^2/2\epsilon_0$ in unit area.
Radius $r \to r - dr$.

$$W = P_e \cdot dV$$

$$= \frac{\sigma^2}{2\epsilon_0} \cdot 4\pi r^2 dr$$ (पहले के बा. में रखने)

कार्य ⇒ E. → संचित conserved.

∴ stored energy $U_e \cdot 4\pi r^2 dr$

U_e → energy density of field E

$$U_e \cdot 4\pi r^2 dr = \frac{\sigma^2}{2\epsilon_0} \cdot 4\pi r^2 dr$$

$$\therefore U_e = \frac{\sigma^2}{2\epsilon_0} = \frac{1}{2\epsilon_0} (\epsilon_0 E)^2$$

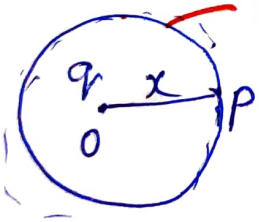
$\because \sigma = \epsilon_0 E$

$$U_e = \frac{\epsilon_0 E^2}{2}$$

E due to conducting sphere in Uni.

$P_t \to 0$, charge q

Gaussian surface



flux $\phi = \iint E \cdot da = E \cdot 4\pi x^2$

Gauss's law $\phi = \frac{1}{\epsilon_0} q$.

$$E \cdot 4\pi x^2 = \frac{1}{\epsilon_0} q$$

$$E = \frac{1}{4\pi\epsilon_0} \frac{q}{x^2}$$

Per unit area of the surface of conductor in an electric field

विद्युत क्षेत्र में एक चालक के पृष्ठ पर प्रति एकांक क्षेत्र बल

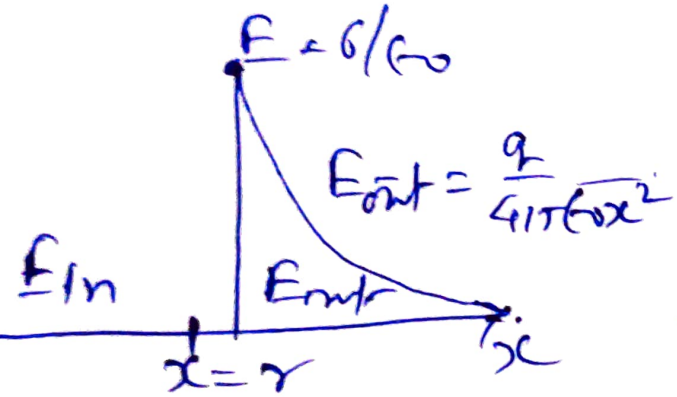
आवेशित पृष्ठ

अवयव

$\sigma \rightarrow$ Surface density

$r \rightarrow$ Radius

चालक गोला $q = 4\pi r^2 \sigma$



$\therefore E_{in} = 0$

$E_{out} = \frac{q}{4\pi\varepsilon_0 x^2}$

गोले के ठीक पास → बाहर → $E = \frac{q}{4\pi\varepsilon_0} = \frac{\sigma}{\varepsilon_0}$

$\Rightarrow$ त्रिज्यीय

da area $E_{in} = 0$, $E_{out} = \frac{\sigma}{\varepsilon_0}$

av. el. field $E_{av} = \frac{E_{in} + E_{out}}{2} = \frac{\sigma}{2\varepsilon_0}$

इस element पर लगने वाला बल

$dF = q \cdot E_{av} = \sigma\, da \cdot \frac{\sigma}{2\varepsilon_0}$

$$\boxed{F = \frac{\sigma^2}{2\varepsilon_0} dq}$$

Objective type questions

1 इस विद्युत द्विध्रुव को विद्युत क्षेत्र में की दिशा में 180° घुमाने में किया गया कार्य ...

2 गॉस के प्रमेय का अवकलन रूप है ...

3 एक समान आवेशित खोखले गोले के कारण विद्युत क्षेत्र किस स्थान पर शून्य होता है ...

4 समविभव पृष्ठ एवं विद्युत बल रेखाओं के बीच बनने वाला कोण ...

5 यदि कोई पृष्ठ विद्युत क्षेत्र के समांतर है तो इससे संबंधित विद्युत फ्लक्स ...

6 विद्युत क्षेत्र में ही द्विध्रुव आघूर्ण वाले द्विध्रुव पर लगने वाला बल आघूर्ण ...

7 विद्युत क्षेत्र तथा विभवांतर में संबंध ...

8 गॉस की विद्युत क्षेत्र के लिए संबंध ...

9 दूरी पर समान आवेश q है, तीसरा आवेश $-2q$ उनके बीच में रखा गया है, स्थितिज ऊर्जा का मान ...

10 इकाई धनावेश को E की दिशा के समांतर d दूरी पर विस्थापित करने में किया गया कार्य ...

Page No.:
Date:

Long/Short Type Qu.

1 गॉस के नियम को समझाओ

2 आवेशित गोलीय चालक के कारण विद्युत क्षेत्र की तीव्रता ज्ञात करो.

3 एक समान आवेशित अनंत चालक के कारण विद्युत क्षेत्र की तीव्रता तथा विभव ज्ञात करें.

4 असंपर्कित अनंत चालक के सामने एक बिंदु आवेश के कारण E तथा V के मान की गणना करो.

5. विद्युत क्षेत्र में एक चालक के पृष्ठ पर प्रति इकाई क्षेत्रफल बल ज्ञात करो.

Page No.:
Date:

Feed back qu.

Qu.1 गॉस के नियम का concept इस video से समझने में . .

Qu.2 गॉस के नियमो के अनुप्रयोगो से आप संतुष्ट है

Qu.3 आप गॉस के नियमो से संबंधित एक अनुप्रयोग बताए

Qu.4 Electrostatic energy को इस video के आधार पर परिभाषित करे.

Qu.5 इस video को update करने के संबंध में सुझाव

E-Content

DEPARTMENT OF PHYSICS

GOVT. V.Y.T.PG AUTONOMOUS COLLEGE DURG 491001 CHHATTISGARH

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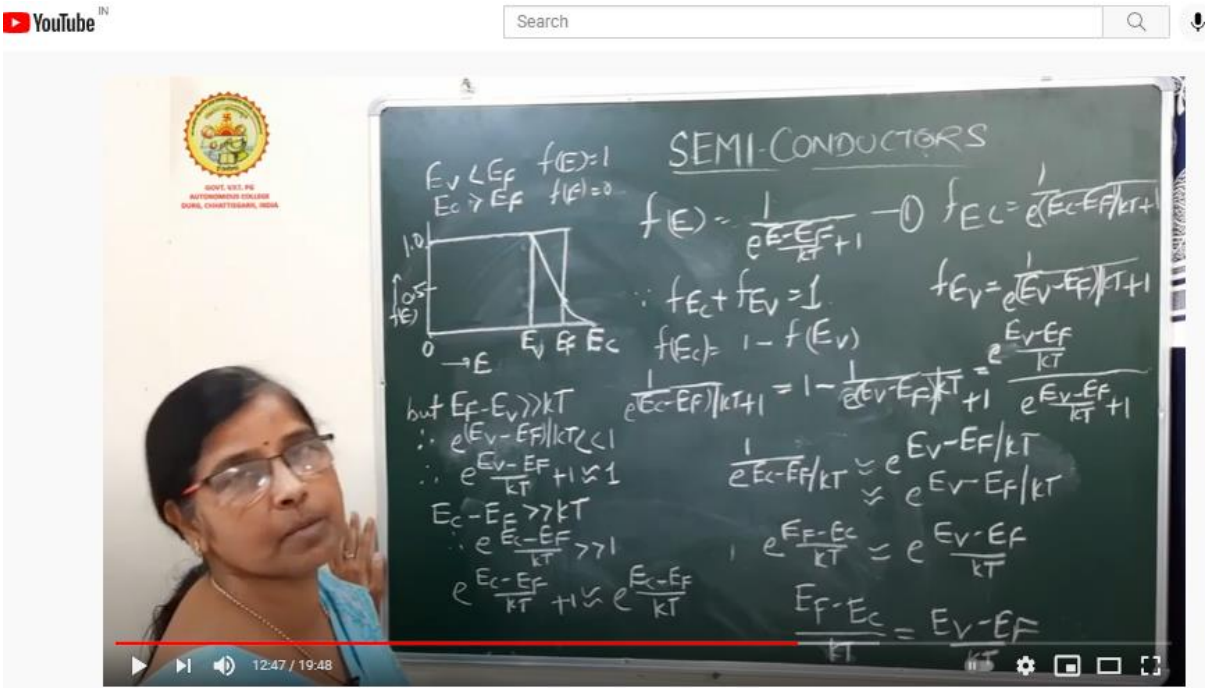
Module: Concept of Semiconductor & PN Junction Diode

Module is divided in four sections:

1. **VIDEO CONTENT**
2. **MATERIAL**
3. **OBJECTIVE QUESTION BASED ON MODULE**
4. **SUBJECTIVE ASSIGNMENT BASED ON MODULE**
5. **FEEDBACK SECTION**

Video Content: https://youtu.be/NddYK4lncJQ

In this video I explained basic concept of Semiconductor and Junction Diode



5

अर्द्ध-चालक डायोड

[SEMICONDUCTOR DIODE]

पाठ्यक्रम— आन्तर या शुद्ध अर्द्ध-चालक, ऊष्मीय संतुलन में आवेश वाहकों की सान्द्रता, फर्मी स्तर, अशुद्ध अर्द्ध-चालक, दाता तथा ग्राही स्तर, डायोड समीकरण, सन्धि भंजन, अवक्षय चौड़ाई तथा सन्धि धारिता, अकस्मात् सन्धि, टनल डायोड, जेनर डायोड, प्रकाश उत्सर्जक डायोड, सौर सेल (सोलर सेल)।

द्वि-ध्रुवी ट्रान्जिस्टर, PNP तथा NPN ट्रान्जिस्टर, ट्रान्जिस्टर के अभिलाक्षणिक, विभिन्न विधाएँ, धारा प्रवर्धन गुणांक, FET।

परिचय (Introduction)

इलेक्ट्रॉनिक्स के विकास में अर्द्ध-चालक पदार्थों का योगदान महत्वपूर्ण है। प्रकृति में अर्द्ध-चालक पदार्थों की बहुतायत एवं इनके विशेष गुणों के कारण ही इलेक्ट्रॉनिक्स पर आधारित युक्तियों एवं उपकरणों का आकार एवं लागत दिनों-दिन कम होते जा रही है। विभिन्न ठोस अवस्था इलेक्ट्रॉनिक युक्तियों (Solid state electronic devices) जैसे—डायोड, ट्रांजिस्टर, इंटिग्रेटेड परिपथ (Integrated circuits) इत्यादि की कार्य-विधि को समझने हेतु अर्द्ध-चालक पदार्थों के गुणों का अध्ययन आवश्यक है। अर्द्ध-चालक वे पदार्थ हैं जो न ही चालक पदार्थों की श्रेणी में आते हैं और न ही कुचालक पदार्थों की श्रेणी में। अर्द्ध-चालक पदार्थों में मुक्त इलेक्ट्रॉनों की संख्या चालकों की तुलना में कम होती हैं, किन्तु अर्द्ध-चालक पदार्थों में एक अन्य आवेश वाहक होल या विवर की उपस्थिति इसे महत्वपूर्ण बना देती है। प्रस्तुत अध्याय में अर्द्ध-चालक पदार्थों के विभिन्न भौतिक गुणों विशेष रूप से इस पर ताप एवं अशुद्धियों के प्रभाव की विस्तृत व्याख्या की गई है।

आधुनिक इलेक्ट्रॉनिक्स में अनेक P अथवा N-प्रकार के अर्द्ध-चालक की उपयोगिता सीमित है। यदि किसी अर्द्ध-चालक क्रिस्टल के कुछ भाग में दाता अशुद्धि तथा शेष भाग में ग्राही अशुद्धि इस प्रकार मिश्रित की गई हो कि अशुद्धि की सान्द्रता में अकस्मात् सांतत्य आ जाये तो उस स्थान पर P-N सन्धि (P-N Junction) बन जाती है। अर्द्ध-चालक युक्तियों जैसे—डायोड, ट्रांजिस्टर आदि की कार्य-विधि में P-N सन्धि का बहुत अधिक महत्व है, क्योंकि इन युक्तियों में महत्वपूर्ण घटनाएँ सन्धि क्षेत्र में ही घटती हैं एवं धारा का नियन्त्रण भी सन्धि द्वारा होता है। अर्द्ध-चालक युक्तियों में एक या एक से अधिक P-N सन्धि होती है। अर्द्ध-चालक में P-N सन्धि के निर्माण हेतु विशेष विधियों (एलाइंग-Alloying, ग्रोइंग-Growing, विसरण-Diffusion) का उपयोग किया जाता है। हालाँकि P-N सन्धि का निर्माण P-प्रकार एवं N-प्रकार के अर्द्ध-चालक को ब्लॉक की भाँति जोड़कर नहीं किया जाता, किन्तु P-N सन्धि में अवक्षय पर्त के बनने आदि घटनाओं की सुलभ व्याख्या करने के लिए सन्धि को चित्र 5·11 के अनुसार प्रदर्शित किया जाता है, जिससे प्रतीत होता है कि P-N सन्धि का निर्माण P-प्रकार के अर्द्ध-चालक के एक सिरे को N-प्रकार के अर्द्ध-चालक के एक सिरे से जोड़कर किया गया है।

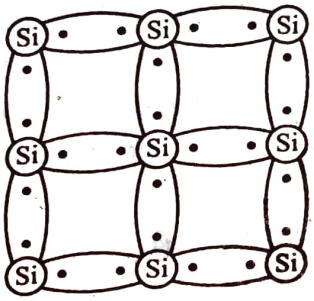
प्रस्तुत अध्याय में P-N सन्धि की क्रिया-विधि सम्बन्धित भौतिक सिद्धान्तों एवं विभिन्न प्रकार की एक सन्धि अर्द्ध-चालक युक्तियों की विस्तृत व्याख्या की गई है।

§ 5·1 आन्तर या शुद्ध अर्द्ध-चालक (Intrinsic or Pure Semiconductors)

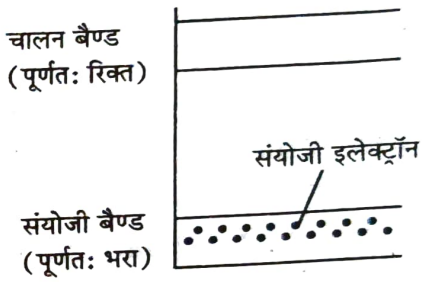
आन्तर या शुद्ध अर्द्ध-चालक ऐसे पदार्थ होते हैं, जिनमें किसी भी प्रकार की अशुद्धियाँ नहीं होती हैं तथा इनकी चालकता पूर्णतया ऊष्मीय प्रक्षोभों तथा उत्पन्न आवेश वाहकों पर निर्भर करती है। केवल सिलिकॉन (Si, परमाणु संख्या Z = 14) तथा जर्मेनियम (Ge, परमाणु संख्या Z = 32) ही शुद्ध अर्द्ध-चालक पदार्थ हैं।

ये दोनों तत्त्व आवर्त सारिणी के चतुर्थ समूह (group) में हैं तथा इनकी क्रिस्टल संरचना डायमण्ड के समान चतुष्फलकीय (tetrahedral) होती है, जिसमें चतुष्फलक के प्रत्येक शीर्ष पर एक-एक तथा केन्द्र पर एक Si (या Ge) का परमाणु स्थित होता है। शुद्ध अर्द्ध-चालकों की चालकता ताप पर निर्भर करती है इसे निम्नानुसार समझा जा सकता है—

(i) परम शून्य ताप पर—सिलिकॉन के परमाणु में नाभिक के बाहर 14 इलेक्ट्रॉन होते हैं तथा परमाणु में विभिन्न कोशों में इलेक्ट्रॉन वितरण 2, 8, 4 है। जर्मेनियम परमाणु में विभिन्न कोशों में इलेक्ट्रॉन वितरण 2, 8, 18, 4 है। इस प्रकार इन परमाणुओं के बाहरी कक्ष में चार इलेक्ट्रॉन होते हैं, इन्हें संयोजी इलेक्ट्रॉन (valence electron) कहते हैं। किसी परमाणु के चारों संयोजी इलेक्ट्रॉनों में से प्रत्येक इलेक्ट्रॉन अपने निकटतम परमाणु के एक संयोजी इलेक्ट्रॉन से साझा कर सह-बन्धन (covalent bond) बना लेते हैं। इस प्रकार प्रत्येक परमाणु के बाह्य कक्ष में आठ इलेक्ट्रॉन हो जाते हैं और कोई भी इलेक्ट्रॉन स्वतंत्र शेष नहीं रहता [चित्र 5·1 (a)]। इस प्रकार निम्न या परम शून्य ताप पर इन पदार्थों में विद्युत् धारा का प्रवाह सम्भव नहीं होता, क्योंकि इस अवस्था में चालन बैण्ड पूरी तरह रिक्त एवं संयोजी बैण्ड पूरी तरह भरे होते हैं [चित्र 5·1(b)]। फलस्वरूप परम शून्य ताप पर अर्द्ध-चालक, कुचालक की भाँति व्यवहार करते हैं।

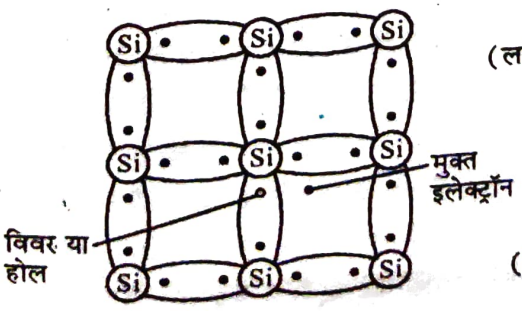


चित्र 5·1 (a) 0°K पर अर्द्ध-चालक की परमाणु में सह-बन्धन

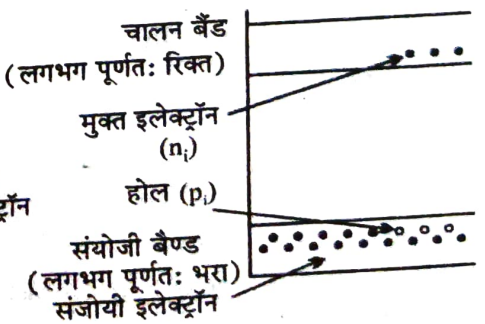


चित्र 5·1 (b) 0°K पर अर्द्ध-चालक की पदार्थों का ऊर्जा बैण्ड आरेख

(ii) कमरे के ताप पर—अर्द्ध-चालकों का ताप बढ़ाने पर (या कमरे के ताप पर) इलेक्ट्रॉनों की गतिज ऊर्जा बढ़ती है, जिसके फलस्वरूप ऊष्मीय प्रक्षोभों द्वारा कुछ सह-बन्धन टूट जाते हैं तथा कुछ इलेक्ट्रॉन धारा प्रवाह के लिये मुक्त हो जाते हैं [चित्र 5·2(a)]। जब कोई इलेक्ट्रॉन सह-बंधन से अलग होता है तो इससे इलेक्ट्रॉन की रिक्तता उत्पन्न हो जाती है जिसे विवर या होल (hole) कहा जाता है। होल को धनावेशित माना जाता है जिसका परिमाण इलेक्ट्रॉन के आवेश के बराबर होता है। इस प्रकार मुक्त इलेक्ट्रॉन की ऊर्जा अधिक होने के कारण वे वर्जित ऊर्जा अन्तराल को पार कर चालन बैण्ड में पहुँच जाते हैं एवं अपने स्थान पर संयोजी बैण्ड में होल छोड़ जाते हैं। जैसे-जैसे अर्द्ध-चालक का ताप बढ़ता है, मुक्त इलेक्ट्रॉन-होल जोड़े उत्पन्न होते जाते हैं। शुद्ध अर्द्ध-चालकों में मुक्त इलेक्ट्रॉनों की संख्या n_i होल की संख्या p_i के बराबर होती एवं विद्युत् चालन में



चित्र 5·2 (a) कमरे के ताप पर शुद्ध अर्द्ध-चालक परमाणु में सह-बन्धन टूटने से मुक्त इलेक्ट्रॉन-होल युग्म



चित्र 5·2 (b) कमरे के ताप पर शुद्ध अर्द्ध-चालक पदार्थों का ऊर्जा बैण्ड आरेख

इलेक्ट्रॉन और होल दोनों भाग लेते हैं। इस प्रकार ताप बढ़ने से आवेश वाहकों की संख्या बढ़ने के कारण शुद्ध अर्द्ध-चालक पदार्थों की चालकता बढ़ती है (या प्रतिरोधकता घटती है)। कमरे के ताप पर अर्द्ध-चालक पदार्थों में मुक्त इलेक्ट्रॉन होल युग्म (free electron-hole pair) बनने की घटना को ऊर्जा बैण्ड आरेख [चित्र 5·2 (b)] द्वारा समझा जा सकता है।

नोट—यह प्रश्न स्वाभाविक है कि अर्द्ध-चालकों का ताप बढ़ने पर केवल कुछ इलेक्ट्रॉन ही ऊर्जा प्राप्त कर संयोजी बैण्ड से चालन बैण्ड में क्यों चले जाते हैं ? सारे संयोजी इलेक्ट्रॉन चालन बैण्ड में क्यों नहीं पहुँचते ? इसे निम्नानुसार समझा जा सकता है—जब कोई इलेक्ट्रॉन सह-बंधन तोड़कर मुक्त इलेक्ट्रॉन हो जाता है, तो शेष बचे हुए इलेक्ट्रॉनों का नाभिक के साथ आकर्षण तीव्र हो जाता है जिससे अन्य इलेक्ट्रॉनों का बंधन तोड़कर मुक्त होना कठिन हो जाता है।

§ 5·2. शुद्ध अर्द्ध-चालक में धारा प्रवाह (होल धारा की अवधारणा) [(Flow of Current in Intrinsic Semiconductor (Concept of Hole Current)]

चालक पदार्थों में विद्युत् धारा का प्रवाह पूरी तरह से मुक्त इलेक्ट्रॉनों की गति के कारण होता है, जबकि अर्द्ध-चालकों में धारा के प्रवाह में मुक्त इलेक्ट्रॉनों के साथ विवर या होल भी आवेश वाहकों का कार्य करते हैं। होल वास्तव में कोई यथार्थ कण नहीं है यह केवल एक कल्पना है। संयोजी इलेक्ट्रॉनों द्वारा ऊष्मीय प्रक्षोभों से वर्जित ऊर्जा अन्तराल के बराबर या ज्यादा ऊर्जा ग्रहण कर चालन बैण्ड में जाने से, संयोजी बैण्ड में निर्मित रिक्तता (vacancy) को होल या विवर कहते हैं। चूँकि विवर इलेक्ट्रॉन की रिक्तता से उत्पन्न होते हैं अत: इनका व्यवहार धनावेशित कण के समान होता है तथा इनका द्रव्यमान इलेक्ट्रॉन के द्रव्यमान के बराबर माना जाता है। अर्द्ध-चालकों के सिरों पर विद्युत् क्षेत्र लगाने पर जहाँ मुक्त इलेक्ट्रॉन चालन बैण्ड में धन इलेक्ट्रोड की ओर गति करते हैं वहीं होल का प्रवाह संयोजी बैण्ड में ऋण इलेक्ट्रोड की ओर होता है, इस तरह अर्द्ध-चालकों में धारा प्रवाह में मुक्त इलेक्ट्रॉन एवं होल दोनों भाग लेते हैं।

