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# Biophysical Properties and Spin Transport in Hemoglobin, Heme Along the Easy Magnetic Fe-N Symmetric Axis

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***Abstract***

*Many physical processes that take place in human and animal hemoglobin are associated with a transport of minerals, air, charge carriers, ions, and spin. They are greatly influenced by external electric and magnetic fields, the concentration of mineral intake, pH value, thermal conditions, and the structure of hemoglobin. In this research, emphasis is given to spin transport in hemoglobin, where a weak spin transport is noticed. In order to clarify the nature of spin transport, the magnetic states are first identified. Then, by developing spin diffusion equations, we investigate the spin diffusion transport in the hemoglobin. This transport is associated with the transition of spin from the high-spin state (deoxyhemoglobin) to the low-spin state (oxygenated hemoglobin). The spin transition is caused by oxygen binding to the heme, resulting in heme–heme interaction of cooperative binding. Hence, the effect of magnetic fields, concentrations, and pH on spin transport is visualized. The spin diffusion transport is then compared with the nature of billiards and ballistic transport in hemoglobin. Whence, factors hindering the spin transport along the Fe-N magnetically easy axis are explored. Then the significant roles of myoglobin (Mgb), in carrying oxygen, spin transport, and as a medium spin generator are demystified. Then, the impact of Fe concentrations and Fe-N magnetic easy axis on the transport process is visualized. Finally, the biophysical properties of hemoglobin and the potential role of spin transport in maintaining metabolic processes and biomedical engineering are envisioned.*

**Keywords:** Ballistic transports, billiard transport, charge carriers, hemoglobin, spin

## INTRODUCTION

In the science of hematology, the hemoglobin molecule is one of the major focus areas of study and research. Hemoglobin is an allosteric protein in the red blood cell which consists of four protein (globin) chains, to each of which is attached a heme moiety, and an iron-porphyrin compound. As discussed by Toddle *et al*. [1] and Ahme *et al.* [2], hemoglobin is a tetrameric protein, where the four long polypeptide chains are equal in pairs. This tetramer consists of four peptide chains with two alpha (α) and two beta (β) subunits, which form a complete hemoglobin molecule. Both α-chains are formed by 141 amino acids, while β-chains are hemoglobin dimers formed from 146 amino acids. Hemoglobin is spherical in shape and 5.5 nm in size. However, as Erickson revealed, the size of a single hemoglobin molecule is 5 nm [3]. The iron is kept at the center of the cube, forming Heme.

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Hemoglobin is developed in the bone marrows that become red blood cells. Fatal Hemoglobin (HbF) transports oxygen from the mother's bloodstream to organs and tissues in the fetus. The human hemoglobin molecules are a set of very closely related proteins formed by the symmetric pairing of a dimmer polypeptide chain and the globins. Despite their similarity in tertiary level,

 

these proteins crystallize in different space groups.

Hemoglobin and myoglobin form a homogenous series of chromotrypsin and trypsin. Hemoglobin transports oxygen, while myoglobin stores and releases oxygen. Hemoglobin (Hb) is also responsible for the delivery of oxygen to the tissues. As Henny illustrated, the normal Hb level for males is 14 to 18 g/dl and for females is 12 to 16 g/dl [4].

When red cells die, hemoglobin is broken up: iron is salvaged and transported to the bone marrow by transferrin proteins. Many blood-related diseases, such as sickle-cell anemia, leukemia, and blood disorders, and blood disorders are caused by alterations or mutations of hemoglobin. When the cell structure is distorted, it no longer carries as much oxygen in the correct way as a normal blood cell. These problems are greatly related to the spin transport, spin drag, and transport of some molecules such as $O_2$, $CO_2$, and $N_2$ in the hemoglobin.

The oxygen-combining property of hemoglobin depends on a single atom of iron present at the center of four heme groups within the hemoglobin molecule. The iron in the heme binds reversibly to oxygen. This mechanism allows efficient iron delivery to tissues that need it for energy production. It also facilitates oxygen transport.

Paoli *et al.* described that Hemoglobin determines the roles of heme signaling to the surrounding protein environment [5, 6]. As discussed by Schechter, research has shown paradigms shift in transport, laboratory, and clinical studies of disease related to hemoglobin [7]. To this end, researches are anticipated in the growth, development, and improvements in molecular medicine. This research delves into the nature of spin transport in the hemoglobin molecule and factors impacting such mechanism of transport. Moreover, it presents potential roles of demystifying spin transport in preventing hematopathologic disease (Figure 1).

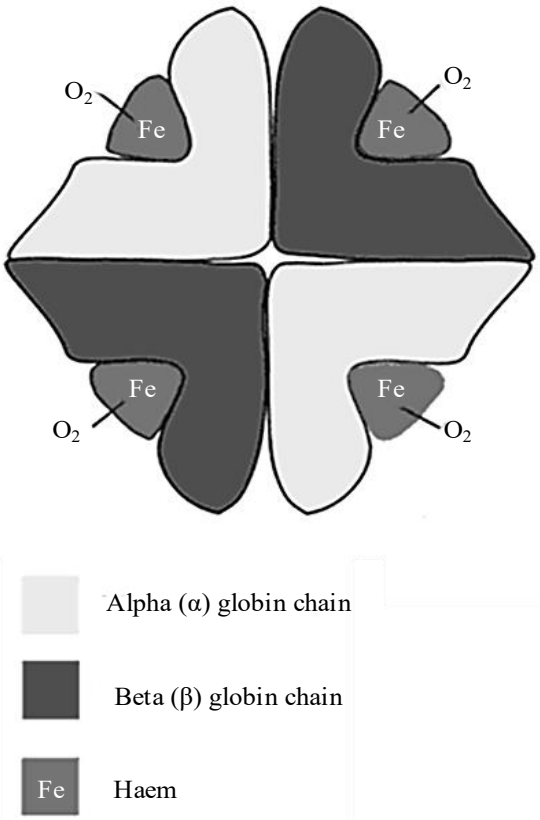


**Figure 1.** Heme in 3D systems [5].

 

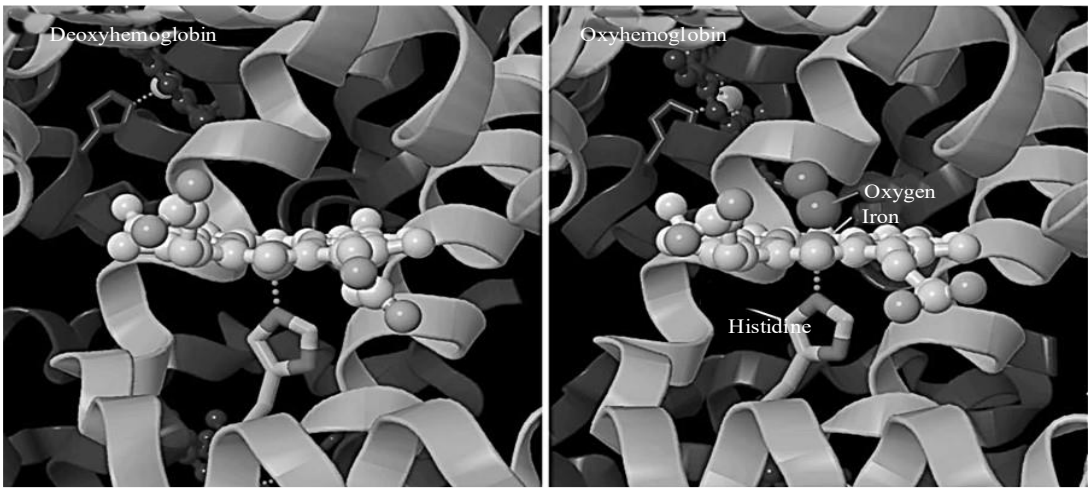


**Figure 2.** Side-by-side comparison of two protein–ligand conformations showing subtle shifts in the bound molecule and surrounding residues.

Heme is a cofactor for molecular oxygen transport. The oxidation of Fe from the ferrous ($Fe^{2+}$) state to the ferric ($Fe^{3+}$) state in the heme releases mobile electrons. This oxidation forms methemoglobin. However, this process does not carry oxygen. Brena *et al*. revealed that the spin density of Fe in deoxygenated hemoglobin is higher than in oxyhemoglobin [8]. This difference in spin density causes a spin transition. This spin transition is crucial for the cooperative binding of oxygen to hemoglobin, which increases the oxygen affinity to bind other subunits of protein molecules.

**Energy Landscape in HB**

The energy landscapes enable spin transport by dictating the path of spin, the rate of electron transitions, and 3D conformations of ligand binding. In Hemoglobin, the energy landscape can also determine the stability of different spin states. The energy landscape makes one spin state more favorable than the other. When oxygen binds to hemoglobin, it shifts the energy landscape, favoring the low-spin (diamagnetic) state of iron. When oxygen is released, the energy landscape shifts toward the high-spin or paramagnetic state. An energy landscape enables visualizing how allosteric effects are transmitted through Hemoglobin. Allosteric effects here describe how binding at one site affects binding at another site, analogous to mutual inductance. It can also be influenced by oxygen binding, temperature, and pH. Different experimenters had determined the pH of hemoglobin at different times. For instance, as Huang *et al*. verified, the pH value of Hb can vary depending on the surroundings; it can be acidic, i.e., pH<6.5, or alkaline, i.e., pH>8.0 [10]. Besides, Hb can further dissociate from dimer to monomer (Figure 2).

Nelson and Cox realized that Myoglobin (Mgb) stores oxygen in the red muscle, while hemoglobin transports oxygen [11]. As Alayash revealed, the oxidation reaction of acellular Hemoglobin is the case of a hemoglobin-based oxygen carrier [12]. Electronically controlled reactions of atom-by-atom occur when carbon monoxide binds to the iron atom at the heme, making an interplay between theory and experiment. As Bowman and Bren investigated, reduction potential can be affected by iron spin states [13]. However, the reaction is influenced by the ligand field strength of the (histidine–iron interaction) interaction in the oxidized state and heme-reduced states.