पदार्थों में विद्युत् क्षेत्र आरोपित करने पर आवेश वाहकों का अनुगमन वेग (drift velocity) v_d, आरोपित क्षेत्र की तीव्रता E के अनुक्रमानुपाती होता है। अर्थात्

$$v_d \propto E$$

या

$$v_d = \mu E$$

जहाँ नियतांक μ को आवेषित कणों की गतिशीलता (mobility) कहते हैं। इसकी इकाई मीटर^2 वोल्ट$^{-1}$ से$^{-1}$ होती है। शुद्ध अर्द्ध-चालकों के चालन बैण्ड में मुक्त इलेक्ट्रॉनों की गतिशीलता μ_n, संयोजी बैण्ड में होल की गतिशीलता μ_p से अधिक होती है, क्योंकि चालन बैण्ड में इलेक्ट्रॉनों पर नाभिक के कारण लगने वाला आकर्षण बल अपेक्षाकृत नगण्य होता है तथा ये लगभग खाली बैण्ड में गति करते हैं।

माना किसी अर्द्ध-चालक के चालन बैण्ड में मुक्त इलेक्ट्रॉन घनत्व (प्रति एकांक मुक्त इलेक्ट्रॉनों की संख्या) n है अत: चालन बैण्ड के एकांक आयतन में उपलब्ध आवेश ne होगा, यह आवेश विद्युत् क्षेत्र E में अनुगमन वेग $v_n = -\mu_n E$ से गति करेगा (यहाँ ऋणात्मक चिन्ह प्रदर्शित करता है कि इलेक्ट्रॉनों का अनुगमन वेग, विद्युत् क्षेत्र की दिशा के विपरीत है)। अत: इन इलेक्ट्रॉनों के अनुगमन से उत्पन्न धारा घनत्व $J_n = -nev_n$ (यहाँ ऋणात्मक चिन्ह यह बताता है कि धारा घनत्व J_n की दिशा, इलेक्ट्रॉनों की गति की दिशा के विपरीत है)।

अत:

$$J_n = -nev_n = ne\mu_n E$$

इसी प्रकार संयोजी बैण्ड के प्रति एकांक आयतन में उपस्थित p होलों द्वारा उत्पन्न धारा घनत्व

$$J_p = pe\mu_p E$$

स्पष्ट है कि पदार्थ में इलेक्ट्रॉन के अनुगमन तथा होल के अनुगमन से उत्पन्न धारा समान दिशा में होती है। अत: अर्द्ध-चालक में कुल धारा घनत्व

$$J = J_n + J_p = ne\mu_n E + pe\mu_p E$$
$$= (ne\mu_n + pe\mu_p)E$$

चूँकि $J = \sigma E$ (σ पदार्थ की चालकता है)

अत: $\sigma = ne\mu_n + pe\mu_p$

चूँकि शुद्ध अर्द्ध-चालकों में इलेक्ट्रॉन व होलों की संख्या समान होती है अत: $n = p = n_i$ (माना)।

अत: अर्द्ध-चालक की चालकता

$$\sigma = n_i e(\mu_n + \mu_p)$$

उल्लेखनीय है कि अर्द्ध-चालकों का ताप बढ़ने पर इलेक्ट्रॉन-होल की सान्द्रता n_i भी परिवर्तित हो जाती है अर्थात्

$$n_i = AT^{3/2}e^{-Eg/2KT}$$

जहाँ A एक नियतांक है जिसका मान अर्द्ध-चालक की प्रकृति पर निर्भर करता है। उपर्युक्त समीकरण में T पदार्थ की परमताप, E_g पदार्थ में वर्जित ऊर्जा अन्तराल एवं K बोल्ट्जमैन नियतांक है।

महत्वपूर्ण तथ्य यह है कि शुद्ध अर्द्ध-चालकों में ऊष्मीय प्रक्षोभों से जो इलेक्ट्रॉन-होल युग्म उत्पन्न होते हैं, अनियमित गति के कारण उनके पुन: संयोग (recombine) करने की सम्भावना बनी रहती है अर्थात् मुक्त इलेक्ट्रॉन किसी टूटे हुए संयोजी बंध में होल का स्थान लेकर पुन: सह-बन्धन बना लेता है। इस प्रकार संयोग से कम-से-कम E_g ऊर्जा मुक्त होती है। सामान्यत: तापीय साम्य में इलेक्ट्रॉन-होल युग्म के उत्पत्ति की दर उसके पुन: संयोग की दर के बराबर होती है।

§5.3. ऊष्मीय संतुलन में इलेक्ट्रॉन तथा होल सान्द्रता; फर्मी स्तर (Electron and Hole Concentration in Thermal Equilibrium; Fermi Level)

ऊष्मीय संतुलन की स्थिति में शुद्ध अर्द्ध-चालकों में इलेक्ट्रॉन तथा होल की सान्द्रता ज्ञात करने में क्वाण्टम यांत्रिकी के सिद्धान्तों का उपयोग किया जाता है। क्वाण्टम सांख्यिकी के अनुसार, अर्द्ध-चालकों के चालन बैण्ड की तली में उपलब्ध अवस्थाओं का ऊर्जा घनत्व (energy density of states) निम्नानुसार होता है—

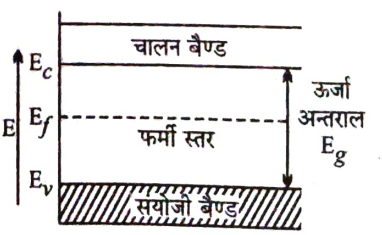
$$Z(E) = \frac{4\pi}{h^3}(2m_e^*)^{3/2}(E - E_c)^{1/2} \quad ...(1)$$

उपर्युक्त समीकरण में h प्लांक नियतांक, E_c चालन बैण्ड की निम्नतम ऊर्जा (अर्थात् चालन बैण्ड की तली की ऊर्जा) तथा m_e^* चालन बैण्ड में इलेक्ट्रॉन का प्रभावी द्रव्यमान है। चालन बैण्ड में गतिशील इलेक्ट्रॉन पर समीपस्थ परमाणुओं एवं अन्य इलेक्ट्रॉनों की गति के प्रभाव के कारण इलेक्ट्रॉन का प्रभावी द्रव्यमान (Effective mass) m_e^*, स्वतंत्र इलेक्ट्रॉन के द्रव्यमान m_e से भिन्न होता है।

इसी प्रकार, यदि संयोजी बैण्ड की उच्चतम ऊर्जा (संयोजी बैण्ड के शीर्ष पर) E_v हो एवं होल का प्रभावी द्रव्यमान m_e^* हो, तो संयोजी बैण्ड के ऊपरी सिरे पर अवस्थाओं का ऊर्जा घनत्व

$$Z'(E) = \frac{4\pi}{h^3}(2m_h^*)^{3/2}(E_v - E)^{1/2} \quad ...(2)$$

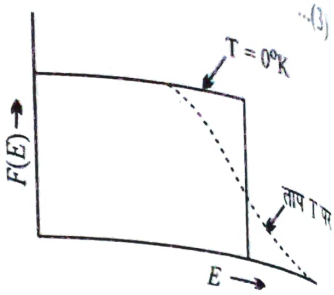
चूँकि इलेक्ट्रॉन पॉली के अपवर्जन नियम (Pauli's exclusion principle) का पालन करते हैं जिसके अनुसार, किसी एक अवस्था में एक से अधिक इलेक्ट्रॉन नहीं हो सकते हैं। अत: यदि इलेक्ट्रॉन की कुल संख्या नियत हैं तथा निकाय की कुल ऊर्जा भी नियत है, तो फर्मी-डिराक सांख्यिकी (F-D Statistics) के अनुसार, फर्मी फलन $F(E)$ अर्थात् ऊर्जा स्तर E के भरे होने की प्रायिकता निम्नलिखित समीकरण द्वारा दी जाती है—



चित्र 5.3—शुद्ध अर्द्ध-चालक में फर्मी स्तर

$$F(E) = \frac{1}{e^{(E-E_F)/KT} + 1} \quad ...(3)$$

यहाँ E_F फर्मी स्तर (अर्द्ध-चालकों में इलेक्ट्रॉनों की औसत ऊर्जा) की ऊर्जा, K बोल्ट्जमैन स्थिरांक ($1{\cdot}38 \times 10^{-23}$ जूल /केल्विन) तथा T परम ताप है। यदि ऊर्जा स्तर E की सभी अवस्थाएँ खाली हो तो $F(E) = 0$ तथा ऊर्जा स्तर E की सभी अवस्थाएँ भरी होने पर $F(E) = 1$ होता है। इसी प्रकार $F(E) = 0{\cdot}5$ का अर्थ है कि ऊर्जा स्तर की सभी अवस्थाओं के भरे होने की प्रायिकता 50% है। फर्मी फलन $F(E)$ का मान ऊर्जा E तथा अर्द्ध-चालक के ताप T पर निर्भर करता है (चित्र 5·4)। फर्मी फलन का मान अवस्थाओं के ऊर्जा घनत्व पर निर्भर नहीं करता है।



चित्र 5·4

चालन बैण्ड में इलेक्ट्रॉन सान्द्रता (Electron Concentration in Conduction Band)

यदि ऊर्जा स्तर E में ऊर्जा अवस्थाओं का घनत्व $Z(E)$ है तो ऊर्जा परास E व $E+dE$ में उपलब्ध ऊर्जा अवस्थाओं की संख्या $Z(E)dE$ होगी। चूँकि फर्मी फलन $F(E)$ इन अवस्थाओं के भरे होने की प्रायिकता है। अत: ऊर्जा परास E व $E+dE$ में उपलब्ध भरी अवस्थाओं की संख्या

$$N(E)dE = Z(E)F(E)dE \quad ...(4)$$

अत: चालन बैण्ड में इलेक्ट्रॉन सान्द्रता अथवा घनत्व

$$n_e = \int_{E_c}^{\infty} N(E)dE = \int_{E_c}^{\infty} Z(E)F(E)dE \quad ...(5)$$

यहाँ समाकलन की सीमायें इलेक्ट्रॉनों द्वारा चालन बैण्ड में भरे निम्नतम ऊर्जा स्तर (E_c) से ऊर्जा बैण्ड की उच्चतम ऊर्जा (∞) तक ली गई है। चालन बैण्ड की अधिकतम ऊर्जा, अनन्त (∞) गणितीय हल को सुविधाजनक बनाने के उद्देश्य से ली जाती है, क्योंकि यदि $E >> E_g$ हो, तो $F(E) = 0$ होगा, अत: अधिकतम सीमा को अनन्त मानने पर n_e के मान में विशेष परिवर्तन नहीं होता है।

समी. (2) एवं (3) से क्रमश: $Z(E)$ एवं $F(E)$ का मान समी. (5) में रखने पर,

$$n_e = \frac{4\pi}{h^3}(2m_e^*)^{3/2} \int_{E_c}^{\infty} \frac{(E-E_c)^{1/2}\,dE}{e^{(E-E_F)/KT} + 1}$$

यदि $(E-E_F)/KT >> 1$ हो, तो $\dfrac{1}{e^{(E-E_F)/KT} + 1} \approx e^{-(E-E_F)/KT}$

$$\therefore \quad n_e = \frac{4\pi}{h^3}(2m_e^*)^{3/2} \int_{E_c}^{\infty} (E-E_c)^{1/2} . e^{-(E-E_F)/KT} dE$$

या $$n_e = \frac{4\pi}{h^3}(2m_e^*)^{3/2} \int_{E_c}^{\infty} (E-E_c)^{1/2} . e^{(E_F-E)/KT} dE$$

या $$n_e = \frac{4\pi}{h^3}(2m_e^*)^{3/2} . e^{\frac{(E_F-E_c)}{KT}} \int_{E_c}^{\infty} (E-E_c)^{1/2} . e^{\frac{(E_c-E)}{KT}} dE$$

यदि $\dfrac{E-E_c}{KT} = x$ हो, तो $dE = KTdx$

$$\therefore \quad n_e = \frac{4\pi}{h^3}(2m_e^*)^{3/2} . e^{\frac{(E_F-E_c)}{KT}} \int_0^{\infty} x^{1/2} (KT)^{1/2} . e^{-x} KTdx$$

$$= \frac{4\pi}{h^3}(2m_e^*)^{3/2}.(KT)^{3/2}.e^{\frac{(E_F-E_c)}{KT}} \int_0^\infty x^{1/2}.e^{-x}dx$$

चूँकि प्रामाणिक समाकलन $\int_0^\infty x^{1/2}.e^{-x}dx = \left(\frac{\pi}{4}\right)^{1/2}$

अत:
$$n_e = \frac{4\pi}{h^3}(2m_e^*)^{3/2}.(KT)^{3/2}.e^{\frac{(E_F-E_c)}{KT}} \frac{\pi^{1/2}}{2}$$

या
$$n_e = 2\left(\frac{2\pi m_e^* KT}{h^2}\right)^{3/2}.e^{\frac{(E_F-E_c)}{KT}} \quad ...(6)$$

जी बैण्ड में होल सान्द्रता (Hole Concentration in Valence Band)

संयोजी बैण्ड में विवरों या होल की सान्द्रता ज्ञात करने के लिये फर्मी फलन $F(E)$ के स्थान पर फलन $F(E)]$ का उपयोग किया जाता है। इसका कारण यह है कि होल चूँकि इलेक्ट्रॉन द्वारा रिक्त किये गये स्थान $F(E)$ किसी ऊर्जा E की अवस्था के भरे होने की प्रायिकता है। अत: ऊर्जा E की अवस्था के रिक्त होने (अर्थात् होल की) प्रायिकता $[1-F(E)]$ होगी। इस प्रकार संयोजी बैण्ड में होल की सान्द्रता

$$n_h = \int_{-\infty}^{E_v} Z'(E)[1-F(E)]dE$$

यहाँ भी ऊर्जा की न्यूनतम सीमा $-\infty$ केवल सुविधा के लिये ली गई है, E_v संयोजी बैण्ड की शीर्ष ऊर्जा

यदि $E_F - E >> KT$ हो, तो

$$[1-F(E)] = 1 - \frac{1}{e^{(E-E_F)/KT}+1}$$
$$= 1-[1+e^{(E-E_F)/KT}]^{-1}$$
$$= 1-[1-e^{(E-E_F)/KT}]$$
$$= e^{(E-E_F)/KT}$$

स्पष्ट है कि संयोजी बैण्ड में $E < E_F$ होने के कारण फलन का मान चरघातांकी नियमानुसार घटता है। ा अर्थ यह है कि होल, संयोजी बैण्ड के शीर्ष के निकट ही उपस्थित होते हैं। संयोजी बैण्ड के शीर्ष के ऊर्जा अवस्थाओं का घनत्व

$$Z(E) = \frac{4\pi}{h^3}(2m_h^*)^{3/2}(E_v - E)^{1/2}$$

अत: समी. (7) से,

$$n_h = \frac{4\pi}{h^3}(2m_h^*)^{3/2}\int_{-\infty}^{E_v}(E_v - E)^{1/2}.e^{(E-E_F)/KT}.dE$$
$$= \frac{4\pi}{h^3}(2m_h^*)^{3/2}.e^{(E_v-E_F)/KT}\int_{-\infty}^{E_v}(E_v-E)^{1/2}e^{(E-E_v)/KT}.dE$$

माना $\frac{E_v - E}{KT} = x$ हो, तो $dE = -KTdx$

अत:
$$n_h = \frac{4\pi}{h^3}(2m_h^*)^{3/2}.e^{(E_v-E_F)/KT}\int_{\infty}^{0}(KT.x)^{1/2}.e^{-x}.(-KT)dx$$

या $$n_h = \frac{4\pi}{h^3}(2m_h^*)^{3/2}(KT)^{3/2}.e^{(E_v-E_F)/KT}\int_0^\infty x^{1/2}.e^{-x}dx$$

या $$n_h = \frac{4\pi}{h^3}(2m_h^*)^{3/2}(KT)^{3/2}.e^{(E_v-E_F)/KT}\frac{\pi^{1/2}}{2}, \quad \text{(प्रामाणिक समाकलन से)}$$

या $$n_h = 2\left[\frac{2\pi m_h^* KT}{h^2}\right]^{3/2}.e^{(E_v-E_F)/KT} \quad ...(8)$$

फर्मी ऊर्जा स्तर (Fermi Energy Level)

आन्तर या शुद्ध अर्द्ध-चालकों में मुक्त इलेक्ट्रॉनों की संख्या, होल की संख्या के बराबर होती है, अत:

$$n_e = n_h$$

या $$2\left[\frac{2\pi m_e^* KT}{h^2}\right]^{3/2}.e^{(E_F-E_c)/KT} = 2\left[\frac{2\pi m_h^* KT}{h^2}\right]^{3/2}.e^{(E_v-E_F)/KT}$$

या $$(m_e^*)^{3/2}.e^{(E_F-E_c)/KT} = (m_h^*)^{3/2}.e^{(E_v-E_F)/KT}$$

या $$e^{(2E_F-E_c-E_v)/KT} = \left(\frac{m_h^*}{m_e^*}\right)^{3/2}$$

लघुगणक लेने पर,

$$\frac{2E_F-E_c-E_v}{KT} = \frac{3}{2}\log\left(\frac{m_h^*}{m_e^*}\right)$$

या $$E_F = \left(\frac{E_c+E_v}{2}\right)+\frac{3}{4}KT\log\left(\frac{m_h^*}{m_e^*}\right) \quad ...(9)$$

यदि इलेक्ट्रॉन एवं होल का प्रभावी द्रव्यमान समान हो, तो $m_h^* = m_e^*$

अत: $$E_F = \frac{E_c+E_v}{2} \quad ...(10)$$

अत: आन्तर या शुद्ध अर्द्ध-चालक में फर्मी स्तर संयोजी बैण्ड के शीर्ष एवं चालन बैण्ड की तली के ठीक मध्य में (अर्थात् वर्जित ऊर्जा अन्तराल के मध्य में) होता है।

वास्तव में m_h^* का मान m_e^* से थोड़ा अधिक होता है, अत: समी. (9) के अनुसार, ताप बढ़ाने पर फर्मी स्तर, थोड़ा ऊपर की ओर विस्थापित हो जाता है।

विद्युत् चालकता (Electrical Conductivity)

शुद्ध अर्द्ध-चालकों की चालकता

जहाँ $$\sigma = n_i e(\mu_n+\mu_p)$$

$$n_i = n_e = n_h$$

अत: $$\sigma = 2\left(\frac{2\pi KT}{h^2}\right)^{3/2}(m_e^*)^{3/2}.e^{(E_F-E_c)/KT}.e.(\mu_n+\mu_p)$$

चूँकि $m_e^* \approx m_e^{*1/2} m_h^{*1/2}$ एवं $E_F - E_c = -\frac{E_g}{2}$, ($E_g$ = वर्जित ऊर्जा अन्तराल)

अतः $$\sigma = 2\left(\frac{2\pi KT}{h^2}\right)^{3/2} (m_e^* m_h^*)^{3/4} . e^{-E_g/2KT} . e.(\mu_n + \mu_p)$$

या $$\sigma = A . T^{3/2} . e(\mu_n + \mu_p) . e^{-E_g/2KT}$$

जहाँ A = नियतांक $= 2\left(\frac{2\pi KT}{h^2}\right)^{3/2} (m_e^* m_h^*)^{3/4}$ ...(11)

उपर्युक्त समीकरण (11) से स्पष्ट है कि ताप बढ़ने पर अर्द्ध-चालक की चालकता बढ़ती है।

समी. (6) एवं (7) से शुद्ध अर्द्ध-चालकों के लिए,

$$n_e = n_h = n_i$$

या $$n_i^2 = n_e \times n_h$$

$$= 4\left(\frac{2\pi KT}{h^2}\right)^3 . (m_e^* m_h^*)^{3/2} . e^{(E_v - E_c)/KT}$$

या $$n_e \times n_h = 4\left(\frac{2\pi KT}{h^2}\right)^3 . (m_e^* m_h^*)^{3/2} . e^{-E_g/KT} \quad ...(12)$$

उपर्युक्त समीकरण से स्पष्ट है कि इलेक्ट्रॉन एवं होल संख्या (सान्द्रता) का गुणनफल केवल अर्द्ध-लक के ताप एवं वर्जित ऊर्जा अन्तराल पर निर्भर करता है। इसका मान फर्मी ऊर्जा स्तर की स्थिति पर निर्भर ं करता है। राशि n_i को आन्तर वाहक घनत्व (Intrinsic carrier density) कहते हैं।

यदि n एवं p क्रमशः चालन बैण्ड, संयोजी बैण्ड में इलेक्ट्रॉन एवं होल की कुल संख्या को प्रदर्शित करते तो $n_e = n$ एवं $n_h = p$.

अतः $$n_e n_h = np = n_i^2 = 4\left(\frac{2\pi KT}{h^2}\right)^3 . (m_e^* m_h^*)^{3/2} . e^{-E_g/KT}$$

= स्थिरांक (नियत ताप पर)

स्पष्ट है कि किसी निश्चित पदार्थ के लिये नियत ताप पर इलेक्ट्रॉन तथा होल सान्द्रता का गुणनफल यांक होता है। यदि अर्द्ध-चालक में इलेक्ट्रॉनों की संख्या n बढ़ाने हेतु अशुद्धि मिलाई जाय तो np का मान यर होने हेतु पदार्थ में होल की संख्या p कम हो जाती है। इसी तरह अशुद्धि के कारण होल की संख्या p बढ़ाने , चालन बैण्ड में इलेक्ट्रॉन की संख्या n कम हो जाती है। इस नियम को द्रव्यमान क्रिया नियम (Law of ass action) कहते हैं। यह नियम शुद्ध एवं अशुद्ध दोनों ही प्रकार के अर्द्ध-चालकों पर लागू होता है।

5·4. बाह्य या अशुद्ध अर्द्ध-चालक (Extrinsic or Impure Semiconductor)

आंतर या शुद्ध अर्द्ध-चालक का उपयोग ताप एवं प्रकाश सुग्राही प्रतिरोध बनाने में किया जाता है, किन्तु म्नलिखित कारणों से ये इलेक्ट्रॉनिक युक्तियों (Electronic devices) के निर्माण में विशेष उपयोगी नहीं —

(i) इनकी चालकता कमरे के ताप पर कम होती है।

(ii) इनकी चालकता ताप पर अत्यधिक निर्भर करती है जिसे नियन्त्रित करना अपेक्षाकृत कठिन है।

यदि शुद्ध अर्द्ध-चालक में कुछ विशिष्ट अशुद्धियों की सूक्ष्म मात्रा (लगभग 10^6 जर्मेनियम या सिलिकॉन ं परमाणुओं में 1 अशुद्ध परमाणु) में मिला दिया जाय, तो ऐसे अशुद्ध अर्द्ध-चालकों की चालकता बहुत (लगभग 10^3 गुनी) बढ़ जाती है। इस प्रकार के अशुद्धि मिश्रित अर्द्ध-चालक को बाह्य अथवा अशुद्ध अर्द्ध-ालक (extrinsic or impure semiconductor) कहा जाता है तथा अशुद्धि मिलाने की क्रिया को डोपिंग

(doping) कहते हैं। बाह्य अर्द्ध-चालक की चालकता मिलायी गई अशुद्धि की मात्रा, उसकी प्रकृति एवं उसके शुद्ध अर्द्ध-चालक में वितरण पर निर्भर करती है। शुद्ध अर्द्ध-चालक में अशुद्धि मिलाने पर उसकी चालकता में वृद्धि, आवेश वाहकों (charge carriers) की संख्या में परिवर्तन के कारण होती है। अशुद्धियाँ मिलाने पर अर्द्ध-चालक में आवेश वाहकों (इलेक्ट्रॉन एवं होल) के परिवर्तन को तालिका 5·1 में दर्शाया गया है।

तालिका 5·1 : अर्द्ध-चालकों में आवेश वाहकों का घनत्व

पदार्थ	प्रकार	चालन इलेक्ट्रॉनों का घनत्व (m^{-3})	होल का घनत्व (m^{-3})
ताँबा	चालक	9×10^{28}	0
सिलिकॉन	आंतर अर्द्ध-चालक	7×10^{15}	7×10^{15}
10^6 सिलिकॉन परमाणुओं में 1 परमाणु फॉस्फोरस	N-प्रकार का अर्द्ध-चालक	5×10^{22}	1×10^{9}
10^6 सिलिकॉन परमाणुओं में 1 परमाणु ऐल्युमिनियम	P-प्रकार का अर्द्ध-चालक	1×10^{9}	5×10^{22}

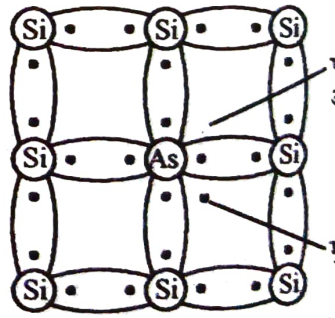
शुद्ध अर्द्ध-चालक में मिलाये गये अशुद्धि की प्रकृति के आधार पर बाह्य अर्द्ध-चालक दो प्रकार के होते हैं—

(i) N- प्रकार के अर्द्ध-चालक

(ii) P-प्रकार के अद्ध-चालक।

(i) N-प्रकार के अर्द्ध-चालक (N-type Semiconductor)

यदि शुद्ध जर्मेनियम अथवा सिलिकॉन में पाँचवें समूह के किसी तत्व जैसे—फॉस्फोरस, ऐण्टीमनी, आर्सेनिक आदि को अशुद्धि के रूप में मिलाया जाय तो प्राप्त क्रिस्टल को N-प्रकार के अर्द्ध-चालक कहते हैं। N-प्रकार के अर्द्ध-चालक में अशुद्धि तत्व के परमाणु, क्रिस्टल लैटिस में, सिलिकॉन के कुछ परमाणुओं को हटाकर उनका स्थान ग्रहण कर लेते हैं। पाँचवें समूह के परमाणु के बाह्य कक्ष में पाँच संयोजी इलेक्ट्रॉन होते हैं। इन पाँच इलेक्ट्रॉनों में से चार इलेक्ट्रॉन निकटतम चार सिलिकॉन परमाणुओं के संयोजी इलेक्ट्रॉनों के साथ सह-बन्धन बना लेते हैं (चित्र 5·5) तथा अशुद्धि तत्व का पाँचवाँ इलेक्ट्रॉन शेष रह जाता है। अशुद्धि तत्व के परमाणु की बाह्य कक्षा में इलेक्ट्रॉनों की संख्या पूर्ण हो जाने के कारण, इसके नाभिक द्वारा, पाँचवें इलेक्ट्रॉन पर आकर्षण कम हो जाता है। नाभिक से इस इलेक्ट्रॉन को मुक्त करने के लिये बहुत कम ऊर्जा (सिलिकॉन के लिये 0·05 eV तथा जर्मेनियम के लिए 0·01 eV) की आवश्यकता होती है। यह ऊर्जा इलेक्ट्रॉन को साधारण कमरे के ताप पर वातावरण से प्राप्त हो जाती है और इलेक्ट्रॉन मुक्त हो जाता है जो आवेश वाहक का कार्य करता है। इलेक्ट्रॉन के मुक्त हो जाने से अशुद्धि तत्त्व का परमाणु धनावेशित हो जाता है जो क्रिस्टल में अचर (immobile) रहता है। मुक्त इलेक्ट्रॉन की अपने परमाणु से संयोग (recombine) की सम्भावना शेष बचे इलेक्ट्रॉनों के आवरण प्रभाव

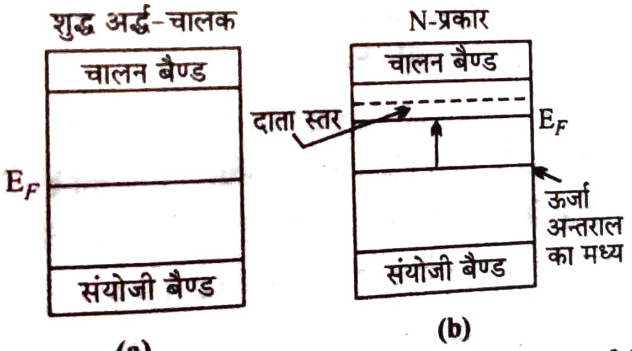


चित्र 5·5—N-प्रकार के अर्द्धचालक में सह-बन्धन

(shielding effect) के कारण काफी क्षीण होती है। इस प्रकार अशुद्धि का प्रत्येक परमाणु क्रिस्टल में आवेश
वाह हेतु एक इलेक्ट्रॉन उपलब्ध करता है। यही कारण है कि पाँचवें समूह की अशुद्धि को दाता अशुद्धि (donor
mpurity) कहते हैं। इस प्रकार के अशुद्धि युक्त अर्द्ध-चालक को N-प्रकार के अर्द्ध-चालक कहते हैं, क्योंकि
समें ऋणात्मक (negative) आवेश के कारण चालकता बढ़ती है।

ाता स्तर (Donar Levels)

शुद्ध जर्मेनियम अथवा सिलिकॉन में पंचसंयोजी तत्त्व की अशुद्धि मिलाने पर चालकता में वृद्धि को ऊर्जा
ण्ड आरेख द्वारा भी समझा जा सकता है। पंचसंयोजी तत्व के परमाणु के पाँच में से चार इलेक्ट्रॉनों द्वारा, निकट
सिलिकॉन परमाणुओं के चार इलेक्ट्रॉनों के साथ सह-बन्धन स्थापित करने पर शेष पाँचवें इलेक्ट्रॉन की ऊर्जा,
ह-बन्धन द्वारा बँधे हुए इलेक्ट्रॉनों की अपेक्षा अधिक होती है। इस तरह वर्जित ऊर्जा बैण्ड में चालन बैण्ड की
ली के कुछ नीचे नये ऊर्जा स्तर उत्पन्न हो जाते हैं तथा दाता परमाणु के पाँचवें इलेक्ट्रॉन इन्हीं ऊर्जा स्तरों में
थान ग्रहण करते हैं। इन ऊर्जा स्तरों को ही दाता स्तर (donor levels) कहते हैं। चूँकि अशुद्धि परमाणु, क्रिस्टल
रचना में सिलिकॉन परमाणु की तुलना में दूर स्थित होते हैं अत: यह स्तर विविक्त होता है एवं ऊर्जा बैण्ड
ारेख में इसे टूटी रेखा (dashed line) द्वारा प्रदर्शित किया जाता है (चित्र 5·6)। चालक बैण्ड की तली से, दाता
तर का अन्तर बहुत कम (जर्मेनियम के लिये 0·01eV तथा सिलिकॉन 0·5 eV) होता है, अत: कमरे के ताप
र ही ऊष्मीय उत्तेजन के कारण दाता स्तर से इलेक्ट्रॉन तुरन्त चालन बैण्ड में चले जाते हैं, चालन बैण्ड में
लेक्ट्रॉनों की संख्या बढ़ने के कारण फर्मी स्तर (जिसके भरे होने की प्रायिकता $\frac{1}{2}$ होती है एवं यह अर्द्ध-
ालकों में इलेक्ट्रॉनों की औसत ऊर्जा को प्रदर्शित करता है) अब ऊर्जा अन्तराल के मध्य में नहीं रह पाता तथा
ालन बैण्ड की ओर विस्थापित हो जाता है। अशुद्धि की मात्रा जितनी अधिक होती है, फर्मी स्तर उतना ही
धिक चालन बैण्ड की ओर विस्थापित होता है।

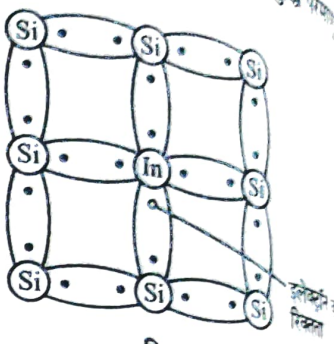


चित्र 5·6—(a) शुद्ध अर्द्ध-चालक के लिए E_F ऊर्जा अंतराल के मध्य होगा तथा इसकी स्थिति ताप पर निर्भर नहीं होती।
(b) N- प्रकार अर्द्ध-चालक में E_F चालन बैंड की ओर विस्थापित हो जाता है।

शुद्ध अर्द्ध-चालक में पंचसंयोजी अशुद्धि मिलाने पर चालन बैण्ड में इलेक्ट्रॉन की संख्या में वृद्धि होती
है, किन्तु संयोजी बैण्ड में होल की संख्या, शुद्ध अर्द्ध-चालक की अपेक्षा कम हो जाती है। (देखें तालिका 5·1
चालन बैण्ड में इलेक्ट्रॉनों की संख्या अधिक होने पर क्रिस्टल लैटिस में इसके होल के साथ संयोग करने की दर
बढ़ने के कारण ही होल की संख्या घट जाती है (संयोग प्रायिकता इलेक्ट्रॉनों की संख्या के समानुपाती होती है)
इस प्रकार, N प्रकार के अर्द्ध-चालकों में इलेक्ट्रॉनों की संख्या अधिक होने के कारण इसे बहुसंख्यक आवेश
वाहक (majority charge carriers) एवं होल को अल्पसंख्यक आवेश वाहक (minority charge carrriers)
कहते हैं।

(ii) P- प्रकार के अर्द्ध-चालक (P-type Semiconductor)

यदि शुद्ध जर्मेनियम अथवा सिलिकॉन में तृतीय समूह के तत्वों जैसे— बोरॉन, गैलियम, इंडियम, ऐल्युमिनियम आदि को अशुद्धि के रूप में मिलाया जाय तो प्राप्त क्रिस्टल P- प्रकार के अर्द्ध-चालक कहलाता है। त्रिसंयोजी अशुद्धि (Trivalent impurity) परमाणु के बाह्य कक्ष में तीन इलेक्ट्रॉन होते हैं, ये तीनों इलेक्ट्रॉन क्रिस्टल में निकटवर्ती तीन सिलिकॉन परमाणुओं के इलेक्ट्रॉनों के साथ सह-बन्धन स्थापित कर लेते हैं, परन्तु चौथा सह-बन्धन एक इलेक्ट्रॉन के अभाव में अधूरा रह जाता है। इस प्रकार क्रिस्टल लैटिस में अशुद्धि परमाणु में एक इलेक्ट्रॉन की रिक्तता उत्पन्न हो जाती है।

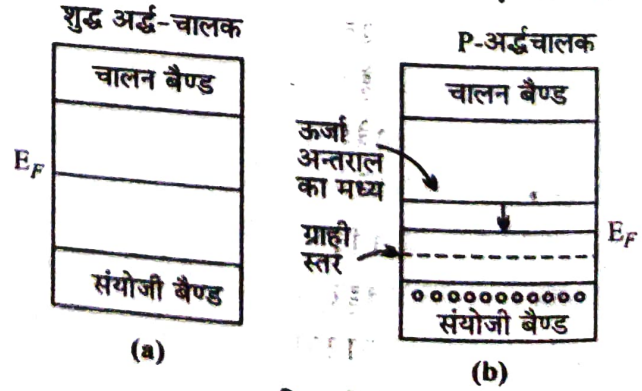


चित्र 5-7

अशुद्धि परमाणु अपने बाह्य चक्र में इलेक्ट्रॉनों की संख्या पूर्ण करने के लिये एक इलेक्ट्रॉन किसी निकटवर्ती सिलिकॉन परमाणु से छीन लेता है। इस तरह वह ऋण आयन में परिवर्तित हो जाता है जो क्रिस्टल लैटिस में अचर होता है, किन्तु निकटवर्ती परमाणु में एक इलेक्ट्रॉन की रिक्तता या होल उत्पन्न कर देता है। चूँकि अशुद्धि का प्रत्येक परमाणु इसी तरह एक इलेक्ट्रॉन ग्रहण कर होल उत्पन्न करता है। अत: इसे ग्राही अशुद्धि (acceptor impurity) कहते हैं। अशुद्धि के कारण अर्द्ध-चालक में होल की संख्या बढ़ने के कारण प्राप्त अर्द्ध-चालक को P-प्रकार के अर्द्ध-चालक कहते हैं, क्योंकि होल धनावेशित (Positive) कण माने जाते ध्यान रहे कि कमरे के ताप पर ऊष्मीय प्रक्षोभों के कारण भी अर्द्ध-चालक के चालन बैण्ड में अल्प संख्या इलेक्ट्रॉन तथा संयोजी बैण्ड में होल उपलब्ध होते हैं। इस प्रकार P- प्रकार के अर्द्ध-चालक में बहुसंख्य आवेश वाहक होल तथा अल्पसंख्यक आवेश वाहक इलेक्ट्रॉन होते हैं।

ग्राही स्तर (Acceptor Levels)

P- प्रकार के अर्द्ध-चालक का ऊर्जा बैण्ड आरेख चित्र 5·8 में प्रदर्शित है। P-प्रकार के अर्द्ध-चालक त्रिसंयोजी परमाणु को अपने सभी सह-बन्धन पूर्ण करने के लिये एक इलेक्ट्रॉन की आवश्यकता होती निकटवर्ती सिलिकॉन परमाणु के इलेक्ट्रॉनों द्वारा इस रिक्तता को पूर्ण करने में बहुत कम ऊर्जा की आवश्यक होती है। इस तरह अशुद्धि परमाणुओं द्वारा, वर्जित ऊर्जा अन्तराल में, संयोजी बैण्ड के ठीक ऊपर इलेक्ट्रॉनों लिये एक नयी ऊर्जा अवस्था निर्मित हो जाती है। इस ऊर्जा अवस्था को ग्राही स्तर (acceptor levels) जाता है। क्रिस्टल में कमरे के ताप पर ही ऊष्मीय प्रक्षोभों से संयोजी बैण्ड के इलेक्ट्रॉन ग्राही स्तर में आ जाते जिससे अशुद्धि परमाणु का बाह्य चक्र पूर्ण हो जाता है एवं वे ऋण आयनित हो जाते हैं। संयोजी बैण्ड से इलेक्ट्रॉन के ग्राही स्तर में चले जाने से उनके स्थान पर बैण्ड में एक होल उत्पन्न हो जाता है। इस प्रकार क्रिस्टल में जितने अशुद्धि परमाणु होते हैं, उतनी ही संख्या में होल, चालन बैण्ड में बढ़ जाते हैं।



चित्र 5-8

(a) शुद्ध अर्द्ध-चालक के लिए E_F ऊर्जा अंतराल के मध्य होगा।
(b) P- प्रकार अर्द्ध-चालक में E_F संयोजी बैंड की ओर विस्थापित हो जाता है।

यह भी ध्यान देने योग्य है कि ग्राही अशुद्धि मिश्रित करने पर फर्मी स्तर अब वर्जित ऊर्जा अन्तराल के मध्य में न रहकर नीचे (संयोजी बैण्ड) की ओर विस्थापित हो जाता है। फर्मी स्तर का विस्थापन अशुद्धि की सान्द्रता पर निर्भर करता है। अशुद्धि की सान्द्रता जितनी अधिक होती है, फर्मी स्तर का विस्थापन भी उतना ही अधिक होता है।

विशेष

(1) N एवं P- प्रकार के अर्द्ध-चालकों पर आवेश

बाह्य अर्द्ध-चालक (N- प्रकार एवं P- प्रकार) विद्युत् रूप से उदासीन होते हैं, क्योंकि शुद्ध जर्मेनियम अथवा सिलिकॉन विद्युत् रूप से उदासीन होते हैं एवं इनमें मिश्रित अशुद्धियाँ परमाणु (पंचसंयोजी एवं त्रिसंयोजी) भी विद्युत् उदासीन होते हैं। दाता परमाणु चालन बैण्ड में चालन हेतु इलेक्ट्रॉन उपलब्ध कर स्वयं धन आवेशित हो जाते हैं। फलतः सम्पूर्ण अर्द्ध-चालक विद्युत् रूप से उदासीन होता है। इसी तरह ग्राही परमाणु द्वारा संयोजी बैण्ड से इलेक्ट्रॉन प्राप्त कर स्वयं ऋण आवेशित होने के साथ संयोजी बैण्ड में एक होल उत्पन्न कर देने से अर्द्ध-चालक विद्युत् रूप से उदासीन बना रहता है।

(2) बाह्य अर्द्ध-चालक की चालकता पर ताप का प्रभाव

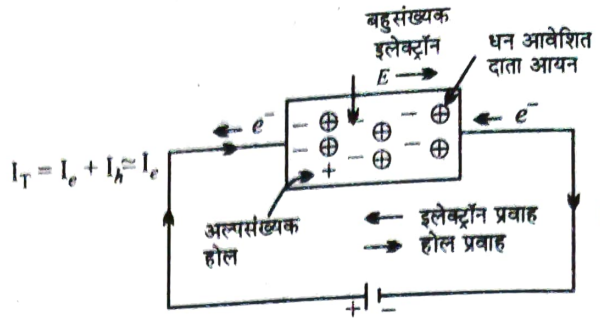
बाह्य अर्द्ध-चालक का निर्माण शुद्ध अर्द्ध-चालक में अशुद्धियाँ मिश्रित कर किया जाता है। N- प्रकार के अर्द्ध-चालक में संयोजी बैण्ड से इलेक्ट्रॉन को चालन बैण्ड में जाने हेतु कम-से-कम E_g ऊर्जा की आवश्यकता होती है जबकि दाता परमाणु से इलेक्ट्रॉन को चालन बैण्ड में जाने हेतु अपेक्षाकृत कम ऊर्जा (Ge के लिए 0·01eV, Si के लिए 0·05 eV) की आवश्यकता होती है। अतः यदि अर्द्ध-चालक का ताप 0 K से बढ़ाया जाय तो कम तापों पर दाता ऊर्जा स्तर से इलेक्ट्रॉन संयोजी बैण्ड में पहुँचकर बाह्य अर्द्ध-चालक की चालकता बढ़ाते हैं। इन तापों पर संयोजी बैण्ड के इलेक्ट्रॉनों को इतनी ऊर्जा नहीं मिल पाती कि ये चालन बैण्ड पहुँच सकें। अतः कम तापों पर आन्तर चालकता का गुण क्षीण हो जाता है। चूँकि दाता परमाणु द्वारा दान किये गये इलेक्ट्रॉनों की संख्या नियत होती है। अतः अर्द्ध-चालक का ताप बढ़ाते जाने से एक अवस्था ऐसी आती है कि सभी दाता परमाणुओं के इलेक्ट्रॉन चालन बैण्ड में पहुँच जाते हैं। अब ताप बढ़ाने पर अशुद्धि के कारण चालकता अचर हो जाती है, किन्तु बढ़े हुए ताप के कारण संयोजी बैण्ड के इलेक्ट्रॉनों को अब वर्जित ऊर्जा अन्तराल (E_g) को पार करने योग्य ऊर्जा मिलनी प्रारम्भ हो जाती है। फलस्वरूप अधिक ताप पर अर्द्ध-चालक की चालकता आन्तर चालकता के कारण बढ़ती है एवं अशुद्धियों (बाह्य-चालकता) का प्रभाव गौण हो जाता है। इसी प्रकार P- प्रकार के अर्द्ध-चालकों पर ताप के प्रभाव की व्याख्या की जा सकती है।

§5·5 बाह्य अर्द्ध-चालक में धारा प्रवाह की प्रक्रिया (Mechanism of Current Flow in Extrinsic Semiconductor)

बाह्य विद्युत् क्षेत्र की अनुपस्थिति में N एवं P- प्रकार के अर्द्ध-चालकों में आवेश वाहक, अपनी ऊष्मीय ऊर्जा के कारण अनियमित रूप से गति करते हैं। किसी निश्चित समय पर जितने आवेश वाहक एक निश्चित दिशा में गतिशील होते हैं लगभग उतने ही आवेश इसके विपरीत दिशा में भी गतिशील होते हैं। फलतः किसी दिशा विशेष में आवेश वाहकों का नेट प्रवाह (विद्युत् धारा) नगण्य होती है। अर्द्ध-चालकों पर बाह्य विद्युत् क्षेत्र आरोपित करने पर आवेश वाहकों पर निश्चित दिशा में बल लगने के कारण वे एक दिशा विशेष में अनुगमन वेग (drift velocity) से चलने लगते हैं एवं विद्युत् धारा का प्रवाह होने लगता है। बाह्य अर्द्ध-चालकों में विद्युत् क्षेत्र (विभवान्तर) आरोपित करने पर इनमें धारा प्रवाह की प्रक्रिया निम्नानुसार होती है—

(i) N- प्रकार के अर्द्ध-चालक में धारा प्रवाह

N-प्रकार के अर्द्ध-चालक में (i) बहुसंख्यक आवेश वाहक इलेक्ट्रॉन, (ii) समान संख्या में निश्चल (immobile) दाता धनात्मक आयन तथा (iii) अल्पसंख्यक आवेश होल होते हैं।

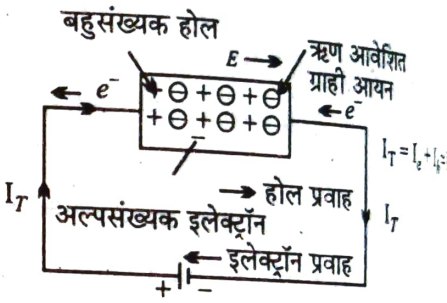


चित्र 5·9

यदि N- प्रकार के अर्द्ध-चालक पर चित्र 5·9 के अनुसार बाह्य विभवान्तर लगायें तो उसमें विद्युत् क्षेत्र प्रभाव में बहुसंख्यक इलेक्ट्रॉन धन सिरे की ओर चलने लगते हैं तथा अल्पसंख्यक होल ऋण इलेक्ट्रोड की ओ परन्तु इनके कारण धारा नगण्य होती है। जब इलेक्ट्रॉन धन सिरे पर पहुँचते हैं तो बैटरी के इलेक्ट्रोड को आवेश दे देते हैं। परन्तु पदार्थ में उपस्थित धन आयन उदासीन नहीं रह पाते और बैटरी के ऋण इलेक्ट्रोड से इलेक्ट्रॉन ग्रहण कर लेते हैं। इस प्रकार N- प्रकार के अर्द्ध-चालक में धारा इलेक्ट्रॉन की गति के कारण प्रवा होती है।

(ii) P- प्रकार के अर्द्ध-चालक में धारा प्रवाह

P- प्रकार के अर्द्ध-चालक में (i) बहुसंख्यक आवेश वाहक होल, (ii) समान संख्या में निश्चल ग्राही ऋण आयन एवं (iii) अल्पसंख्यक इलेक्ट्रॉन होते हैं।



चित्र 5·10

यदि P- प्रकार के अर्द्ध-चालक पर चित्र 5·10 के अनुसार विभवान्तर आरोपित किया जाये तो उसमें विद्युत् क्षेत्र के प्रभाव के कारण बहुसंख्यक होल ऋण सिरे की ओर चलने लगते हैं जबकि अल्पसंख्यक इलेक्ट्रॉन धन सिरे की ओर। ऋण सिरे की ओर पहुँचकर होल बैटरी के ऋण इलेक्ट्रोड से इलेक्ट्रॉन ग्रहण कर लु (disappear) हो जाते हैं। ठीक इसी समय धन इलेक्ट्रोड के समीप क्षेत्र के प्रभाव से एक इलेक्ट्रॉन उदासी परमाणु से अलग होकर धन इलेक्ट्रोड में प्रवेश करता है तथा अपने पीछे अर्द्ध-चालक में होल छोड़ जाता है ऋण इलेक्ट्रोड की ओर गति करता है। धन सिरे पर होल उत्पत्ति की वही दर होती है जो ऋण सिरे पर होल लुप्त होने की। इस प्रकार P- प्रकार के अर्द्ध-चालक में धारा होल के कारण प्रवाहित होती है। अल्पसंख्य इलेक्ट्रॉनों के कारण धारा नगण्य होती है। ध्यान रहे कि होल के कारण धारा केवल P-प्रकार के अर्द्ध-चालक के अर्द्ध-चालक के अन्दर ही प्रवाहित होती है। बाह्य परिपथ में धारा इलेक्ट्रॉनों की गति के कारण ही होती है

विशेष

(1) अर्द्ध-चालकों में इलेक्ट्रॉन का प्रवाह चालन बैण्ड में एवं होल का प्रवाह संयोजी बैण्ड में होता है

(2) चालन बैण्ड में इलेक्ट्रॉन लगभग खाली या आंशिक भरे हुए बैण्ड में गति करता है जबकि होल लगभग भरे हुए संयोजी बैण्ड में गति करता है। अत: इलेक्ट्रॉन की गतिशीलता, होल की अपेक्षा अधिक होती है। यही कारण है कि यदि शुद्ध अर्द्ध-चालक में समान सान्द्रता में पंचसंयोजी एवं त्रिसंयोजी अशुद्धि मिश्रित क्रमश: N एवं P- प्रकार के अर्द्ध-चालक बनाये जायें तो N- प्रकार के अर्द्ध-चालक की प्रतिरोधकता, P-प्रकार के अर्द्ध-चालकों की प्रतिरोधकता के लगभग आधी होती है।

Page No.:
Date:

Objective type qn.