In multimeric proteins, including hemoglobin, the interface between the subunits is not frustrated in either form. However, in the region of high frustration, interaction occurs internally in each subunit around heme binding. Hemoglobin is frustrated at the heme binding site where weak spin transport takes place. Frustration in protein-DNA linkages may create an energy landscape and an alternate energy state, which have lower values. As Ferreiro *et al*. explained, frustration enters into protein biochemistry like in magnets, hetero polymers, and in neural network models [14]. It is also applicable in areas from spintronics and microelectronics to drug delivery.

 

**Existence of Magnetism**

The magnetic property of hemoglobin is closely associated with unpaired electron states. It is verified that ox-hemoglobin and carbon monoxide-hemoglobin have no unpaired electrons. However, ferrohemoglobin has four unpaired electrons per heme. Oxy-hemoglobin exhibits a magnetic moment corresponding to two parallel electron spins for each $FeO_2$ group. The existence of an unpaired electron corresponds to O-O bond and the other to the Fe-O bond. Such unpaired electrons per heme and the heme-heme interaction tend to stabilize the parallel magnetic moment. The oxygenated form has low spin states, so that the magnetic moment of $Fe^{2+}$ and superoxide radicals maintains antiferromagnetic coupling. However, the deoxygenated form has high spin states and maintains paramagnetism.

It is also shown that the spin and the crystal field parameters of the iron ions are described by spin spin-dependent Heisenberg Hamiltonian approach. In a Hemoglobin crystal, the symmetry along the Fe-N axis allows a high ground state degeneracy. As Nagamine *et al*. observed, the Hemoglobin macromolecules contain positive muons, $\mu^+$ in the heme-Fe protein, which helps detect the existence of magnetism [15]. As Fe ions interact with each other and with the surrounding porphyrin ring, their magnetic phases can be expressed by magnetic spin states, which are presented in detail in the succeeding section.

**Magnetic States**

Heme rotation in conjunction with the displacement of the iron atom within the porphyrin ring causes spin transitions in hemoglobin. As Jensen illustrated, this transition is operated via steric interactions and changes in the ligand field [16]. This spin transition is accompanied by a shift of the iron atom from out-of-plane to in-plane with respect to the porphyrin ring.

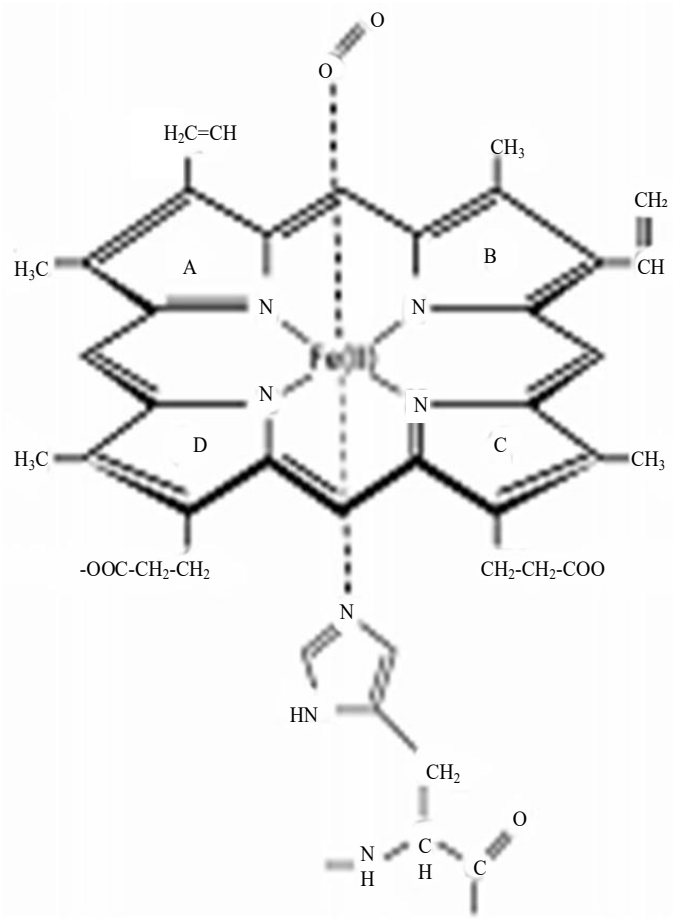


**Figure 3.** Heme about the Fe-N easy symmetric axis.

 