1. एक Ge परमाणु में ... इलेक्ट्रान होते है।

2. चालकों, कुचालकों एवं अर्धचालकों के बीच अंतर का प्रमुख कारक ...

3 शुद्ध अर्धचालक में विद्युत चालकता ताप के साथ ...

4. P प्रकार के अर्धचालक में .. प्रकार के अपमिश्रण मिलाए जाते है।

5. शुद्ध Ge में Sb मिलाने से ... बनता है।

6 सिलिकान के लिए वर्जित ऊर्जा अंतराल ...

7. अर्धचालक की चालकता अपद्रव्य मिलाने से किस प्रकार प्रभावित होती है।

8. N प्रकार के अर्धचालक में फर्मी स्तर की स्थिति कहां होती है?

9 P प्रकार की अशुद्धि ... कहलाती है

10. P-N संधि में रोधिका निम्न ताप बढ़ाने पर ...

Long / Short type Qu.

1. अर्द्ध अर्धचालक क्या है? N तथा P प्रकार के अर्धचालक का बनना बैंड आरेख द्वारा समझाइये।

2 वर्जित ऊर्जा अंतराल के आधार पर चालक, कुचालक, सुचालक में अंतर समझाइये?

3 फर्मी स्तर के बनने की प्रक्रिया समझाइये

4 ठोसों में बैंड किस प्रकार बनते है?

5 विभव प्राचीर, अवक्षय पर्त, संधि धारिता समझाइये

Page No.:
Date:

Feed back

1. इस video के द्वारा पदार्थ के विभिन्न प्रकार को समझने में आप सक्षम हो सके?

2. फर्मी स्तर तथा वर्जित ऊर्जा अंतराल के concept को यह वीडियो ठीक प्रकार से explain कर सका?

3. Band theory के द्वारा तीनो प्रकार के पदार्थ में अंतर स्पष्ट हुआ?

4. P एवं N प्रकार के अर्धचालक में charge carriers के concept से आप परिचित हुए

5. इस video को और अधिक अच्छे से बनाया जाए इस संबंध में कृपया सुझाव दें

M.Sc II Semester Chemistry

Calculation of Δ_0, inter electronic repulsion parameter (B) & β for d^1, d^9, d^4, d^6, d^2 & d^8 complexes

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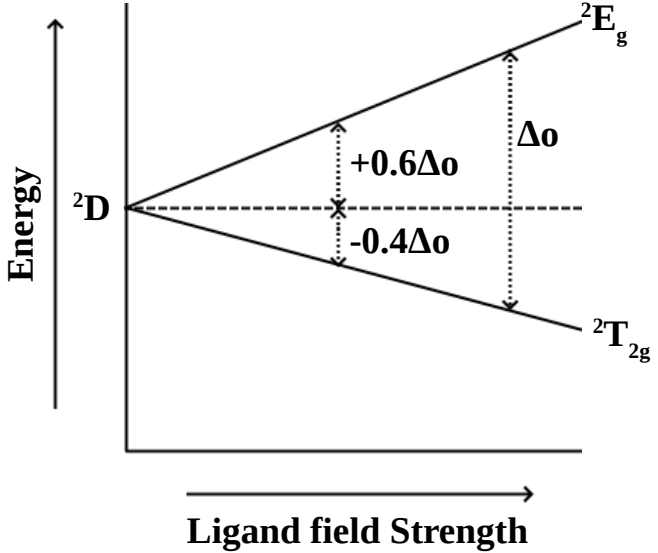
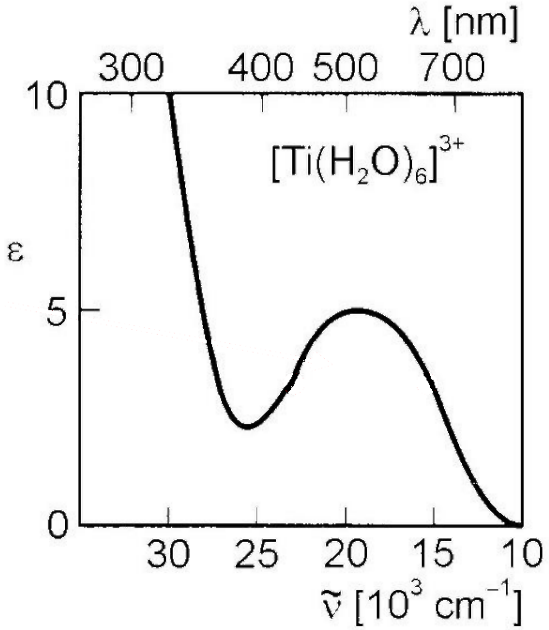
Durg
Chhattisgarh

Interpretation of spectra of 3d transition metal complexes & calculation of 10 Dq, B and β

For all octahedral complexes, except high spin d^5, simple CFT would predict that only one band should appear in the electronic spectrum and that the energy of this band should correspond to the absorption of energy equivalent to 10 dq. This is only observed for those ions which have 'D' term symbol. But when free metal ions have 'F' symbol, 2 or 3 bands are observed in electronic spectra. If the ligand field splitting energy is greater than the pairing energy, then Orgel diagrams fail to explain. In this case Tanabe - Sugano diagrams help us to explain electronic spectra of metal complex. So, both Orgel and Tanabe-Sugano diagrams help us to calculate 10 dq, B (interelectronic repulsion parameter in complex) and β (nephelauxetic ratio, which gives information about covalency character in complex).

d^1 complexes





System with a single d electron is free from interelectronic repulsion. The spectroscopic term for the ground state of gaseous metal ion (example Ti^{3+}) is ^2D , which splits up into T_{2g} and E_g . The T_{2g} state lies 0.4 Δo below and the E_g state 0.6. Δo with respect to 'Bery center'. In d^1 the ground state is triply degenerate, it can be

$(dxy)^1$, $(dxz)^0$, $(dyz)^0$, $(e_g)^0$ or

$(dxy)^0$, $(dxz)^1$, $(dyz)^0$, $(e_g)^0$ or

$(dxy)^0$, $(dxz)^0$, $(dyz)^1$, $(e_g)^0$

and the excited state is doubly degenerate, it can be

$(t_{2g})^0$,$(dx^2\text{-}y^2)^1$,$(dz^2)^0$ or

$(t_{2g})^0$, $(dx^2\text{-}y^2)^0$, $(dz^2)^1$

A single electronic band is expected for d^1 configuration

$$^2T_{2g} \rightarrow {}^2E_g$$

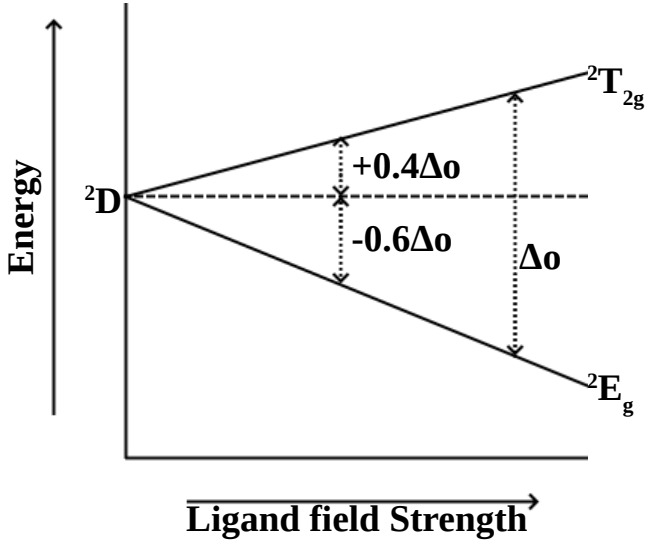
Magnitude of Δo depends on the nature of metal and ligands and affects the energy of transition and hence λ_{max} . Colour of $[Ti(H_2O)_6]^{3+}$ is purple, which is complementary colour of green because energy difference between t_{2g} and e_g levels is 57 kcal (20300 cm^{-1}).

In the absorption spectra of $[Ti(H_2O)_6]^{3+}$ the steep part of the curve from 27000 to 30000 cm^{-1} (in the UV region) is due to charge transfer. The intensity of band is extremely weak (ε ~ 5) because transition is spin allowed but Laporte forbidden. Due to Jahn-Teller distortion absorption band appeared broad, actually this single band formed due to overlapping of two closely spaced bands.

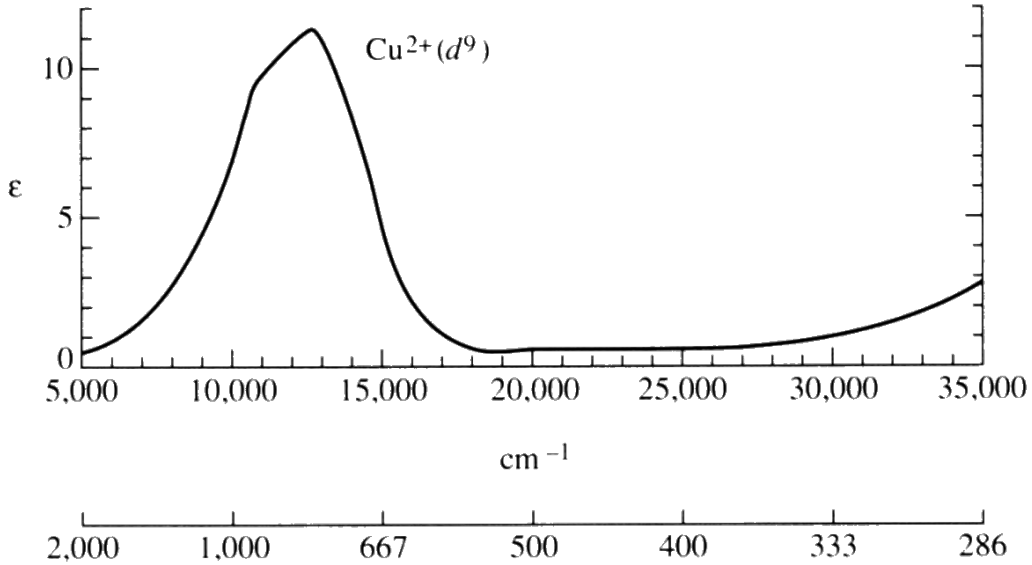
Here only one electron is present in ‘d’ orbital so, no need to calculate ‘B’ or β.

d^9 complexes

In the d^1 case there is a single electron in the lower t_{2g} level, whereas in the d^9 case there is a single hole in the upper e_g level. Thus the transition in the d^1 case is promoting an electron from the t_{2g} level to the e_g level, while in the d^9 case it is simpler to consider the promotion of an electron as the transfer of a hole from e_g to t_{2g} . The energy diagram for d_9 is therefore the inverse of that for a d^1 configuration.

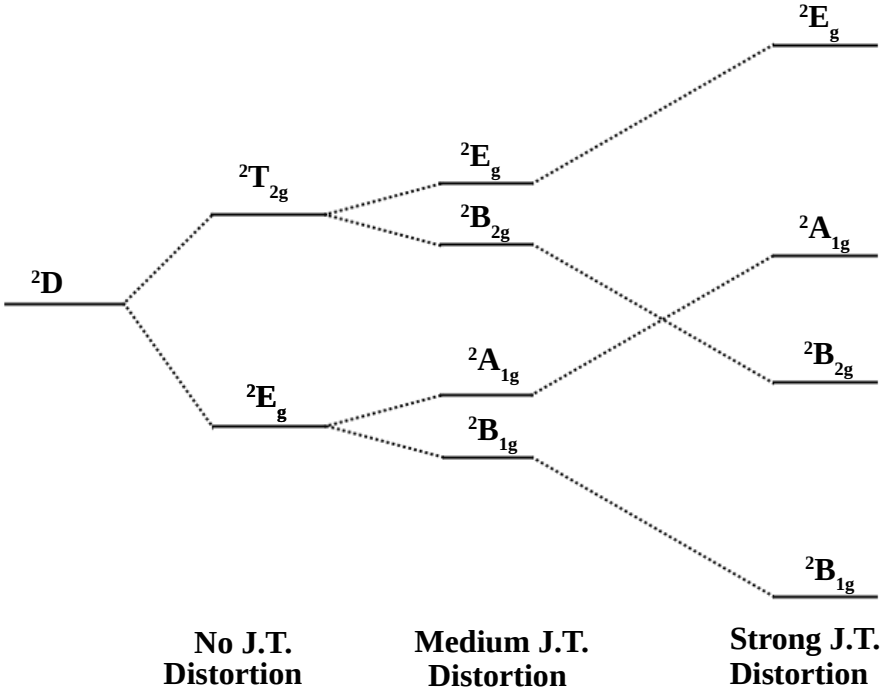


Absorption spectrum of Cu^{++} ion in aqueous solution, which contains $[Cu(H_2O)_6]$ gives one band.



$Cu(H_2O)_6^{2+}$ has a blue colour due to the single $^2E_g \rightarrow {}^2T_{2g}$ electronic transition at ~800 nm

Actually this one broad band consists of closely spaced three bands(800 nm , max 11) . This is due to Jahn-Teller distortion, which causes further splitting of energy levels into a set of four levels and clearly three bands, corresponding to the transition from the lowest to the upper levels are possible.



The energy difference between levels depends on the extent of splitting caused by the ligands. When the ligand field is weak the splitting is small and hence the three bands are nearly superimposed to produce a broad adsorption band as in the case of $[Cu(H_2O)_6]^{2+}$.

In absence of Jahn-Teller distortion only one transition is possible

$$^2E_g \rightarrow {}^2T_{2g}$$

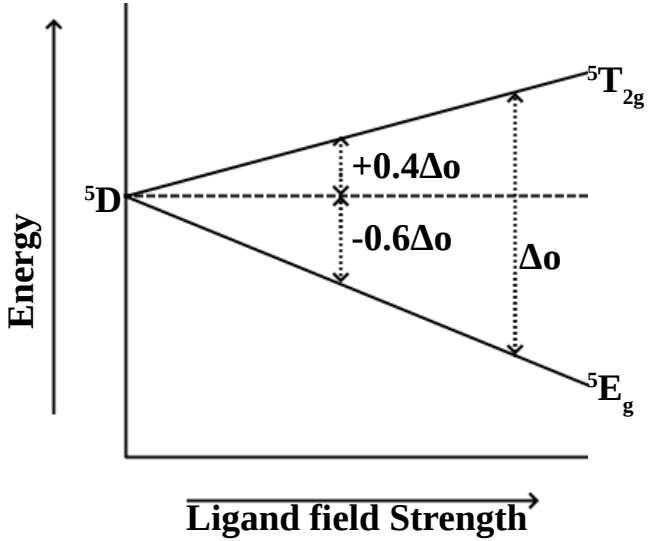
This transition energy is equivalent to 10 dq or Δo

When strong Jahn-Teller distortion occur transitions are :-

$$^2B_{1g} \rightarrow {}^2B_{2g}$$
$$^2B_{1g} \rightarrow {}^2A_{1g}$$
$$^2B_{1g} \rightarrow {}^2E_g$$

d^4 complexes

Metal complex with d^4 configuration have ^5D ground state term symbol in the absence of any ligand field. When six ligands approach in octahedral geometry, the electronic distribution is t_{2g}^3, e_g^1 in weak field and ground state term symbol is ^5E_g. In strong field electronic distribution is t_{2g}^4, e_g^0 and $^3T_{1g}$ is ground state term symbol. The Orgel and Tanabe-Sugano diagram for d^4 configuration can be used to estimate the value of Δ_0 for these complexes.

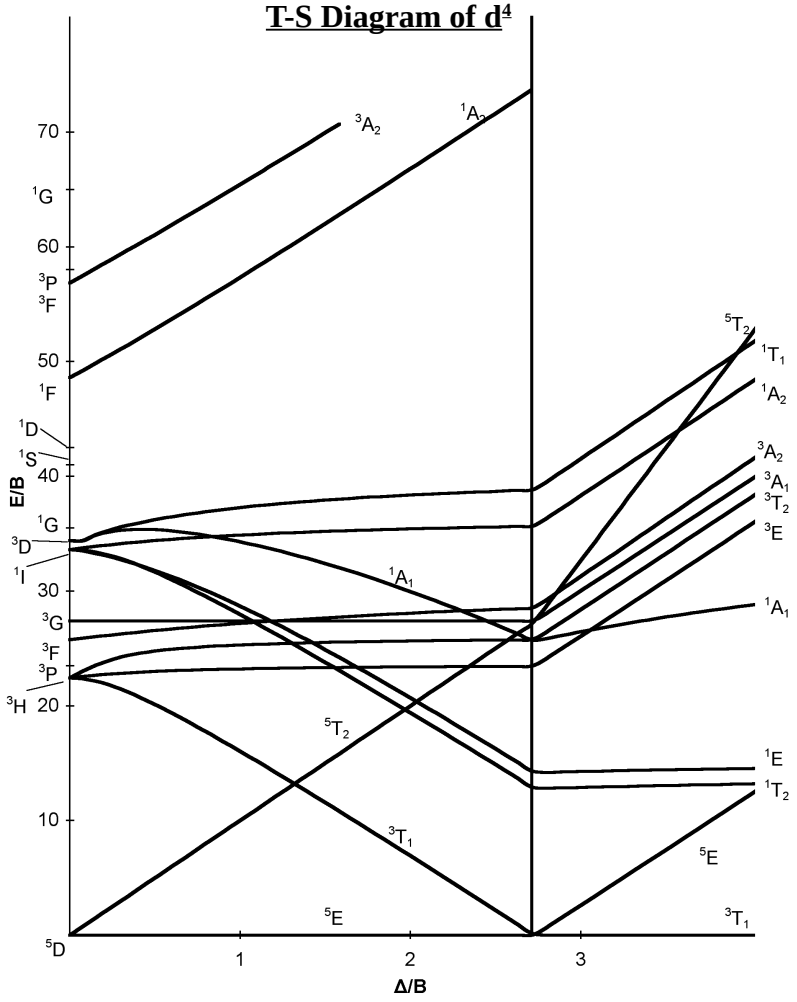


High spin d^4 complex

Splitting pattern of ^5D term is same as d^9 system.
Energy difference between ^5E_g and $^5T_{2g}$ state gives value of 10 dq or Δ_0

Low spin d^4 complexes

It can be explained by taking example of $[Mn(CN)_6]^{3-}$



From T-S diagram it can be seen that the spin-allowed transitions are

$$^3T_{1g}(H) \rightarrow {}^3T_{2g}(H)$$
$$^3T_{1g}(H) \rightarrow {}^3E_g(H)$$
$$^3T_{1g}(H) \rightarrow {}^3A_{1g}(G)$$
$$^3T_{1g}(H) \rightarrow {}^3A_{2g}(F)$$

Three bands are observed at around 27000, 29000 and at 34000 cm^{-1}

The ratio of experimental band energies is

$$\frac{\nu_2}{\nu_1} = \frac{E_2}{E_1} = \frac{E_2/B}{E_1/B} = \frac{29000\,cm^{-1}}{27000\,cm^{-1}} = 1.07$$

When this ratio is 1.07 then $\Delta_0/B = 40$

when $\Delta_0/B = 40$ then

$\frac{E2}{B}$ =38 and $\frac{E1}{B}$ =35

Thus on the T-S diagram, where $\Delta_0/B = 40$,
the value of $^3T_{1g} \rightarrow {}^3T_{2g}$ and $^3T_{1g} \rightarrow {}^3E_g$ are 38 and 35, respectively. The Racah parameter(B) can be calculated from v_2 and v_1

$$\frac{29000\,cm^{-1}}{B} = 38$$

$$B = \frac{29000\,cm^{-1}}{38} = 763cm^{-1}$$

$$\frac{27000\,cm^{-1}}{B} = 35$$

$$B = \frac{27000\,cm^{-1}}{35} = 771cm^{-1}$$

Average value of Racah parameter(B) = $\frac{763+771}{2} = 767cm^{-1}$

Calculation of Δ_0

From the average value of the Racah parameter, the ligand field splitting energy can be calculated as follows

$\frac{\Delta_0}{B}$ = 40 , $\frac{\Delta_0}{767\ cm^{-1}}$ = 40

Δ_0 = 40 ×767 = 30680 cm^{-1}

Calculation of β

Nephelauxetic ratio = β = $\frac{B_{complex}}{B_{free\ ion}}$ = $\frac{767}{1140}$ = 0.673

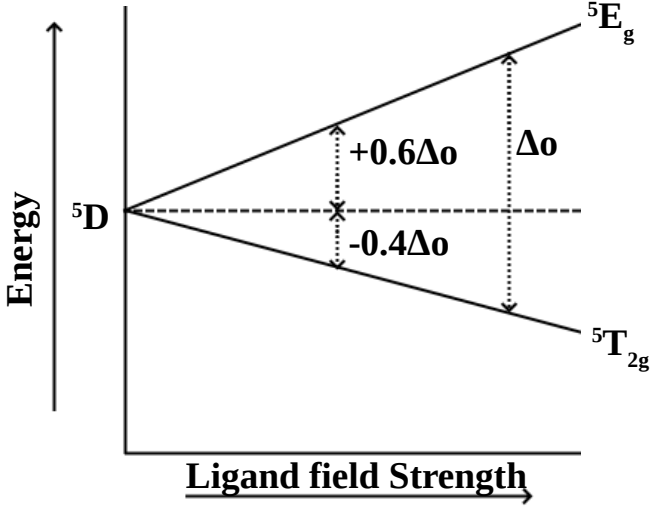
Hence, the inter-electronic repulsion has been decreased during the process of complexation.

d^6 complexes

Metal complex with d^6 configuration have ^5D ground state term symbol in the absence of any ligand field. When six ligands approach in octahedral geometry, in weak field electronic distribution is $t_{2g}^4\ e_g^2$ and ground state term symbol is $^5T_{2g}$. In strong field electronic distribution is $t_{2g}^6\ e_g^0$ and ground state term symbol is $^1A_{1g}$.

Orgel and T-S diagram is used to estimate the value of delta for these complexes.

High spin d^6 complex



Splitting pattern of ^5D term is same as d^1 system. Energy difference between $^5T_{2g}$ and ^5E_g state gives value of Δ_0 or 10 dq.