As Mayda *et al*. analyzed experimentally, both oxygenated and deoxygenated hemoglobin exhibit local magnetic moments [17]. The existence of such moments can be confirmed from magnetic susceptibility measurement, Mossbauer effects, and magnetic circular Dichroism (MCD). The magnetic susceptibility of Heme can be measured using magnetic static techniques (Gouy-balance) in terms of the change in weight of the sample with applied magnetic field. It can also be measured by electron paramagnetic resonance (EPR). The energy required for recoiling particles ($E_R$) is expressed in terms energy of gamma ($\gamma$).

$$E_R = \frac{{E_\gamma}^2}{2m_e c^2} \quad (1)$$

With energy of the gamma ray $E_\gamma$=14.4 keV for $^{57}$Fe, the mass of the emitting or absorbing body, M=57 Da, for $^{57}$Fe, and the square of the speed of light, $c^2 = 931.5eV$, the energy lost as recoil particle, $E_{R,}$ is 0.002 eV for $^{57}$Fe, Nave, C.R. 2005 [18].

Moreover, MCD can measure the magnetic moment by measuring the change in circularly polarized light absorption between left and right. The absorption change is caused by an external magnetic field. This action is then done by determining the electronic band structure and magnetic spin states of iron in the heme (Figure 3). The local crystal field of the hemoglobin arises from the iron site, producing quantization of iron spin. An external magnetic field affects the spin state of each iron, changing the alignment of heme. It then changes the size of the spin-orbit interactions, their conformations, and the spin-tunneling rate.

A spin transport has a significant impact on oxygen transport. Bren noted that the spin state of iron is directly involved in the transport of oxygen by hemoglobin [19]. The effect of oxygen binding is to alter the Fe's spin state from the triplet state to the singlet state. As Kurokawa *et al*. revealed, deoxyhemoglobin and oxyhemoglobin systems have triplet and singlet total magnetizations, respectively [20]. The spin of iron (Fe) dictates interaction with neighboring oxygen. The deoxygenated or higher spin state has a spin, s=2, while the oxygenated state or low spin state has a spin, s=0. A quintet spin state where an energy level or spin state has a total spin quantum number, S=2, and spin multiplicity of 5. This means the state undergoes a splitting of energy level/magnetic moment into five possible spin orientations, corresponding to spin projections (M) of –2, –1, 0, +1, and +2. Essentially, this state has four unpaired electrons with their spins aligned in a parallel configuration.

Ferritin is the principal iron storage molecule. It is a protein shell packed with 100–1000 iron particles. Ferritin is a highly symmetrical, primary intracellular iron storage protein that is formed via self-assembly of 22 subunits. As Lee *et al.* illustrated, Ferritin stores and releases iron while Hemoglobin (myoglobin) stores and releases oxygen [21]. Consequently, Ferritin encapsulates iron, while iron binds oxygen. Ferritin has a high thermal stability up to 80˚C. As Gunhild *et al*. had illustrated, Ferrochelatase catalyzes the terminal step of heme biosynthesis and insertion of ferrous iron into protoporphyrin [22]. Hundreds to thousands of Ferritin particles are combined with amorphous proteins and lipids to form Hemosiderin. Hemosiderin exhibits superparamagnetic properties. It also exhibits magnetic susceptibility much a stronger than the magnetic susceptibility of Ferritin.

In Hemoglobin, the low and high spin states are influenced by the crystal field created by its surrounding ligand (Oxygen). In oxyhemoglobin, at oxygen binding, a strong ligand field produces splitting of the iron's d-orbital, leading to low-spin states. This state exhibits a diamagnetic property and absorbs electromagnetic waves in the blue-green region.

**Carrier Transport: in Hemoglobin**

Simultaneous transport of $O_2$ and $CO_2$ via the hemoglobin molecule can be analyzed and monitored theoretically. This kind of transport is an idealized approach toward a ballistic transport. Ballistic conduction is typically observed in quasi-1D structures, such as carbon nanotubes and silicon nanowires. This is due to the consequence of quantum size effects in these materials. It is a physical phenomenon where charge carriers travel at relatively high speeds within a medium (such as a

 

semiconductor crystal) without scattering from an obstacle. It can encounter scattering from subatomic particles, neutrons, electrons, and protons. Spins can be generated from Heme by attaching a nitroxide radical to the porphyrin ring of heme by a covalent bond. It can produce a spin current in proportion to the electron number density. However, as can be measured in solid state physics, spin current cannot be measured directly in hemoglobin. Rather, it is measured as a spin state of iron and electron number density.

Therefore, the spin transport cannot be directly treated as ballistic transport in hemoglobin since it is a disordered system. However, diffusion current can be detected experimentally by neutron spin echo spectroscopy. This current or spin dynamics is consistent with Brownian motion, a form of diffusion. Therefore, it has the same diffusion coefficient as in the case of red blood cells.

**Spin Transport Mechanism in Hemoglobin**

When the iron atom in the heme group becomes oxidized, i.e., loses an electron, its valence state changes from $Fe^{+2}$ (ferrous) to $Fe^{+3}$ (ferric). This property of hemoglobin makes it useful in describing the spin transport and nanomagnetic characteristics of Hemoglobin. Iron porphyrins are key components of proteins like hemoglobin and myoglobin, where they participate in electron transfer, oxygen binding, and transport. As discussed by Liong *et al.*, reversibility depends critically on retention of the heme prosthetic group [23]. Heme is a polypeptide prosthetic group consisting of protoporphyrin IX and a central iron atom.

Hence, the mechanism of spin transport is studied by enumerating spin states in the hemoglobin molecule. As Kurokawa *et al.* revealed, the spin transition from triplet to quintet singlet states mediates the $O_2$ binding process [20]. Therefore, it is important first to describe the physics of spin transport and technology based on this system. A simple model describing the binding of oxygen to hemoglobin is developed by Lavrinenko *et al*. [24].

In order to make the problem simpler, an easy magnetic axis is preferred for spin transport. Accordingly, the Fe-N bond within the heme group is preferred where iron is situated. This axis is critical for the expected spin transport in the hemoglobin molecule. This direction is also the direction of magnetization.

The mechanism of spin transport and diffusion in hemoglobin is associated with changes in the oxidation state of the iron from ferrous to ferric states within the heme group. The spin state of the iron in one heme group affects heme-heme interaction, leading to cooperative oxygen binding. Consequently, the spin-spin interactions are mediated by the exchange of electrons through J-coupling in the hemoglobin molecules. In hemoglobin, the J-coupling is mediated by chemical bonds. Dixit and Verkhivker suggested that mutation-induced allosteric signaling of hemoglobin may involve a dynamic coupling between minimally frustrated and locally frustrated clusters of residues [25].

Spin-spin interaction also occurs due to photon exchange interactions. Photon interaction is detected during spectroscopic analysis of protein conformation, and photon absorption by heme. Moreover, photons can be absorbed or reemitted during the two-photon quantization of fluorescence in the hemoglobin. Photon interactions can impact the spin transport by changing electronic and spin states as well as inducing allosteric effects.

Research by Freed *et al*. indicates that, in the quantization of solubilized proteins and crude protein crystals spectrum, 8% of spins are mobile in the total population [26]. This shows that spin transport plays a dominant role next to electron and thermal transport. The electron transport in the heme protein in the liquid crystal film is surfactant-enhanced as compared with the protein solution.

Zhendong [27], Sanvito and Rocha [28] had quoted that molecular spintronics can affect the state of the molecule due to its spin-polarized currents. The physics of such a system can best be illustrated in

 

terms of magnetic spins. The iron in deoxygenated hemoglobin is relatively in a high-spin state, while in the oxygenated state is in low low-energy state.

The binding of hemoglobin to $O_2$ has a triplet S=1 ground state, to a final oxygen-bound hemoglobin (Oxy-Hb) state at S=0. As per Kurokawa *et al*., deoxyhemoglobin and oxyhemoglobin systems have triplet and singlet total magnetizations [20]. The spin transition from the triplet state to the singlet state takes place. This process is referred to as phosphorescence and leads to the release of a photon of energy E. The transition process takes place at each of the four-heme sites where 24 electrons undergo pairing upon oxygen binding. The transition spin flip process, which takes place in the hemoglobin, is responsible for oxygen binding. Freisleben *et al*. revealed that any changes in the heme-Iron structural change can be determined by the x-ray absorption fine structure (XAFS) [29].

## EQUATION OF MOTION

### Spin Diffusion Equation

The progress of medical and biophysics has a profound impact on disease modeling and the theory of oxygen binding to hemoglobin. Although this progress is courageous in to investigation of new models and principles to describe spin diffusion, there is no sufficient model to describe some phenomena, such as the spin drag concept. However, current research models have been focused on oxygen binding (e.g., Hill or Adair models). This model is effective at describing hemoglobin cooperatively and allosteric interactions. In this manuscript, the Boltzmann equation is employed to describe the phenomenon of spin transport.

The Boltzmann equation is a theoretical framework used for electron spin transport in bulk materials. Mostly, it is applicable to describe the nature of transport in metals and sophisticated systems like hemoglobin. As Flensberg *et al.* discussed, the Boltzmann equation can be derived for a set of coupled transport equations, including electron-electron coupling, which produces a spin drag effect that enhances the resistivity of the system [30].

In order to explain the spin diffusion, we first calculate the energy difference between triplet states and singlet states. As the canonical ensemble demonstrates, the system's energy can fluctuate, but its temperature must be kept constant. In addition, the spin transition of the iron within hemoglobin due to oxygen binding is subjected to energy exchanges. The energy change corresponds to the spin transition.

$$\Delta E = (E_t - T_s) = K_B T_s \quad (2)$$

$\Delta E$ is the energy difference between the energy of the high-spin state or deoxyhemoglobin ($E_t$) and the energy of the low-spin state or oxyhemoglobin state ($E_s$). $T_s$ is the standard body temperature, and Es and Et are energies of singlet and triplet states, respectively. The rate of spin diffusion and path length of spin transport are determined by the energy barrier in the energy landscape. As Kurokawa *et al*. revealed, the energy activation barrier for $O_2$ binding is 0.38 eV, whereas $O_2$ desorption is 0.92 eV [20].