Low spin d^6 complex

It can be explained by taking example of $[Co(en)_3]^{3+}$

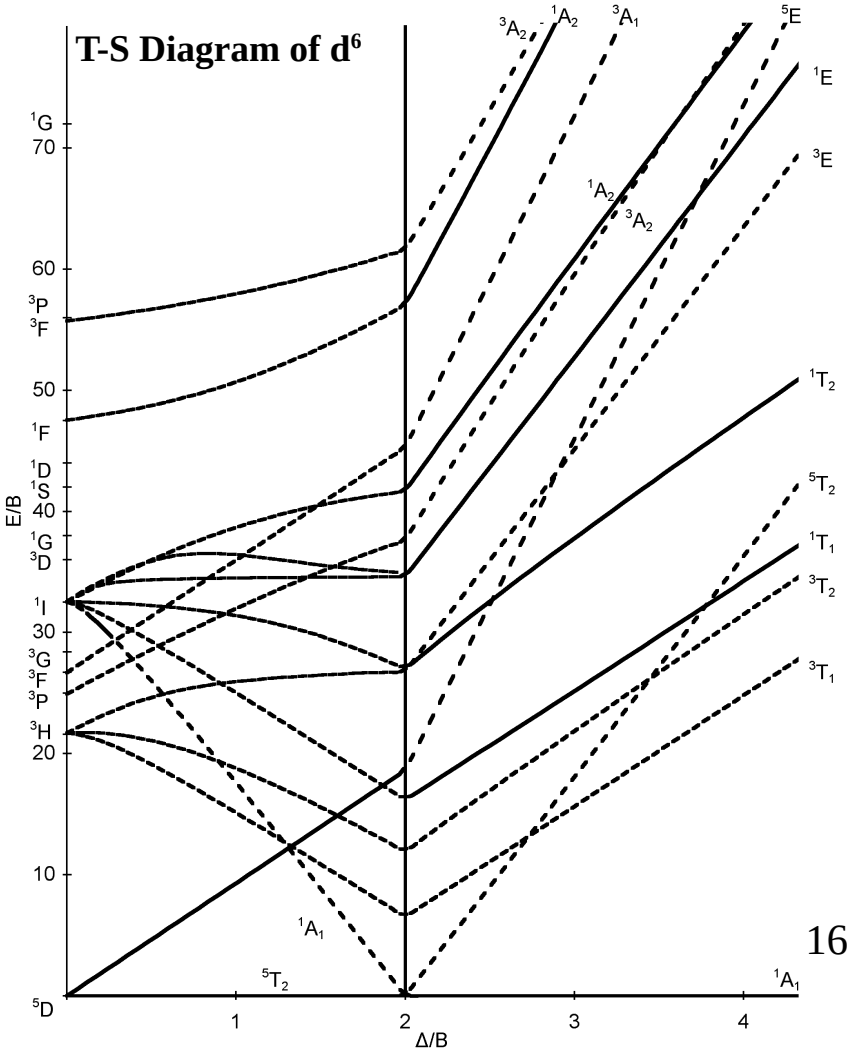
Calculation of B

From T-S diagram it can seen that the spin allowed transitions are

$^1A_{1g}$ (I) → $^1T_{1g}$ (I)

$^1A_{1g}$ (I) → $^1T_{2g}$ (I)

These bands are observed at around 21450 and at 29450 cm^{-1}.



The ratio of experimental band energies is $\frac{v_2}{v_1} = \frac{E_2/B}{E1/B} = \frac{29450\,cm^{-1}}{21450\,cm^{-1}}$ =1.37

When this ratio is 1.37 then $\frac{\Delta_0}{B}$ = 40

When $\frac{\Delta_0}{B}$ = 40

$\frac{E_2}{B}$ =52 and $\frac{E_1}{B}$ = 38

The Racah parameter can be calculated from v_2 and v_1

$\frac{29450}{B}$ = 52 B = $\frac{29450}{52}$ = 566cm^{-1} and

$\frac{21450}{B}$ =38 B= $\frac{21450}{38}$ = 564 cm^{-1}

Average value of B = $\frac{566+564}{2}$ = 565 cm^{-1}

Calculation of Δ_0

From the average value of B we can calculate ligand field splitting energy (Δ_0)

$\frac{\Delta_0}{B}$ =40 ,. $\frac{\Delta_0}{565}$ =40

Δ_0 =565×40 = 22600cm $^{-1}$

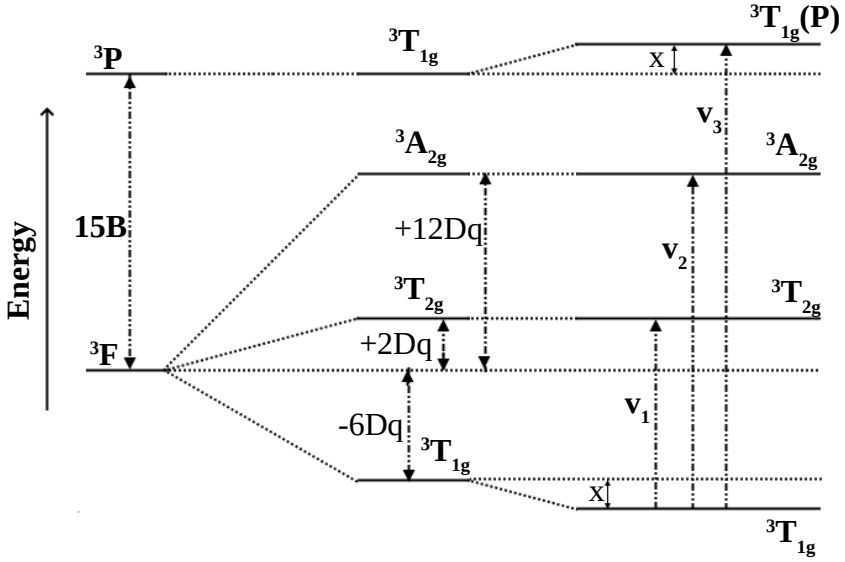
Calculation of β

$\beta = \frac{B_{complex}}{B_{free\ ion}} = \frac{565}{1100} = 0.514$

Value of ‘β’ shows that this complex has more covalent character

d^2 Complexes

Metal complex with d^2 configuration have ^3F ground state term symbol in the absence of any crystal field. However, when six ligands approach in an octahedral coordination, the ground state term symbol becomes $^3T_{1g}$ and remains as such in weak field as well as in strong ligand field. The Orgel and Tanabe-Sugano diagram for d^2 configuration can be used to estimate the value of crystal field splitting energy for these complexes.



The energy level diagram for complexes, where the central metal ion has two d electrons is more complicated. The possible energy states are

Ground state - 3F

Excited state - ^3P, ^1G, ^1D, ^1S

The ^3P, ^1D, and ^1S states contain electrons with opposite spins whereas, in the ground state the two electrons have parallel spins. The transitions from the ground state to ^1G, ^1D or ^1S are spin forbidden, will be very weak and can be ignored.

The only important transitions are. ^3F to ^3P.

From the energy level diagram, we show that, there are three transitions are possible between the triplet states which are spin allowed

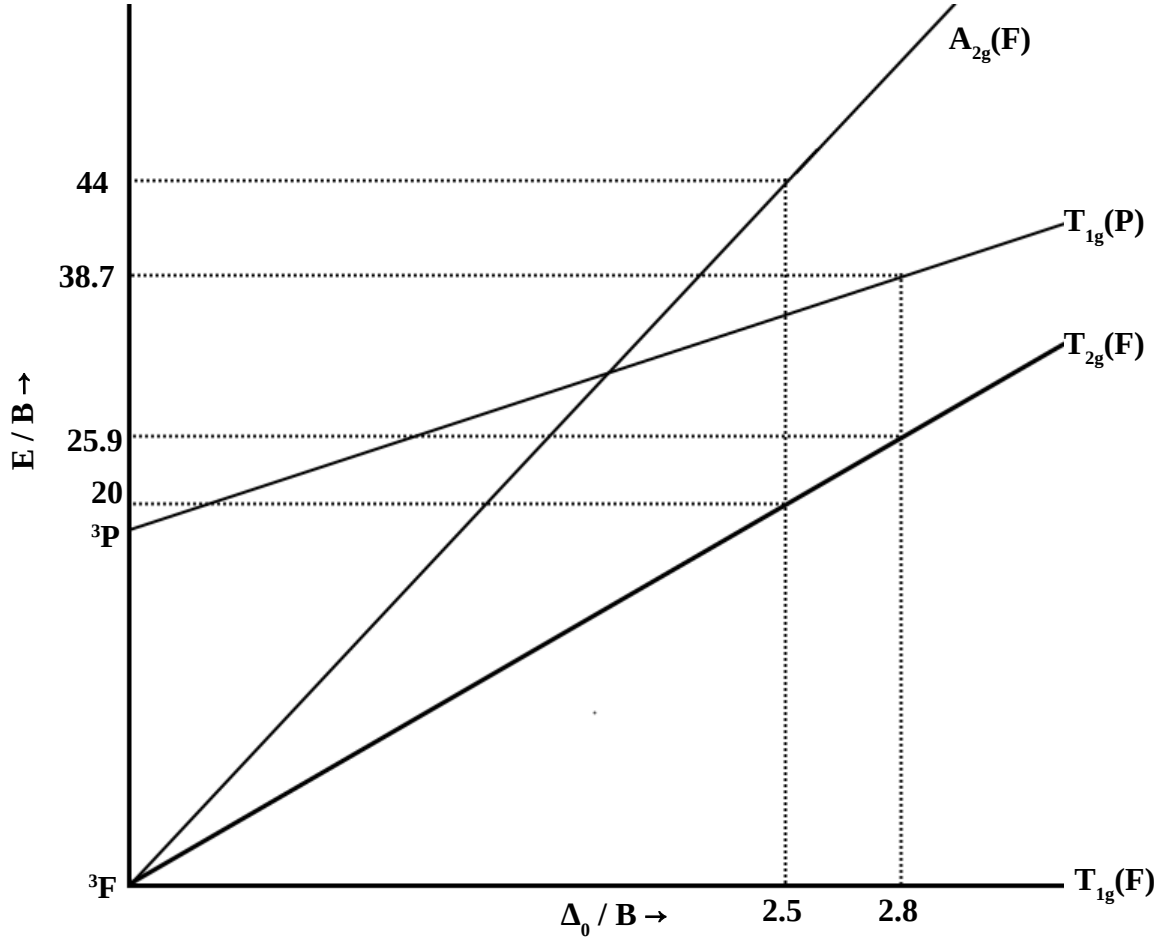
$$^3T_{1g}(F) \text{-----} > {}^3T_{2g}(F) \quad \text{---}\nu_1$$

$$^3T_{1g}(F) \text{-----} > {}^3T_{1g}(P) \quad \text{---}\nu_2$$

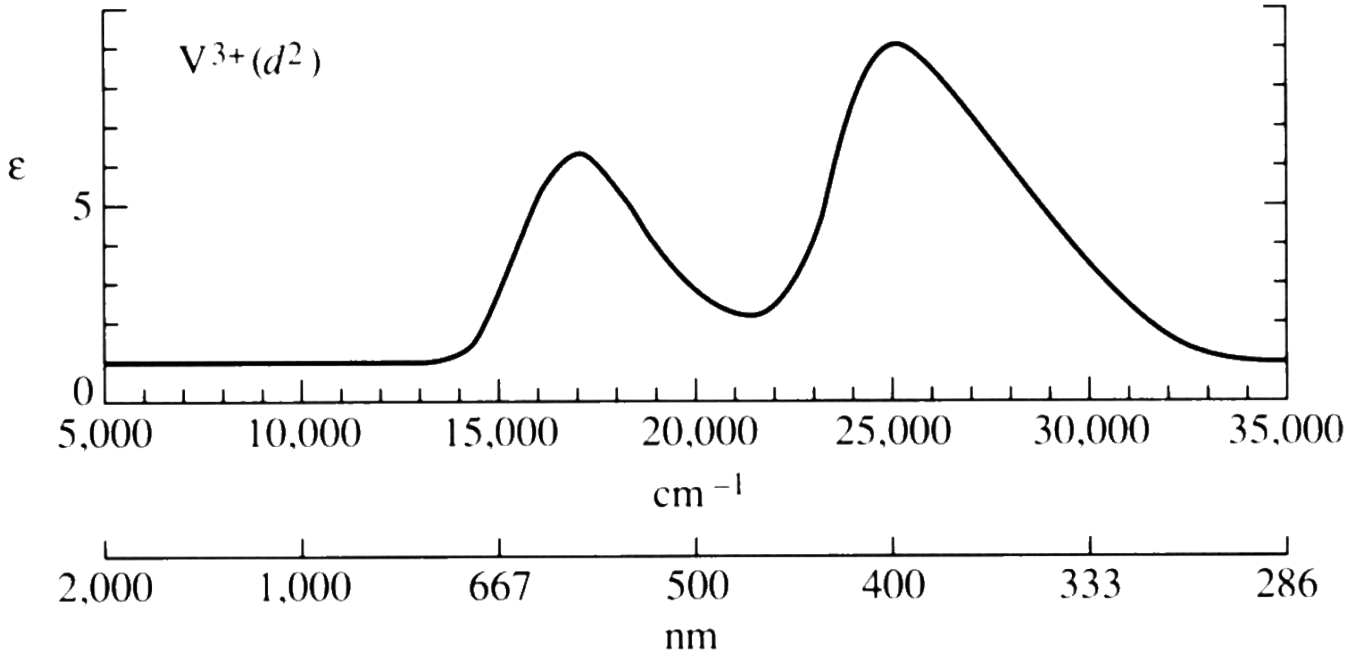
$$^3T_{1g}(F) \text{-----} > {}^3A_{2g}(F) \quad \text{---}\nu_3$$

It can be explained by taking example of $[V(H2O)_6]^{3+}$ ions, which are green in colour. The spectrum consists of broad weak bands at 17,200 cm^{-1} (ε =6) and at 25,600 cm^{-1} (ε = 8). Very weak bands also observed between 20,000 and 30,000 cm^{-1}. The two stronger peaks are due to spin allowed transitions, whereas the very weak bands due to spin forbidden transitions to excited singlet terms.

T-S Diagram of d^2



Uv-vis spectrum of $[V(H_2O)_6]^{3+}$



Calculation of B

There are three transitions are possible from the ground state, hence three peaks should occur in the spectrum, but in the spectrum only two peaks observed, because the ligand field strength of water results in transition occurring close to the $^3A_{2g}$ / $^3T_{1g}$(P) crossover point, hence these two transitions are not resolved into separate peaks. The spectrum shows two main absorption bands are :-

17,200 cm^{-1} ----- $^3T_{1g}$(F) ----------> $^3T_{2g}$(F) (ε =6)

25,600 cm^{-1} ----- $^3T_{1g}$(F) ----------> $^3T_{g1}$(P) or $^3A_{2g}$(F) (ε= 8)

The ratio of experimental band energy is

$$\frac{E_2}{E_1} = \frac{E_2/B}{E_1/B} = \frac{25{,}600}{17{,}200} = 1.49$$

When this ratio is 1.49 then $\frac{\Delta_0}{B}$ = 28

When Δ_0/B = 28 then

$\frac{E_1}{B}$ = 25.9 & $\frac{E_2}{B}$ = 38.7

The Racah parameter (B) can be calculated from both v_2 & v_1

$\frac{25,600}{B}$ = 38.7

B= $\frac{25,600}{38.7}$ = 662cm^{-1}

$\frac{17200}{B}$ = 25.9

B= $\frac{17200}{25.9}$ = 664cm^{-1}

Average Value of B = $\frac{662+664}{2}$ = 663cm^{-1}

Calculate of Δ_0

From T-S diagram $\frac{\Delta_0}{B}$ = 28

$\frac{\Delta_0}{663}$ = 28 Δ_0= 28 x 663 = 18564cm^{-1}

Calculation of β

Free ion value of 'B' for V^{3+} = 860cm^{-1}

$$\beta = \frac{B_{complex}}{B_{free\ ion}} = \frac{663}{860} = 0.771$$

Value of β shows that ~ 25% covalent character present in complex.

If in the spectra of d^2 complexes 3 bands are observed then 'B' can be calculated by this formula

$$B = \frac{v_3 + v_2 - 3v_1}{15}$$ where

$$v_1 = {}^3T_{1g} \rightarrow {}^3T_{2g}$$

$$v_2 = {}^3T_{1g} \rightarrow {}^3A_{2g}$$

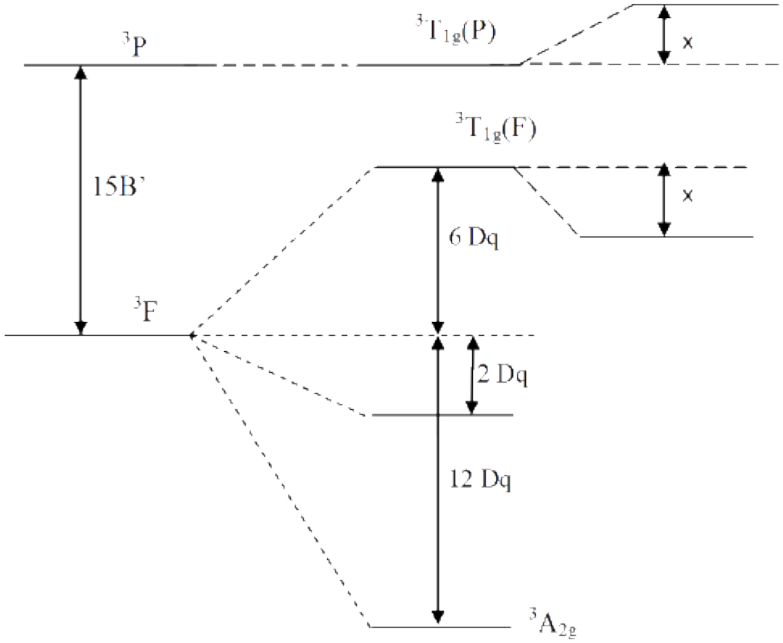
$$v_3 = {}^3T_{1g} \rightarrow {}^3T_{1g}(P)$$

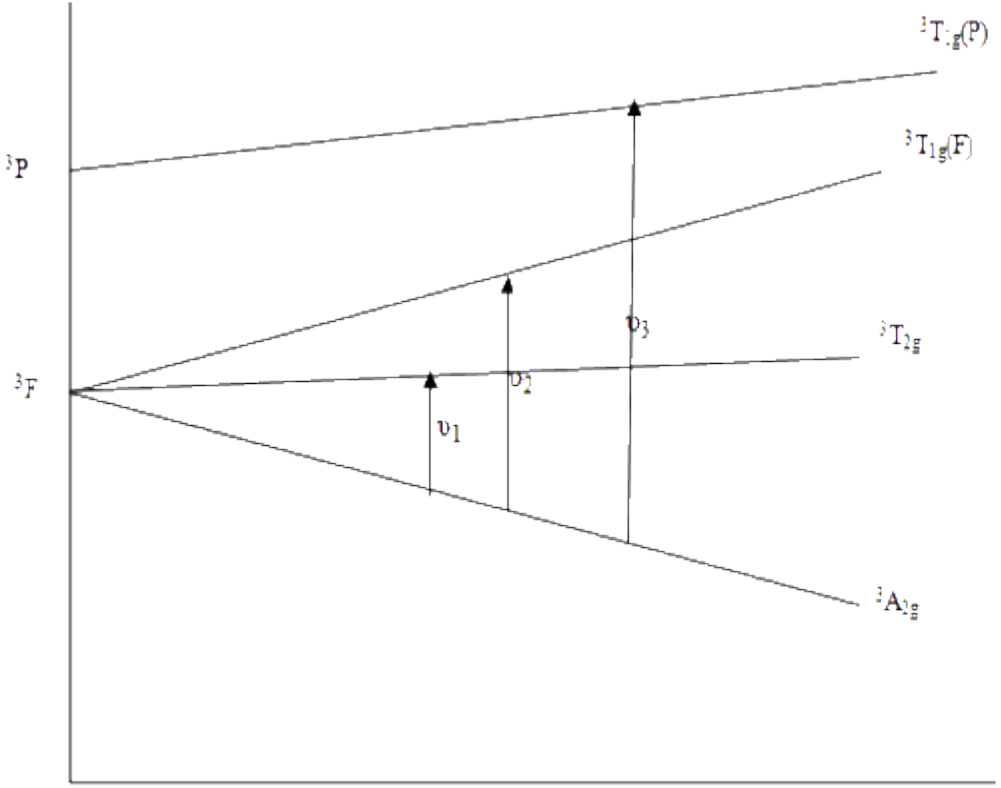
d^8 complexes

For d^8 complexes ground state term is ^3F and excited state is ^3P (of same multiplicity).In octahedral field the transformation of states are-

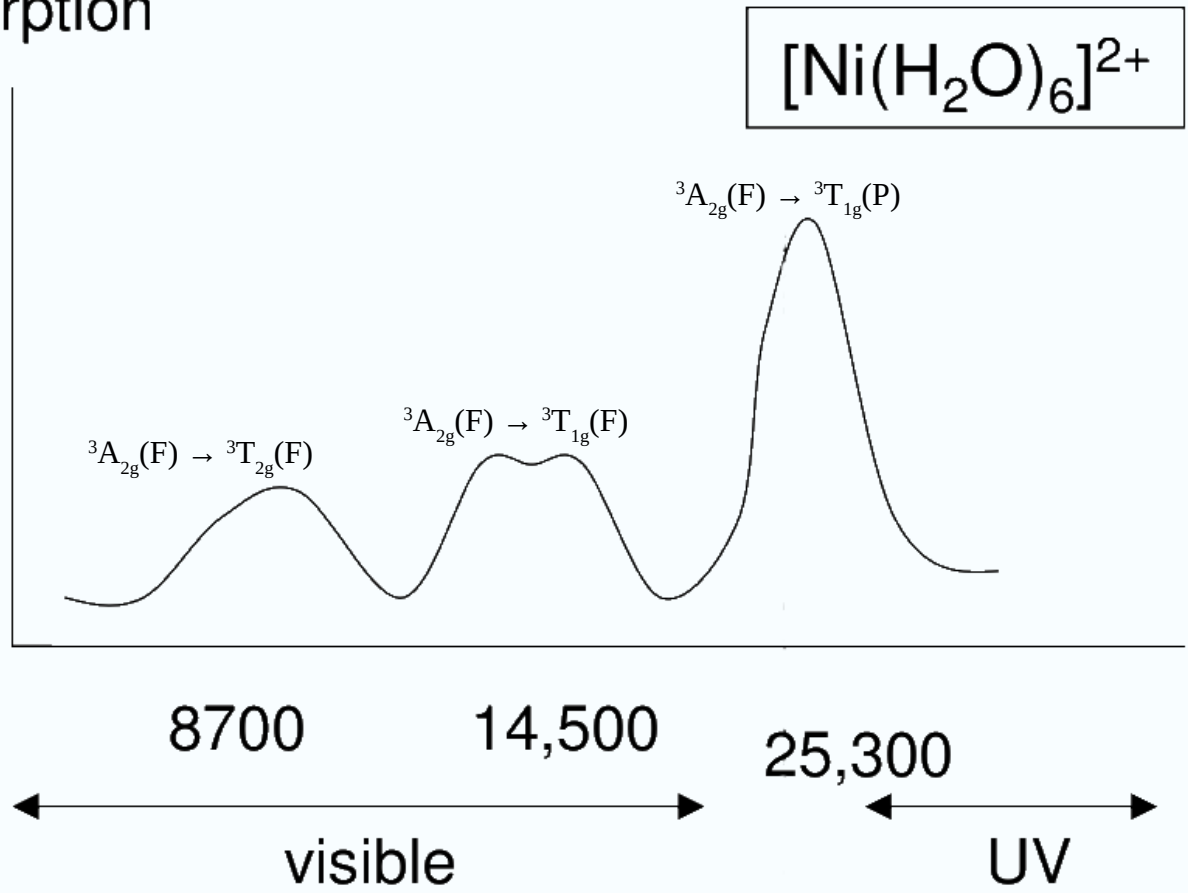
^3P --------- $^3T_{1g}$

^3F --------- $^3A_{2g}$, $^3T_{2g}$, $^3T_{1g}$




$^3T_{1g}(P)$
$^3T_{1g}(F)$
^3P
$^3T_{2g}$
^3F
υ_3
υ_2
υ_1
$^3A_{2g}$
Ligand field strength

Absorption



$\bar{\nu}$ / cm^{-1} (frequency)

Electronic arrangement for d^8 configuration is same in high spin or in low spin, t_{2g}^6, e_g^2. For d^8 configuration ground state has only one arrangement of electrons that's why A_{2g} state (single degenerate) is ground sub state.