The partition function is used in order to determine the relative populations of different spin-dependent states of hemoglobin. The partition function describes the thermodynamic and statistical relation between spin states.

$$z = \sum_i e^{(-\beta E_i)} \quad (3)$$

Where, $\beta = \frac{1}{k_B T}$

The ratios of the probability of triplet and singlet states are:

$$\frac{P(E_t)}{P(E_s)} = e^{\left(\frac{E_t - E_s}{k_B T}\right)} = e^{\left(\frac{\Delta E}{k_B T}\right)} \quad (4)$$

The partition function (z) is incorporated in order to determine the probability of a spin occupying different energy states at a given temperature. This is due to the consequence of the randomness of spin

 

diffusion in the hemoglobin. For humans, the body's red cells are 300 K.

The spin diffusion equation is a mathematical model that describes how spin polarization due to the difference in magnetic moment between triplet and singlet states spreads out. In hemoglobin, the spin of the iron atom responsible for oxygen binding is considered. Hence, the Boltzmann equation can be used to model how polarization spreads within the Hemoglobin molecules and other molecules upon interaction. It is often written as:

$$\partial s/\partial t = \xi\nabla^2 s - (s - s_0)/\tau + O(t) \quad (5)$$

Where:

S is the spin polarization vector, representing the direction and magnitude of the spin imbalance. ξ is the spin diffusion constant, indicating how quickly spin diffuses. τ is the spin relaxation time, representing how long it takes for the spin polarization to decay. $s_0$ is the equilibrium spin polarization (usually zero in the absence of external forces). $\nabla^2 s$ is the Laplacian of the spin polarization, representing diffusion. The last term O(t) represents other potential terms like those related to external magnetic fields or spin-orbit coupling.

Systems like hemoglobin are strongly correlated systems. Due to this correlation, the dynamic mean field approximation can be used to describe the mechanism of transport in hemoglobin. This aspect of hemoglobin enables the use of the dynamic mean field approximation theory. As the work of Sikaris demonstrates, hemoglobin $A_1c$ level is strongly correlated with mean blood glucose levels [31]. This shows a strong correlation between Hemoglobin and hematocrit (hemoglobin volume). Hemoglobin's structure also has a strong correlation with the heme group and electronic distributions in the hemoglobin. This correlation results in cooperative binding.

The microstates can be low-spin oxy-form state or singlet state, the high-spin deoxy-form, or triplet state, and quintet states or intermediate states of iron centers. These states are significantly useful in an in-depth understanding of spin transport and dynamics in hemoglobin.

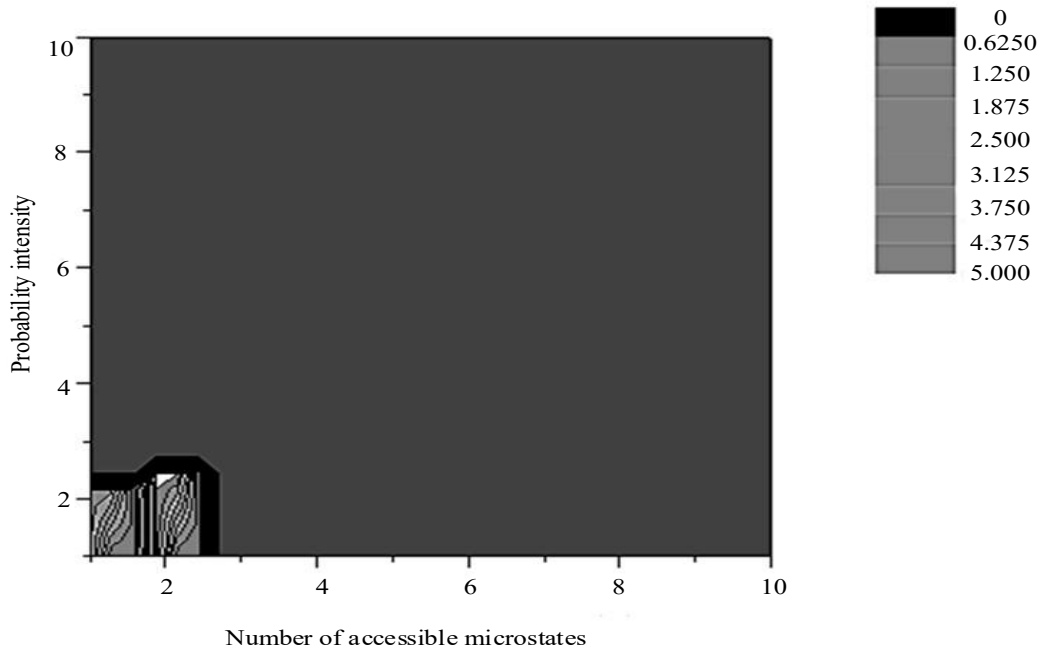


**Figure 4.** The relation between the number of accessible microstates and probability intensity.

In Figure 4, the relation between microstates and probability intensity is illustrated. As the result shows, each number microstate has a probability of a specific energy level. The energy splitting is associated with the central Iron at the Heme. The iron is in the oxidation states $Fe^{+2}$ or $Fe^{+3}$. The figure

 

also demonstrates a measurement of a non-random quantity, probability intensity from a random variable, and microstates. As illustrated in the figure, the hemoglobin microstates emit light intensity through two-photon excited fluorescence. The process allows for label-free imaging of microvasculature, cell imaging and contributes to medical biotechnology.

**Magnetic Field Enhanced Spin Transport Hemoglobin**

The iron is responsible for the characteristic properties of hemoglobin, such as electronic, optical, and magnetic properties. As oxygen approaches the liquid phase, it becomes much closer to paramagnetic phases. Moreover, deoxyhemoglobin exhibits paramagnetic order due to the Fe counterpart. When heme is exposed to a magnetic field, it can exhibit Faraday rotations. While exposed to a magnetic field, the plane of polarization of light rotates in the heme. This magneto-optic effect is the characteristic property of Faraday rotation.

Deoxy-hemoglobin bears iron in its molecular heme, which exhibits magnetic behavior. It can be influenced by an external magnetic field, showing deflection depending on the strength of the magnetic field. Deoxy-hemoglobin has unpaired electrons in the heme iron, which can be attracted by magnetic fields. Magnetic field, therefore, retards the rate of diffusion of molecules in the case of deoxy-hemoglobin. This phenomenon determines how fast an oxygen molecule is delivered to body cells and tissues.

Zablotskii *et al*. revealed that in cells, magnetic force can redistribute paramagnetic free radicals, such as $O_3$, NO, and $NO_2$, and the molecules $FeCl_3$ and $O_2$, thereby altering the cell machinery and cell fate [32]. By using DFT and the Hubbard model, Mohammadi *et al*. were able to determine the energy and revealed the magnetic moments of deoxyhemoglobin and aquomehemoglobin $\mu = 4\mu_B$ and $\mu = 4.72\mu_B$ [33].

A magnetic field is essential to measure the magnetoresistance effect, especially the interaction of spins with organic matter, hemoglobin. Wagemans and Koopmans reveal that the significant use of organic materials in spintronics is due to their long spin time, cheap, easy processing, infinite chemical tunability, and magnetic functionality [34]. Frustration in nearest-neighbor spin interactions causes the Zeeman energy splitting or degenerate energy states.

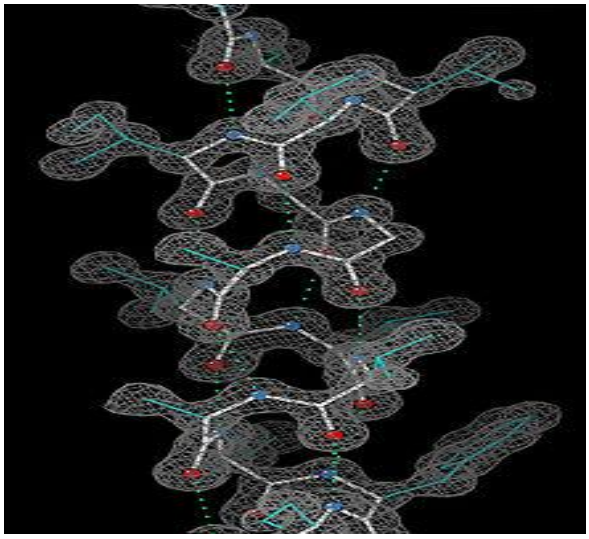

**Figure 5.** Electron number densities of hemoglobin (Myoglobin).

Youxun *et al*. showed that using $Cu^{2+}$ and $Ni^{2+}$ metal ions would help to magnetically separate proteins by affinity chromatography [35]. Caetano had shown that the spin-orbit coupling gives rise to a spin-current induced by canonical momentum rather than kinetic momentum (Figure 5) [36].

 

## DISCUSSION

In the case of spin transport through a frustrated system, it is important to consider both the properties of the valence band and the conduction band. Depending on the band structures, different compounds exhibit the anomalous Hall Effect with different crystal structures. Thus, it is a brilliant activity to determine and analyze the band structures and their properties. The particles' motion within the hemoglobin is greatly influenced by Brownian motion, a zigzag dancing of molecules/particles between successive impacts. This motion is the most probable for molecules/particles in a protein crystal.