Spectra of d^8 complexes can be explained by taking example of $[Ni(H_2O)_6]^{2+}$.Aqueous solution of bivalent nickel salts have a light green colour, which is due to presence of weak bands in the red and the portions of the visible spectrum. The spectrum consists of three bands

v cm^{-1}	ε	
8,700	1.6	v_1
14,500	2.0	v_2
25,300	4.6	v_3

The spin allowed transitions are expected are -----

$^3A_{2g}$ (F) ----------> $^3T_{2g}$(F)

$^3A_{2g}$(F) ----------> $^3T_{1g}$(F)

$^3A_{2g}$(F) ----------> $^3T_{1g}$(P)

Calculation of Δ_0

Energy difference between $^3A_{2g}(F)$ & $^3T_{2g}(F)$ is 10Dq or Δ_0 so transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (v1) gives value of Δ_0

$\Delta_0 = 8{,}700 cm^{-1}$

Calculation of inter electronic repulsion parameter (B)

Value of B is obtained from the relation

$$B = \frac{\nu_2 + \nu_3 - 3\nu_1}{15}$$

B value for $[Ni(H_2O)_6]^{2+}$ complex is

$$B = \frac{(14{,}500 + 25{,}000) - (3 \; X \; 8{,}700)}{15} = 913 cm^{-1}$$

Calculation of β

$$\beta = \frac{B_{complex}}{B_{free\ ion}}$$

'B' for Ni^{2+} free ion is $1030 cm^{-1}$

$$\beta = \frac{913\,cm^{-1}}{1030\,cm^{-1}} = 0.9029$$

The considerable reduction in 'B' value on complex formation is due to attribution of certain degree of covalency of the metal – ligand bond, which causes delocalization of the metal ion electron density into the ligand.

Thank you

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Charge Transfer Spectra

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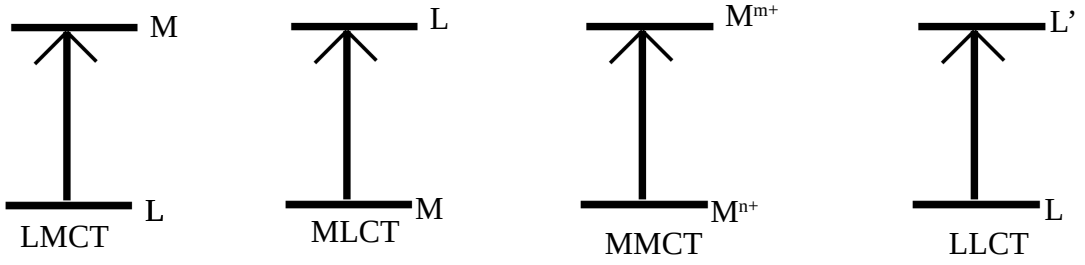
Charge Transfer Spectra

An electronic transition between orbitals that are centred on different atoms is called charge transfer transition and absorption band is usually very strong. These transitions involve electron transfer from one part of a complex to another. More specifically an electron moves from an orbital that is mainly ligand in character to one that is mainly metal in character (ligand-to-metal charge transfer, LMCT) or vice versa (metal-to-Ligand charge transfer, MLCT). Unlike d-d transitions, these are fully allowed and hence give rise to much more intense absorptions. When these absorptions fall within the visible region, they often produce rich colours. In these transitions, the electronic transitions are Laporte and spin allowed, i. e. $\Delta l = \pm 1$ and $\Delta S = 0$

A charge transfer transition may be regarded as an internal redox process.

Types of charge transfer spectra

(1) Ligand to metal charge transfer (LMCT)
(2) Metal to ligand charge transfer (MLCT)
(3) Intermetal charge transfer or metal to metal charge transfer (MMCT)
(4) Interligand charge transfer (LLCT)

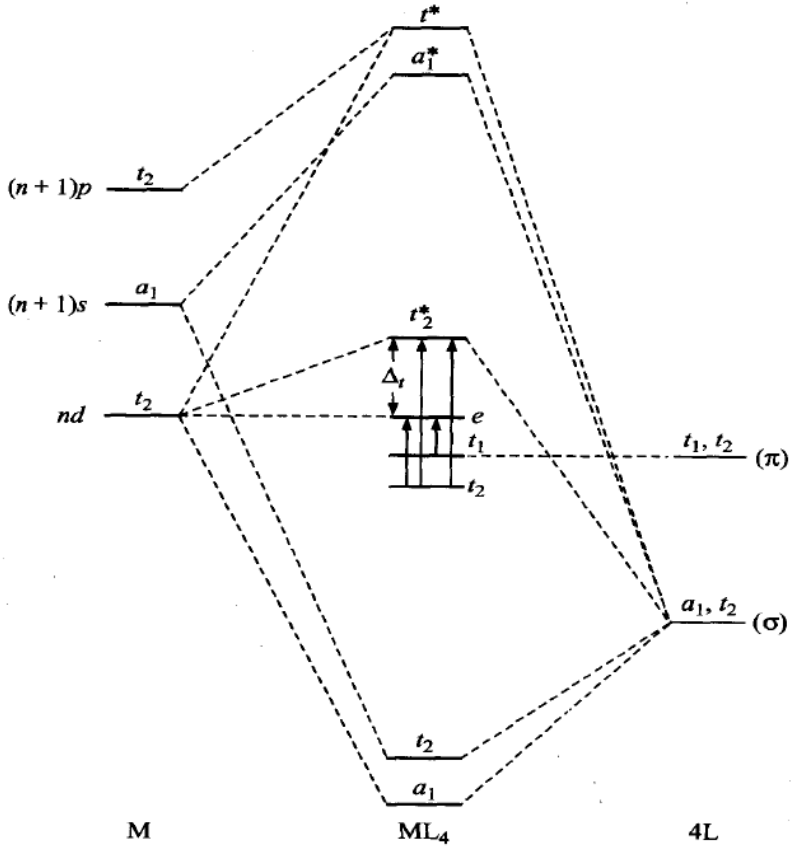


Ligand to metal charge transfer (LMCT)

If the migration of electron is from ligand to metal, then the charge transfer is called ligand to metal charge (LMCT). Some important characteristics of these transitions are:-

(a) Transfer of electrons from filled ligand orbitals to vacant metal orbitals
(b) π-donar ligands show LMCT, e.g. halides, oxides, sulphides, selenides, N_3^-, RO^-
(c) Metal should have high energy vacant orbitals
(d) Metal should be in high oxidation state
(e) Ionization energy of metal should be high
(f) Ligand should have low energy filled orbital
(g) Internal oxidation of ligand and internal reduction of metal takes place
(h) Metal may be of main group, transition metal or inner transition metals

Molecular Orbital Diagram of MnO_4^-



Electronic transitions in metal complexes can be easily explained by taking an example of permanganate ion, MnO_4^-, in which oxidation state of manganese is +7 and combined with four oxide ion. The molecular orbital diagram help us to identify possible LMCT transitions. In any tetrahedral complex, the four lowest energy σ-bonding orbitals are filled and primarily ligand in character. Next there are two sets of σ- nonbonding molecular orbitals, one is ligand centred and one is metal centred. Manganese ion has vacant 3d orbitals, hence there are four possible ligand-to-metal transitions are

$$L\ (t_1) \text{-----} \rightarrow M\ (e)$$

$$L\ (t_1) \text{-----} \rightarrow M\ (t_2^*)$$

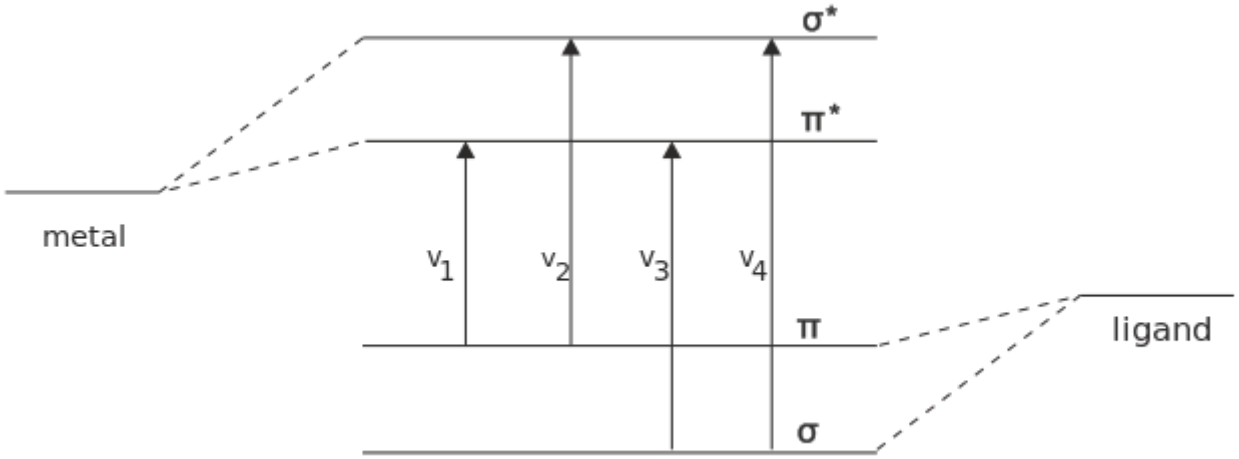
$$L\ (t_2) \text{-----} \rightarrow M\ (e)$$

$$L\ (t_2) \text{-----} \rightarrow M\ (t_2^*)$$

For MnO_4^- all four transitions have been observed: 17,700 cm^{-1} (t_1-----→e), 29,500 cm^{-1} (t_1-----→t_2^*), 30,300 cm^{-1} (t_2-----→e), and 44,400 cm^{-1} (t_2-----→t_2^*). Only the absorption at 17,700 cm^{-1} belongs to visible region, and it is responsible for the deep purple colour of MnO_4^-

Here a partial MO diagram for an octahedral ML6 complex

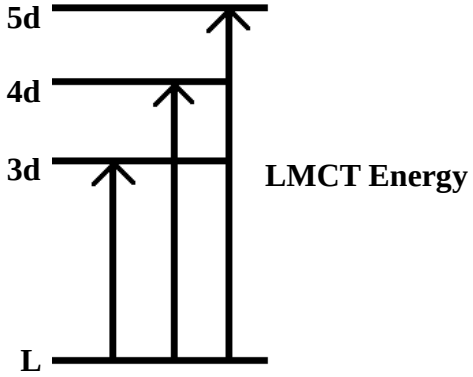
Partial Molecular Orbital Diagram



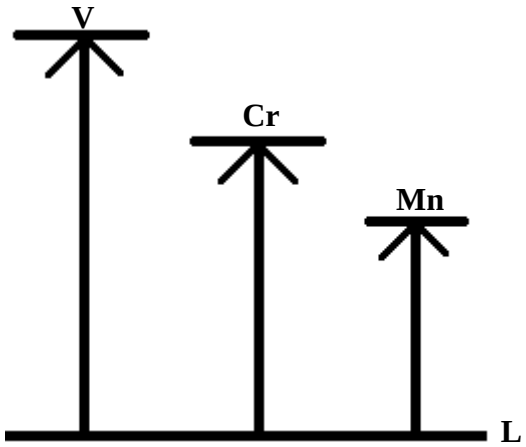
Energy difference between filled ligand orbital and vacant metal orbital is denoted as LMCT energy.

Variation of LMCT energy

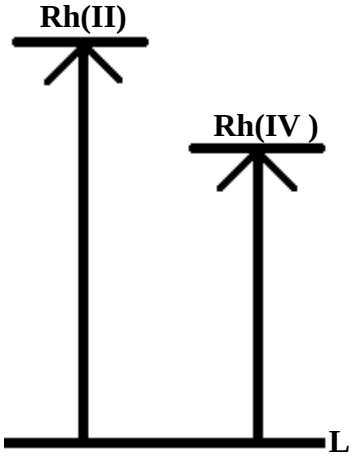
(a) On moving down in a group of transition metals LMCT energy increases.



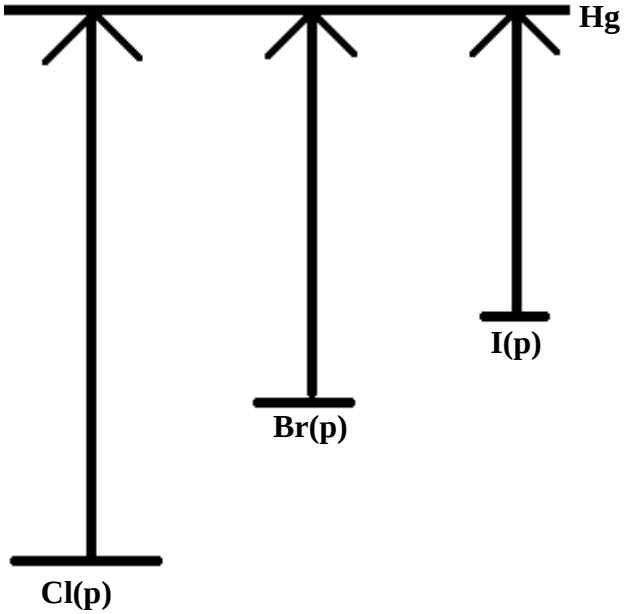
(b) On moving left to right in a period, d-orbital size of atom decreases due to effective nuclear charge and hence LMCT energy decreases, note that ligand should be same.



(c) LMCT energy decreases on increasing oxidation state of metal, if ligand is same.



(d) If ligands are different but metal ion is same then LMCT energy depends on size of ligand. For example in $HgCl_2$, $HgBr_2$, HgI_2 size of iodine is large, so energy of filled orbital of iodine is higher in energy, hence energy difference between ligand orbital and vacant metal orbital is less and LMCT energy decreases.



Colour of mercury halides are :-

1. $HgCl_2$ absorbs from UV region and its colour is white
2. $HgBr_2$ absorbs from violet region and its colour is yellow
3. HgI_2 absorbs from green region and its colour is reduction

Pigment	Primary Orbitals Involved
Cadmium yellow (CdS)	Ligand $\pi_p \longrightarrow$ metal $5s$
Vermilion (HgS)	Ligand $\pi_p \longrightarrow$ metal $6s$
Naples yellow $[Pb_3(SbO_4)_2]$	Ligand $\pi_p \longrightarrow$ metal $5s$ or $5p$
Massicot (PbO)	Ligand $\pi_p \longrightarrow$ metal $6s$
Chrome yellow ($PbCrO_4$)	Ligand $\pi_p \longrightarrow$ metal $3d$
Red and yellow ochres (iron oxides)	Ligand $\pi_p \longrightarrow$ metal $3d$

Metal to ligand charge transfer (MLCT)

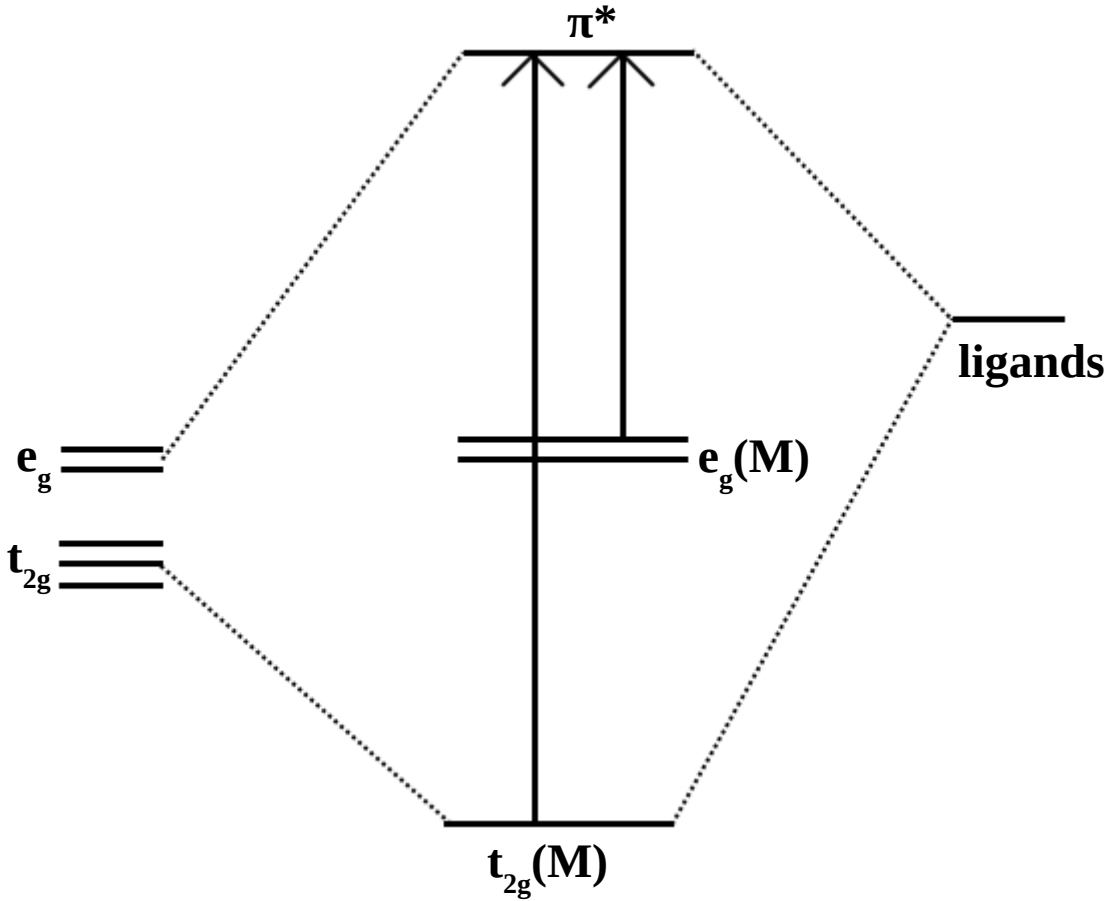
If the migration of electron is from metal to ligand, then charge transfer is called metal to ligand charge transfer (MLCT). Favourable conditions for these transitions are:-

(a) Transfer of electrons from molecular orbital of metal to ligand.

(b) Metal should be in low oxidation state.

(c) Ligand must have vacant orbital, e. g. CO, CN^-, NO, bipy, ph, py, thionate ion, imines, aromatic ligands, ligands having π-bonds.

M.O. Diagram of MLCT



Value of MLCT energy (energy difference between filled metal orbital and vacant ligand orbital) depends on nature of metal orbital

(a) Electron rich metals, which have filled e_g orbitals show coloured complex i. e. it absorbs from visible region.

(b) If metals have filled t_{2g} orbitals then MLCT energy is more, and complex absorbs from uv region and complex will be colourless.

Metal to metal charge transfer (MMCT)

If in a complex same metal ions are present in different oxidation state, then electron transfers between both metal ions is called MMCT.

Some examples are here---

(a) $KFe^{III}[Fe^{II}(CN)_6]$ Prussian Blue

$KFe^{II}[Fe^{III}(CN)_6]$ Turnbull's Blue

(b) Rust (Fe_3O_4) is reddish brown here elctrons transfers from Fe^{2+} ------→ Fe^{3+}

(c) If spinels (mixed oxides) are coloured, it is due to MMCT eg. Pb_3O_4

Ligand to Ligand Charge Transfer (LLCT)

In Complex if ligands are present of different nature, one is electron donor and other is electron accepter then we get LLCT.

Intense absorption bands which are assigned to inter system LLCT transitions appear in the electronic spectra of square planar Ni^{II} ,Pd^{II} & Pt^{II} complexes, which contain a 1,2-ethyldithionate as electron donating and 1,3-diimine as accepting ligand.

Thank You

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Cytochromes

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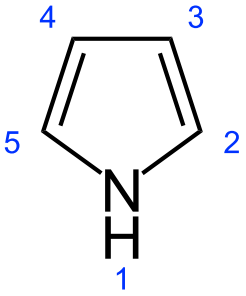
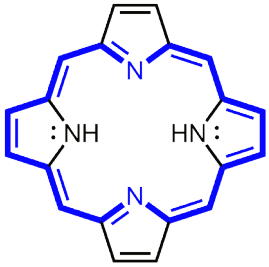
Pyrrole



Pyrrole is a heterocyclic aromatic organic compound, a five-membered ring with the formula C_4H_4NH

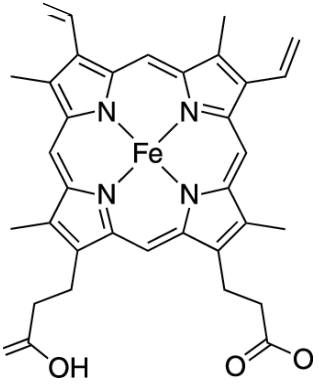
Porphyrin

Porphyrins are a group of heterocyclic macrocycle organic compounds, composed of four modified pyrrole subunits interconnected at their α carbon atoms via methine bridges (=CH−). The parent of porphyrin is porphine, a rare chemical compound of exclusively theoretical interest. Substituted porphines are called porphyrins. With a total of 26 π-electrons, of which 18 π-electrons form a planar, continuous cycle, the porphyrin ring structure is often described as aromatic. One result of the large conjugated system is that porphyrins typically absorb strongly in the visible region of the electromagnetic spectrum, i.e. they are deeply colored. The name "porphyrin" derives from the Greek word which means purple.



Heme

Heme or haem is a coordination complex "consisting of an iron ion coordinated to a porphyrin ring acting as a tetradentate ligand, and to one or two axial ligands." Many porphyrin-containing metalloproteins have heme as their prosthetic group; these are known as hemoproteins. Hemes are most commonly recognized as components of hemoglobin, the red pigment in blood, but are also found in a number of other biologically important hemoproteins such as myoglobin, cytochromes, catalases, heme peroxidase, and endothelial nitric oxide synthase. The word heme is derived from Greek means "blood".



Cytochromes

Cytochromes are proteins containing heme as a cofactor. They are classified according to the type of heme and its mode of binding. Four varieties are recognized by the International Union of Biochemistry and Molecular Biology (IUBMB), cytochromes a, cytochromes b, cytochromes c and cytochrome d. Cytochrome function is linked to the reversible redox change from ferrous (Fe(II)) to the ferric (Fe(III)) oxidation state of the iron found in the heme core. In addition to the classification by the IUBMB into four cytochrome classes, several additional classifications such as cytochrome o and cytochrome P450 can be found in biochemical functions.

Cytochromes are classified according to heme proteins on the basis of the position of their lowest energy absorption band in their reduced state, as cytochromes a (605 nm), b (≈565 nm), and c (550 nm). Within each class, cytochrome a, b, or c, early cytochromes are numbered consecutively, e.g. cyt c, cyt c1, and cyt c2, with more recent examples designated by their reduced state R-band maximum, e.g. cyt c559.

Types of Cytochromes

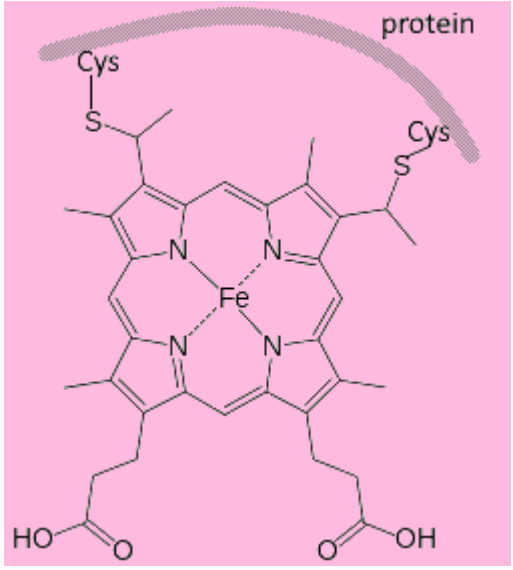
Several kinds of cytochrome exist and can be distinguished by spectroscopy, exact structure of the heme group, inhibitor sensitivity, and reduction potential.

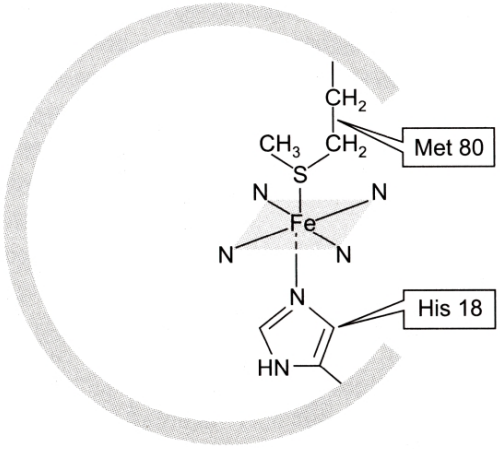
Four types of cytochromes are distinguished by their prosthetic groups:-

Type	Prosthetic group
Cytochrome a	heme A
Cytochrome b	heme B
Cytochrome c	heme C (covalently bound heme b)
Cytochrome d	heme D (Heme B with γ-spirolactone)

Cytochrome c is most important among the four

Cytochrome c





The iron atom of the heme group in cytochrome *c* is bonded to a methionine sulphur atom and a histidine nitrogen atom

$$RCH{=}CH_2 + HSCH_2 \longrightarrow R\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}SCH_2R$$

Vinyl group on heme

Cysteine Residue of protein

Formation of a thioether linkage

The most extensively studied is the cytochrome c. It has a single polypeptide chain of 104 amino acid residues Its active centre is a porphyrin ring with iron at the centre with the oxidation state +2 or +3. Heme is covalently bound to its protein via thioether groups.

Iron is at the centre of the prophyrin ring has histidine as the fifth ligand and the sixth ligand is a methionine segment. The iron sulphur bond is strong enough to prevent the replacement of the methionine legend by oxygen. The heme group is surrounded by several tightly packed hydrophobic side chains.

The heme part of Cyt C is buried deep inside the hydrophobic pocket of the apoprotein. Only an edge part of the heme is near the surface. The fact, that their is a ring of lysine residues of the protein surrounding the exposed part of the heme. The model studies have shown that Cyt C interacts with the inorganic redox partners through the exposed heme edge. Consiquently the reduction potential of Cyt C is also dependent on the stability and the solvent accessibility of the heme crevice and the hydrophobicities of the amino acid residues that form the line around the heme crevice

The reduction potential of cytochrome C is rendered more positive (as

compared to higher electron affinity) by the hydrophobic character of the heme environment when compared to the same heme complex in an aqueous environment. Consequently removal of an electron from cytochrome C becomes energetically more costly from the heme in cytochrome C when compare from a heme in water since the dielectric constant near the iron atom is lower in cytochrome C.

Diagram shows that since there is no vacant coordination position, cytochrome C is unable to bind with oxygen molecule. This is unlike to the situation of iron in haemoglobin and myoglobin. The iron of heme in cytochrome is alternatively oxidize Fe^{3+} and reduced Fe^{2+} which is an essential feature for the electron transport in electron transport chain. This is in contrast to heme iron of haemoglobin and myoglobin which only remains in the ferrous (Fe^{2+}) state.

Both the oxidized and reduced form of cytochrome C have almost similar structures and differ slightly in structure of protein part. The heme prosthetic groups are at a distance of $17A^0$. It has been suggested that electron transfer between these distant hemes occurs through outer sphere electron transfer. This is supported by the fact that iron in both the form is in the low spin configuration of favourable situation for outer sphere electron transfer.

Cytochrome c Oxidase or Cytochrome aa_3

The term cytochrome oxidase is generally used to collectively represent cytochrome a and a_3 which is the terminal component of ETC. Cytochrome oxidase is the only electron carrier, the heme iron of which can directly react with molecular oxygen and reduce it. Cytochrome oxidase is thus the last link in the respiratory chain of electrons flowing from reduced food stuffs to oxygen. Thus (without oxygen) it must be five quardinate in contrast to cytochrome c. Besides heme (with iron), these oxidase also contains copper that undergoes oxidation reduction ($Cu^{2+} \rightleftharpoons Cu^{+}$) during the transport of electrons. In the final stage of ETC, the transported electrons, the free protons and the molecular oxygen combined to produce water.

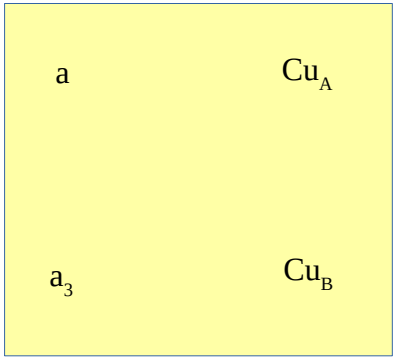
The electron transfer process occurs from cytochrome c in the reduced form to the cytochrome c oxidase. Ultimately the electron is transferred to O_2 by reduced cytochrome c oxidase followed by four electron reduction of O_2 to water. In the transfer of electron from NADH (formed by oxidation of glucose) to O_2, large

amount of energy is released (however, the energy is liberated in controlled steps).

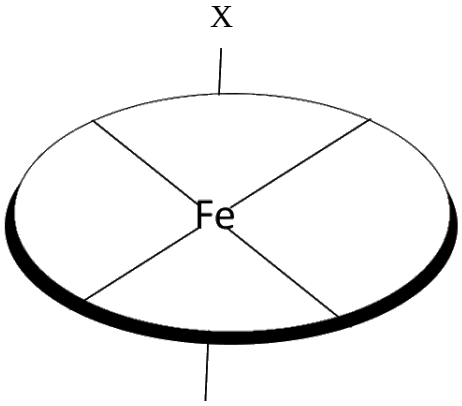
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Chemical Structure

cytochrome c oxidase contains two distinct cytochromes only one type of heme designated heme a can be isolated from it .Thus the different properties of cytochrome a and a_3 must be derived from differences in the binding to the protein part of the enzyme. Cytochrome a has its iron atom in a low spin state. It may probably has to axial protein ligands, like other low spin cytochromes such as cytochrome c. Cytochrome a_3 on the other hand appears to have a free coordination position, as it can interact with dioxygen or various inhibitors and the iron atom is found to be in a high spin state. The environments of heme in cytochrome A and B are shown here:-



Prosthetic groups in the minimal functional unit of cytochrome c oxidase



Schematic representation of the environment of heme
In cyt a X=S(Met), Y=N(His)
In cyt a_3 X= N(His), Y=O_2

The catalytic cycle of cytochrome C oxidase may be studied by considering the following points:

1. The cyt a_3 and Cu_B are separated by 4.5 A^0 ,and both are separated from cyt a and Cu_A by 20 A^0

2. Cytochrome a--Cu_A is the low potential site and hence it receiving the electron.
3. The reduction of cyt a--Cu_A brings in structural changes in the site so, that an electron transfer path is opened for the electrons to be transferred to cyt a_3--Cu_B site
4. The structural change also helps the cyt a_3--Cu_B site to bind O_2 and transfer electrons to it. Thus cyt a_3–Cu_B site can lose electron more easily as compared to cyt a--Cu_A site.
5. Fe(II)a_3 and Cu(I)$_B$ remain close to each other in a geometry, suitable for O_2 binding. Two electrons are released from Fe(II)a_3--Cu(I)$_B$ to bound O_2 forming μ-peroxo complex

$Fe(III)$--O^---O^---$Cu(II)_B$

6. The Fe(III) of the peroxo complex receives one electron from cyt a--Cu_A to form $Fe(III)_{a3}$--$Cu(II)_B$ and resulting in the cleavage of O^---O^- Bond into O and O^{2-}. The oxygen [O] takes two electrons from Fe(II) forming Fe(IV) O^{2-} ion and the other O^{2-} gets bound to two protons to form water, which binds to $Cu(II)_B$
7. Transfer of one more electron from cyt a--Cu_A to $Fe(IV)O^{2-}$ results in the formation of

$$\overset{O}{\underset{\|}{}}Fe(III)a_3\text{-}Cu_B\text{-}OH_2 \text{ complex}$$

8. Transfer of one proton from H_2O of Cu_B to O^{2-} of $Fe(III)a_3$ results in the formation of

$$\overset{OH}{\underset{\|}{}}Fe(III)a_3 - Cu_B\text{-}OH.$$

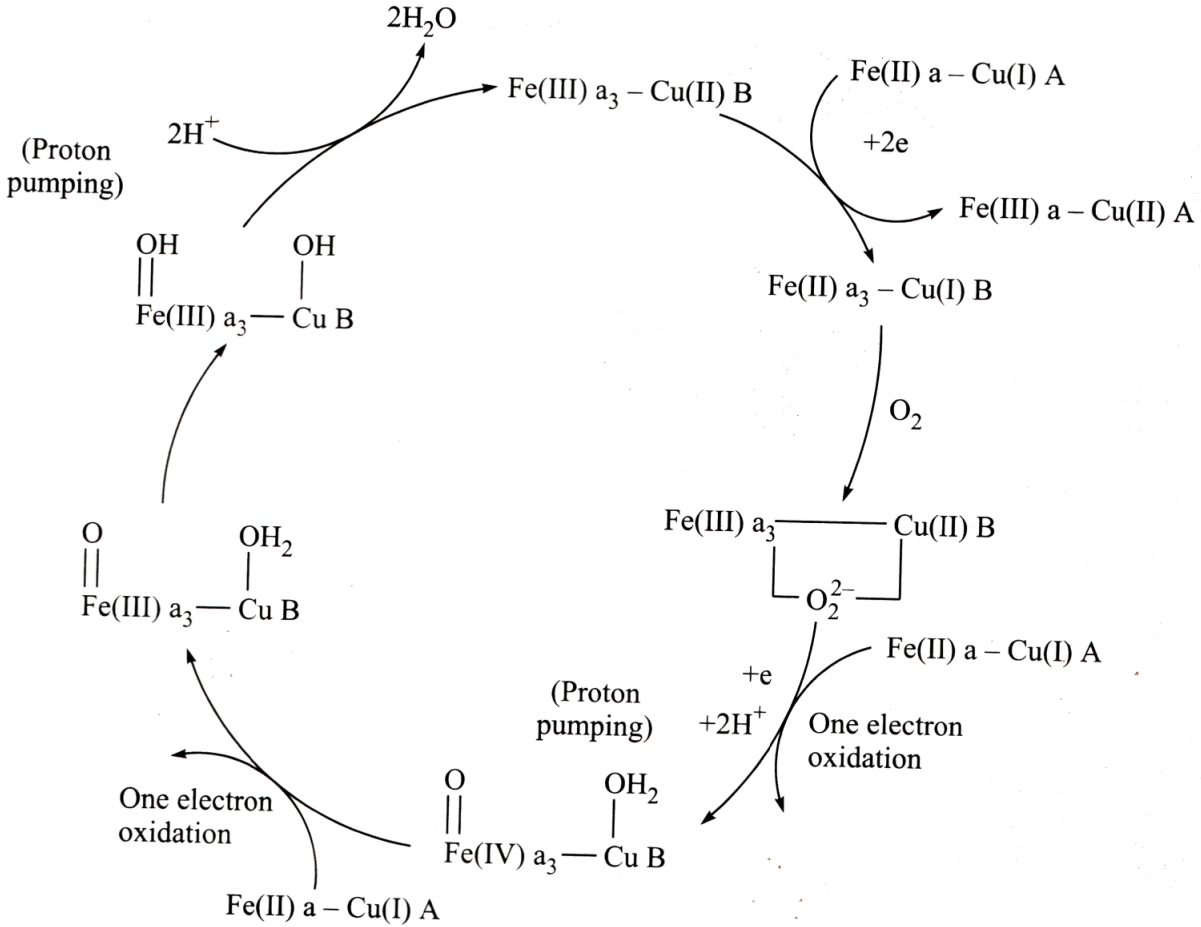
9. Further protonation of the two -OH on the Fe(III) and Cu_B leads to the liberation of two water molecule and regeneration of the cyt a_3--Cu_B

The function of cytochrome c oxidase is not only to reduce O2--->$2O^{2-}$, but also to pump protons across the membrane. The energy released by the reduction of O_2 assists the formation of ATP from ADP.

out of two components of cytochrome c oxidase, only cyta_3-Cu_B part combined with the ligands like CO or CN^- . This is because Fe(III) in cyt a is hexa coordinated, Fe(II) in cyt a_3 is a penta coordinated site.

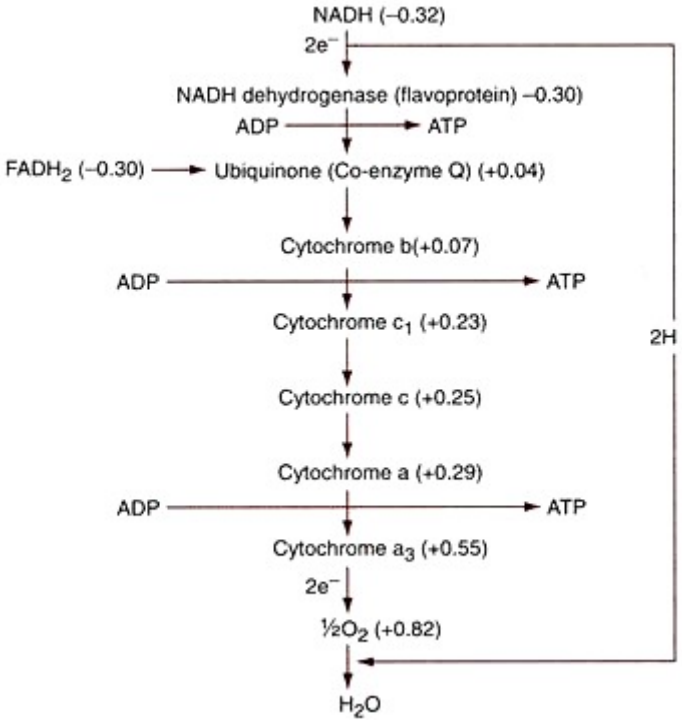
CN^- binds with the reduced Fe(II)a_3 and thus blocks the site from binding with molecular oxygen. Further cyanide stabilizes Cu(I) oxidation state of Cu_B . Thus transfer of electron from reduced cyt a_3-Cu_B to O_2 is blocked.

Thus the terminal oxidation process is stopped and thus cyanide acts as a poison. The fatal effect of cyanide is not due to the blocking of the sixth coordination site in hemoglobin or myoglobin, as these sites are hydrophobic and have least affinity for binding with charged cyanide ion.



Catalytic cycle of cytochrome c oxidase

Path of electron transfer in cytochromes



Thank you

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Nitrogenase

Introduction :- Gaseous form of nitrogen cannot be absorbed by plants. Nitrogen fixation is the process of conversion of Nitrogen to ammonia and subsequently to soluble nitrogen compounds. The enzyme nitrogenase, in plants, plays the vital role of assisting fixation of nitrogen.

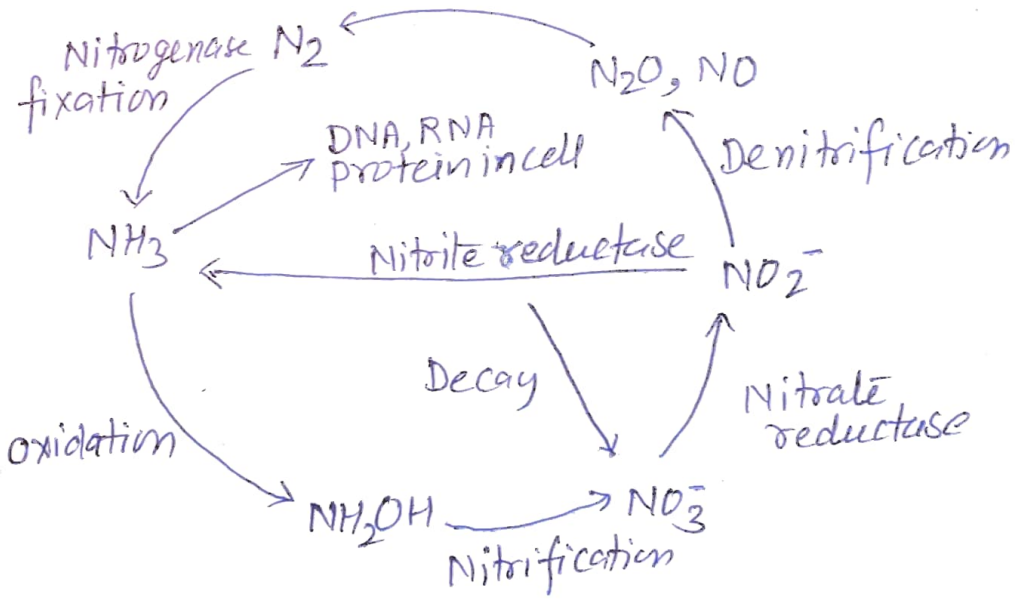
Nitrogenase is obtained in the symbiotic bacteria, living in the root of leguminous plants, like pea and bean. This group of bacteria is called Rizobium. The enzyme is also found in the non-symbiotic bacteria, azotobactor (aerobic) and clostridium pasteurianum (anaerobic), photasynthetic bacteria and some blue green algae and fungi.

Ammonia formed due to Nitrogen fixation is converted to soluble Nitrogen compounds, which can be taken up by the plants for the synthesis of DNA, RNA and proteins. These nitrogenous compound are reconverted to ammonia in due course.

The excess ammonia, not used for the synthesis of biomoleeules is oxidized to hydroxyl amine and further to nitrate by the nitrification process. The nitrate goes to the soil. Soil nitrate is also formed by the decay of nitrogenous organic compounds. A variety of micro organisms and higher plants convert the soil nitrate into ammonia. The soil

nitrate is first reduced to nitrite, using the enzyme nitrate reductase, and nitrite is reduced to ammonia, assisted by the enzyme nitrite reductase. In micro organisms, nitrite may alternatively be reduced to N_2O and to N_2 in the denitrification process. The nitrogen, liberated, goes back to the atmosphere and is reconverted to ammonia by the enzyme nitrogenase.

The cycle of fixation of atmospheric nitrogen into ammonia, its incorporation into biological system due to the formation of nitrogenous biomolecules, their decay into nitrate and the return of N_2 to the atmosphere, due to denitrification of nitrate is called the "Nitrogen Cycle".



Nitrogen Cycle

Chemistry of nitrogen fixation

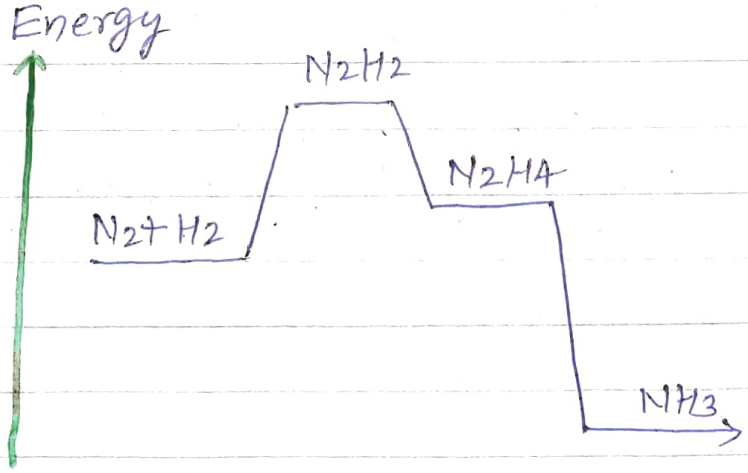
Dinitrogen molecule (N_2) is very stable compound, its bond energy ($N \equiv N$) is high 945 KJ/mol. Though nitrogen molecule is kinetically inert, the reduction of N_2 by H_2 to NH_3 is thermodynamically favourable :-

$$N_2 + 3H_2 \longrightarrow 2NH_3 \;,\; \Delta G = -3.97 \text{ K cal/mole}$$

However, there has to be concerted reaction of 6 electrons and $6H^+$ with N_2, and hence formation of NH_3 is difficult. Hence, the reaction may proceed through the formation of the intermediates N_2H_2 and N_2H_4

$$N_2 + 2H^+ + 2e^- \longrightarrow N_2H_2$$
$$N_2 + 4H^+ + 4e^- \longrightarrow N_2H_4$$
$$N_2 + 6H^+ + 6e^- \longrightarrow 2NH_3$$

However, the formation of intermediates is less probable, because they are thermodynamically less stable. The intemediates are higher in energy, than the reactants ($N_2 + H_2$) and also the product NH_3.



In the nitrogenase assisted nitrogen fixation, the formation of the intermediates may be facilitated, as they are stabilized due to coordination with the metal centers. The formation of the intermediates in the nitrogenase activity may also be assisted by the liberation of energy, due to the hydrolysis of ATP.

In biological systems, the formation of ammonia is always associated with the production of H_2 gas.

$$N_2 + 8H^+ + 8e^- \longrightarrow 2NH_3 + H_2$$

In the absence of N_2, the active nitrogenase reduces H_3O^+ ion into H_2 gas. This is suggested to be due to the presence of metal hydride in the systems, which reacts with H_3O^+ to form H_2.

Nitrogen fixing process requires a source of electrons and a source of energy for the activation of electrons and N_2. Nitrogenase receives the electrons formed by the oxidation of pyruvates (generated from carbohydrates in the respiration process), or other sources. These electrons are carried to the electron receiving site of nitrogenase by the Fe-S protein, ferridoxin. The energy required for the activation of the electrons is provided by the hydrolysis of ATP to ADP.

$$ATP + H_2O \longrightarrow ADP + P_i + \text{energy}$$

This reaction uses up water and hence maintains anhydrous condition, required for nitrogen fixation. 12 to 14 molecules of ATP required to reduce

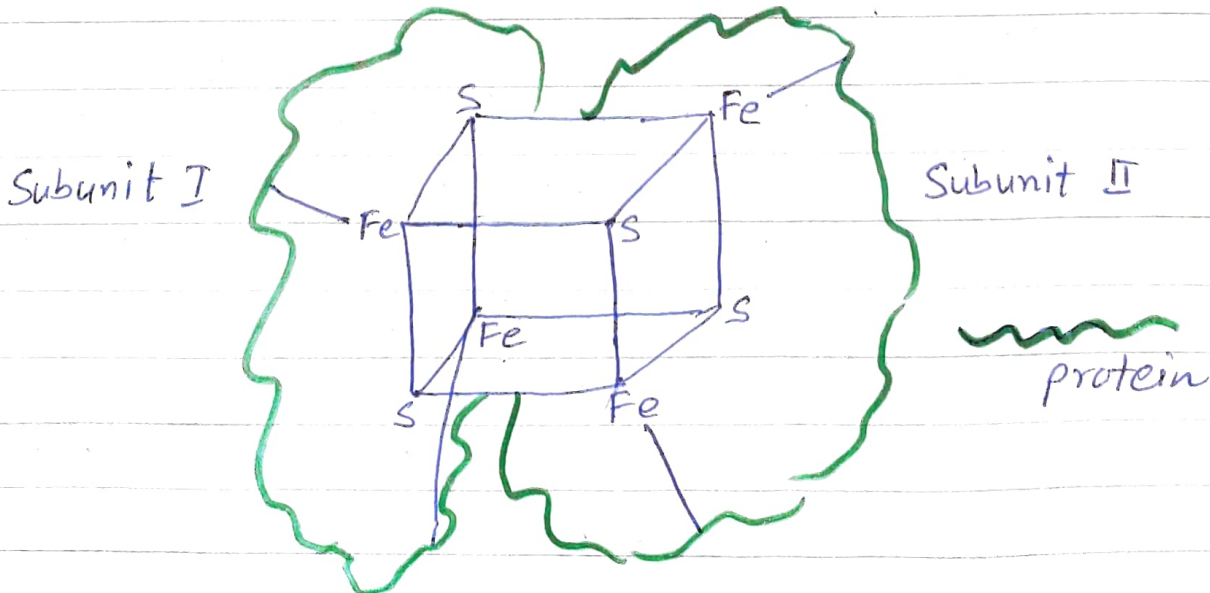
one molecule of N_2.

It has been observed that in the red pods of the leguminous plants, there is a Fe(II) heme protein called leghemoglobin. This binds with O_2 and thus provides anaerobic environment required for the catalytic activity of nitrogenase. The oxygen in oxyleghemoglobin also assists the respiration process of the microorganisms and liberates additional energy for the excitation of electrons.

Structure of nitrogenase

Nitrogenase enzyme consists of two proteins. Both proteins are catalytically inactive, but when present together, they can assist nitrogen fixation.

(1) Iron Protein :- It is made up of two identical subunits of mol. wt. 30,000 daltons. The protein contains four iron and four sulphide ions, which can be extruded as one $[Fe_4S_4]^{2+}$ cluster. This shows that there is one $[Fe_4S_4]^{2+}$ centre, bound, between the two subunits of protein. This has been confirmed by X-ray studies.



Fe_4S_4 is diamagnetic, due to antiferromagnetic interaction between the pairs of Fe(II) and Fe(III) centers through sulphide bridges. It is thus similar to $[Fe_4S_4]^{2+}$ in Ferridoxin with two Fe(III) and two Fe(II).

The Fe_4S_4 centers of iron protein receive electron through Ferridoxin chain and undergo one electron reduction. The reduced form shows epr activity. However, the EPR spectrum of the reduced iron protein shows two spin states $s = 1/2$ and $s = 3/2$, raising the controversy earlier, that there are more than one type of Fe_4S_4 sites. However, it has now been established that the reduced state of same types of Fe_4S_4 site may exist in different spin state. It has been suggested that one of the coupled Fe_2S_2 site in the reduced Fe_4S_4 [1 Fe (III), 3 Fe(II)] is paramagnetic. The spin coupling due to anti ferromagnetic interaction may lead to $s = 1/2$ or $s = 3/2$. However, there is no difference in the redox behaviours of the Fe_4S_4 with different spin states.

During the enzyme turnover, reduced Fe_4S_4 centers of the iron protein transfer electrons to Fe-Mo-protein in one step.

The Fe protein is bound to two molecules of Mg-ATP, at the cleft between the two subunits of the protein. for the transfer of each electron to the Fe-Mo-protein, two Mg-ATP molecules must undergo hydrolysis. Thus hydrolysis of 12 molecules of Mg-ATP is required for the reduction of one molecule of N_2, which requires transfer of six electrons.

Fe protein receives activated electrons and transfer to Fe-Mo-protein. where N_2 gets reduced. Thus the iron protein reduces Fe-Mo-protein to its catalytically active form.

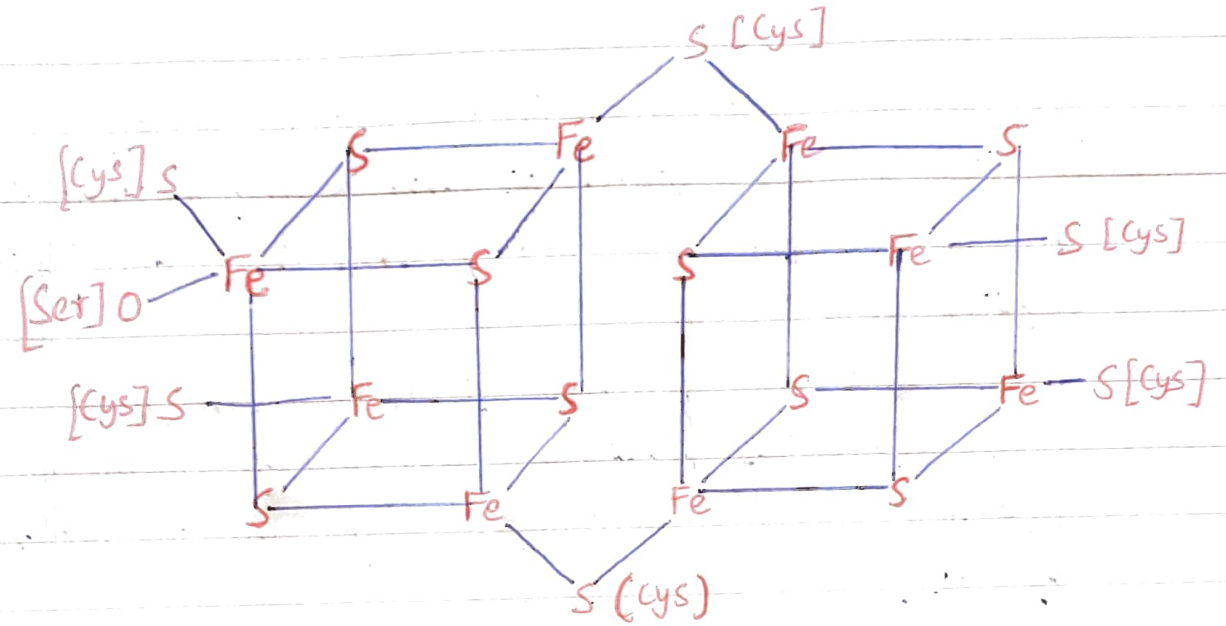
Though the presence of Fe protein is essential for the transfer of electrons, and thus for nitrogenase activity, but only Fe-Mo-protein is responsible for the reduction of N_2.

(2) Fe-Mo-Protein

This protein receives the electron from the iron protein, and its reduced form acts as catalyst for reduction of nitrogen. Fe-Mo-protein contains two types of subunits and has a molecular weight in the range 220,000 to 245,000 daltons. The two types of sub units are called 'P' cluster and 'M' cluster. Both types of centers have specific properties, even after being extracted out of the protein. Their structures and roles are as follows :-

(i) 'P' cluster :- The 'P' cluster consists of four Fe_8S_8 units as pairs of Fe_4S_4. These Fe_4S_4 differ from Fe_4S_4 found in Ferredoxin, as revealed by their electronic spectra and Mössbauer spectra. EPR shows that the P clusters are paramagnetic with $S = 7/2$. This indicates that there is incomplete antiferromagnetic coupling between pairs of Fe(II). M.B. spectra shows that all four irons in Fe_4S_4 are not equivalent. This indicates that the Fe_4S_4 units are highly distorted, unlike the cubane structure in ferredoxin.

The spectroscopic studies of 'P' cluster after extrusion shows that the four clusters are not equivalent.



Structure of one subset of 'P' cluster

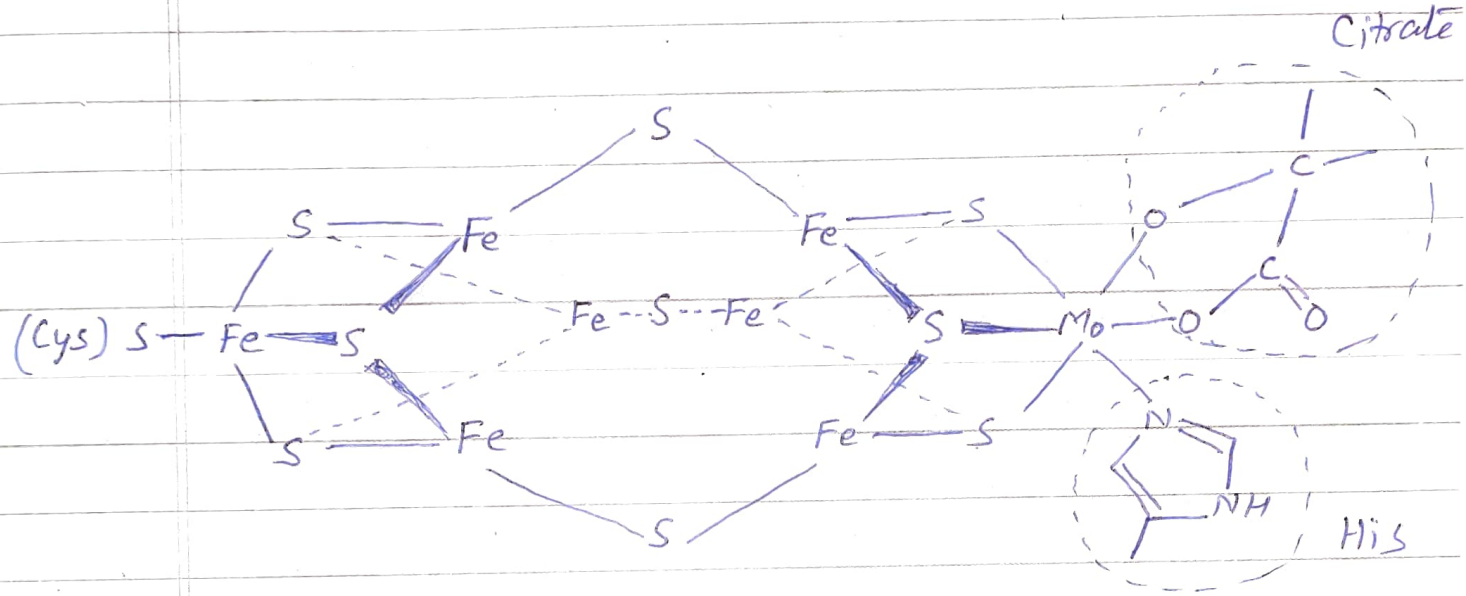
The X-ray crystallographic studies shows that there are four Fe_8S_8 clusters, very close together, each in the form of a pair of Fe_4S_4. Each pair has doubly bridged (through cysteine 'S') double cubane structure. Each cubane has intracubane bridged Fe(II). The third and fourth Fe(II) of one Fe_4S_4 are bound to cysteine 'S' at the fourth coordination site. In the other Fe_4S_4 third iron is bound to 'S' cysteine and the fourth iron is bound to one cysteine sulphur and one serine oxygen. Thus iron is pentacoordinated. The intercubane bridging may be responsible for the unusual properties of the 'P' cluster.

The 'P' clusters are considered to be reservoirs for accepting the high energy (low potential) electrons from Fe-protein, to be passed on to the M cluster, where reduction of nitrogen takes place.

(ii) **'M' cluster :-** The spectroscopic and redox studies show that the presence of Iron and molybdenum in the 'M' cluster and hence it is also known as Fe Mo co factor [Fe Mo co]. The detailed characterisation

of Fe-Mo-co has been carried out by the studies of the unit in vivo in the protein and also in the extracted form, in various organic solvents.

The structure of Fe-Mo-co factor is :-



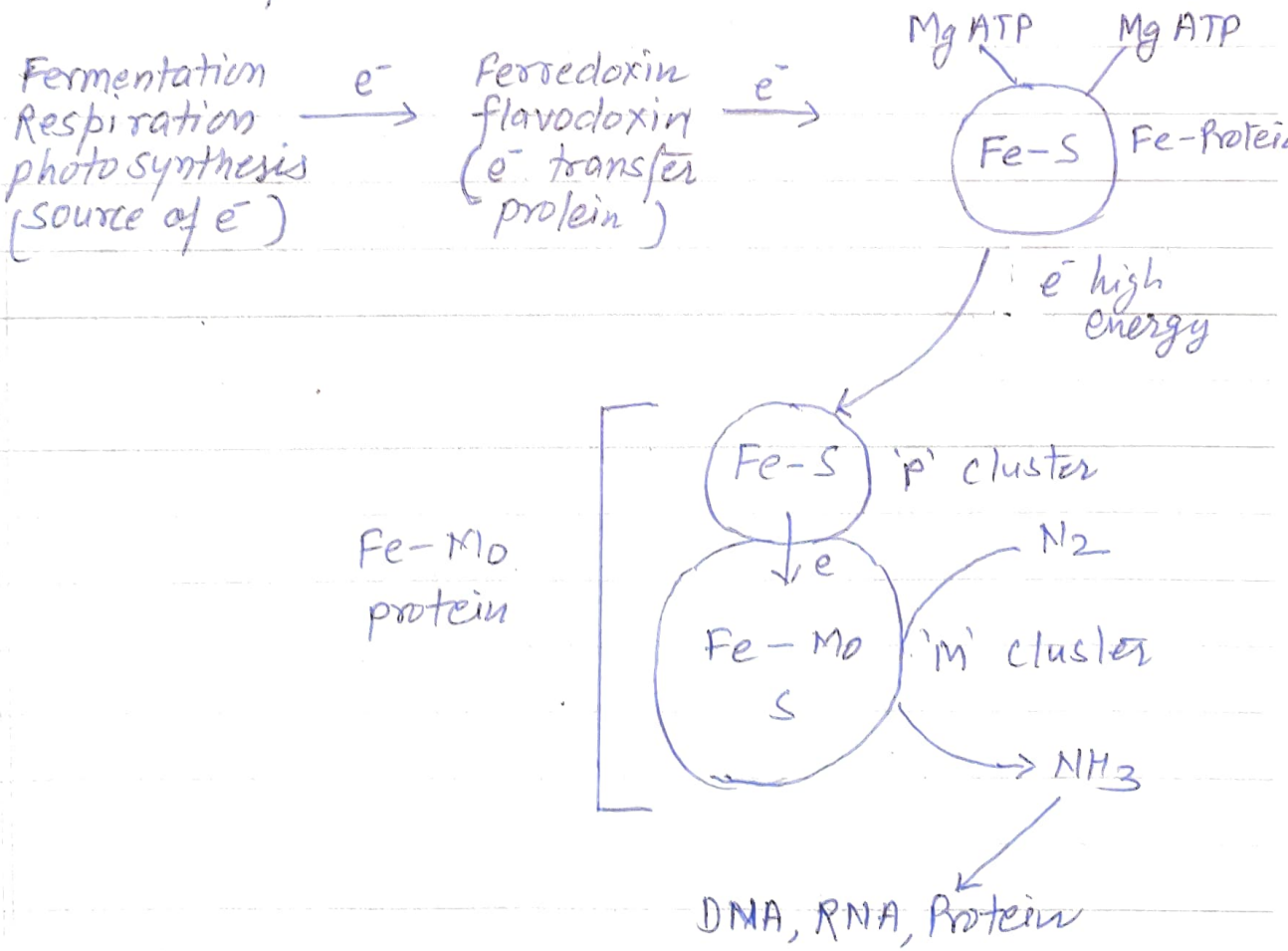
The composition of the M cluster is $Fe_{6-8}S_{7-10}$. The structure of the cluster is not definitely known. Each multiple iron sulphur cluster, contains one molybdenum.

Each Fe Mo cofactor consists of two non-identical clusters (Fe_4S_3) and ($MoFe_3S_3$), which are linked by three sulphide ions. Each Fe Mo cofactor is covalently linked to the protein by one cysteine residue and one histidine residue. Mo is six coordinated, bound to two oxygens of bidentate citrate and N of Histidine.

EXAFS (extended X-ray absorption fine structure) studies show that iron is coordinated to sulphur at a distance of about 2.2 A°, and distant Fe-Fe interactions at about 2.6 A°, Mo—S distance is 2.4 A°, Mo—N or Mo—O distance is 2.2 A° and Mo, Fe distance is about 2.7 A°.

Mechanism of Nitrogen Reduction and ammonia formation

As discussed earlier, iron protein receives the electron generated from the oxidation of pyruvates, through electron transfer protein ferredoxin. The reduced iron protein gets bound to the two molecules of the Mg-ATP. The resulting $(Mg\text{-}ATP)_2$ Fe-protein gets bound with Fe-Mo-protein. There is hydrolysis of two molecules of ATP, providing energy for the excitation of electrons of Fe protein, to be transferred to the 'P' cluster of Fe-Mo protein and subsequently Fe-Mo-cofactor, to which is bound the substrate N_2.



Electrons are successively transferred to the N_2, resulting in steps, in the formation of $[N_2]^{6-}$ ion. These negatively charged nitrogen species combine with H^+, giving a sequence of intermediates

leading to the formation of ammonia.

$$Mo-N\equiv N \xrightarrow[2H^+]{2e^-} Mo-NH=NH \xrightarrow[2H^+]{2e^-} Mo-NH_2-NH_2$$

$$Mo-NH_2-NH_2 \xrightarrow{2H^+ \mid 2e^-} Mo + NH_3$$

$$2NH_3 + 2H^+ \longrightarrow 2NH_4^+$$

Reduction of N_2 to ammonia is thermodynamically favourable. However, hydrolysis of ATP, to provide energy for the excitation of electrons is a kinetic requirement. The two component of nitrogenase, the iron protein and iron molybdenum protein, catalyse the reduction of one molecule of N_2 to $2NH_4^+$, along with the formation of NH_3 and evolution of H_2. Hence the limiting stoichiometry is :-

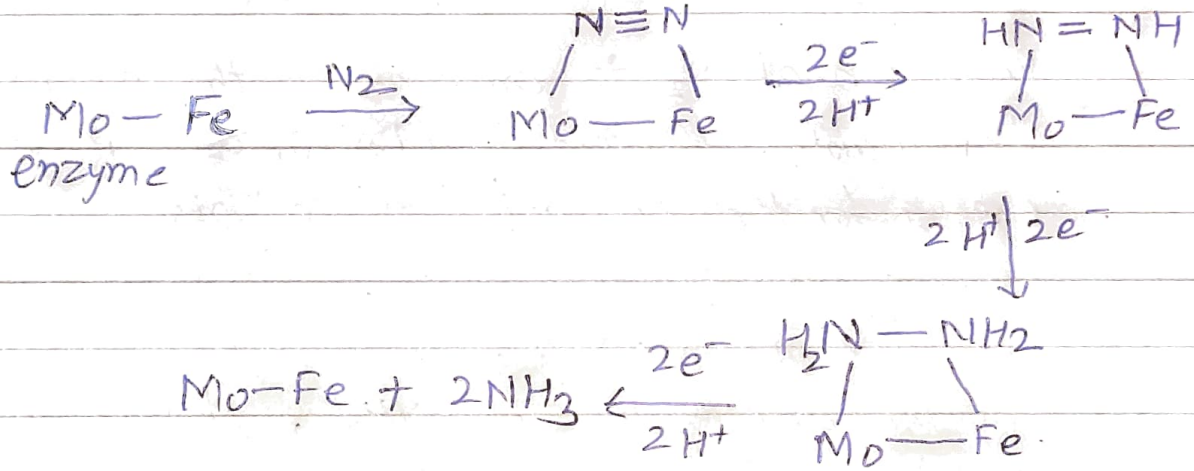
$$N_2 + 10H^+ + 8e^- \longrightarrow 2NH_4^+ + H_2$$

The electrons of the nitrogenase reduce H^+ also, resulting in the formation of molybdenum hydride sites on the enzyme. The hydride ion combines with H^+ of water to form H_2. If N_2 is not present, all the electrons of the enzyme are used for hydrogen evolution.

If carbon monooxide is present, it inhibits reduction of nitrogen and hence, NH_3 formation. But it does not affect H_2 formation. This shows that there are different sites present in the enzyme for N_2 and H^+ reduction.

It is observed, that there is formation of symmetrical intermediate products during the reduction of nitrogen. The formation of di imide $NH=NH$, hydrazine H_2N-NH_2, shows that two nitrogen

atoms are reduced simultaneously. This indicates that N_2 is bound to the two metal centers, through two nitrogen atoms. Thus a binuclear Fe-Mo protein is suitable for N_2 binding. On this basis it was suggested that the reduction may be in steps as shown in equation -



However, more recent X-ray crystallographic studies suggest, that the Mo is coordinatevely saturated and hence may not be the site of nitrogen binding. N_2 molecule may be bound inside the cluster. Thus the mode of binding of N_2 is not finally known.

Since, the iron protein and Fe-Mo protein sites are not solvent exposed, electron transfer, substrate binding and product release should involve structural change in the enzyme, exposing the active sites during the reduction process, similar to the "Gating process."

Nitrogenase also reduces other substrates with triple bond, like acetylene, cyanides and isocyanides.

$$C_2H_2 + 2e^- + 2H^+ \longrightarrow C_2H_4$$

$$HCN + 6e^- + 6H^+ \longrightarrow CH_4 + NH_3$$

$$RNC + 6e^- + 6H^+ \longrightarrow RCH_3 + NH_3$$

$$N_3H + 6e^- + 6H^+ \longrightarrow NH_3 + N_2H_4$$

$$RNC + 6e^- + 6H^+ \longrightarrow RNH_2 + CH_4$$

It has been shown recently, that the Fe-Mo protein part of the nitrogenase can also cause hydrogenation of the dyes, in the presence of molecular hydrogen and thus can act as a hydrogenase. This is the only example, where only one component of nitrogenase shows catalytic activity independently.

Model Systems of nitrogenase

There are no satisfactory Fe-S cluster model for the Fe-Mo protein. However many FeMoS clusters have been synthesized, mimcing FeMoco site (M centre) However, reduction of nitrogen using FeMoS clusters has not been possible, because of the non availability of suitable reductant. It has been reported that certain phosphine complexes of molybdenum containing dinitrogen easily give NH_3 in acidic medium, with grignard reagent as the reducing system.

$$[MoCl_3(thf)_3] + 3e^- + 2N_2 + \text{excess dppe} \longrightarrow [Mo(N_2)_2(dppe)_2] + 3Cl^-$$

$$[Mo(N_2)_2(dppe)_2] + 6H^+ \longrightarrow 2NH_3 + N_2 + Mo^{VI}\text{products}$$

thf = tetrahydrofuran

dppe = 1,2 - bis (diphenyl p phino) ethane

$Ph_2PCH_2 - CH_2PPh_2$

One of the most exciting example of In vitro nitrogen fixation is that of titanium (II) alkoxide. Titanium alkoxide form dinitrogen complex which may then be reduced either to ammonia or hydrazine.

Titanium (II) alkoxide can be obtained from reducing well characterised titanium (IV) alkoxide.

$$Ti(OR)_4 + 2e^- \longrightarrow Ti(OR)_2 + 2RO^- \quad (i)$$

$$Ti(OR)_2 + N_2 \longrightarrow [Ti(OR)_2N_2] \quad (ii)$$

$$[Ti(OR)_2N_2] + 4e^- \longrightarrow [Ti(OR)_2N_2]^{4-} \quad (iii)$$

$$[Ti(OR)_2N_2]^{4-} + 4H^+ \longrightarrow N_2H_4 + Ti(OR)_2 \quad (iv)$$

$$[Ti(OR)_2N_2]^{4-} + 2e^- \longrightarrow [Ti(OR)_2N_2]^{6-} \quad (v)$$

$$[Ti(OR)_2N_2]^{6-} + 6H^+ \longrightarrow 2NH_3 + Ti(OR)_2 \quad (vi)$$

The $Ti(OR)_2$ formed in reaction (iv) and (vi) may be recycled to form dinitrogen complex in reaction (ii). At commercial scale till now Haber process is used for the nitrogen fixation in which yield is very poor as well as we need high temperature and pressure.