### Spin Transport in Billiard Model View

Ancient models assume that spin transport in hemoglobin can take the form of Billiard transport. However, it was not acceptable in reality. Hence, the statement of spin transport in hemoglobin, achieving a billiard model, is not considered reasonable. In order to detect if billiard-like transport is achieved, it is important to first determine the Lyapunov exponent. If the Lyapunov exponent is positive, the spin transport encounters chaotic motion, which in reality is not billiard-like transport. If the Lyapunov exponent is negative, the system comes to a stable, non-chaotic equilibrium. Consequently, the spin transport in hemoglobin is visualized as spin diffusion undergoing chaotic dynamics. As Longville noted, hemoglobin diffusion can be measured from neutron spin echo spin spectroscopy [37].

As Datseris discussed, in a billiard model, a point particle is moving freely on a frictionless curved surface at constant speed until it hits the boundary of the billiard [38]. However, once the particle impinges on the billiard, it will reflect specularly. Hemoglobin animation: since ballistic transport is considered, any nonlinear velocity components are neglected. To enhance the transport (either ballistic or billiard), it is important to break the covalent bond between oxygen and iron ions by (i) reducing the effect of spin drag, (ii) reducing the size of the micro-sized particles to a nano size, (iii) increasing concentrations, and (iv) increasing the pH value.

Introducing an external magnetic field can reinforce mixing of spin states by the hyperfine field to maintain spin blocking. However, the spin transition from the triplet state to the singlet state is responsible for weak spin transport. Moreover, the equation developed in the Boltzmann transport formalism demonstrates the possibility of spin diffusion transport and chaotic dynamics in the hemoglobin molecule.

In hemoglobin, the spin transport can be affected by a various factors. The movement of the iron atom within the porphyrin ring is influenced by carbon monoxide (CO) that encapsulates iron in the hemoglobin molecule. Particularly, in the triplet spin state (deoxyhemoglobin), spin drag retards the transfer rate of iron ions. The spin drag in spin-polarized transport creates a frictional force that tends to decay spin-polarized current. It also retards the rate of energy and momentum transfer. This phenomenon involving electron-electron interactions may result in thermal magneto-resistance.

For the circulation process, assuming the path of the flow along a curve of radius, R, and the steady speed, V,

$$\vec{F}_c = \frac{\eta \rho V.\vec{v}^2}{r} \quad (6)$$

The magnetic forces are responsible for the spin drag, a force:

$$\vec{F}_B = nVe^{-}\vec{V}\vec{B} \quad (7)$$

$$n = \frac{\eta \rho \omega}{e^{-}\vec{B}} \quad (8)$$

$$\omega = \frac{\xi e^{-}\vec{B}}{\eta}.r \quad (9)$$

Defining, $\xi = \frac{n}{\rho}$, to be the ratio of electron number density to mass density, $\omega$ is the frequency of vibration, $\eta$ is the coefficient of micro viscosity, ρ-is the density of hemoglobin, n-electron number density, $e^{-}$ is the charge carried by an electron, and $\vec{B}$ Is the magnetic field.

 

Figure 6 demonstrates the relation between spin relaxation frequency and magneto-rheological properties of hemoglobin. As magnetorheological fluid allows spin diffusion from the central heme, Fe, as illustrated in Figure 6, the spin relaxation frequency increases with increasing magnetic field. Moreover, the spin frequency is associated with the induction of a small magnetic field from heme porphyrins. It then behaves as a paramagnetic fluid.

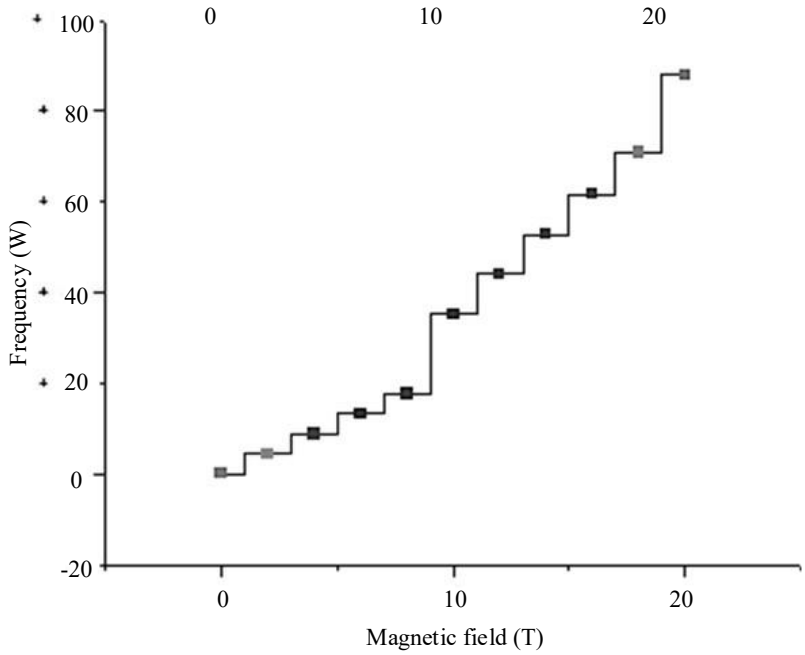


**Figure 6.** Spin relaxation frequencies as a function of magnetic field.

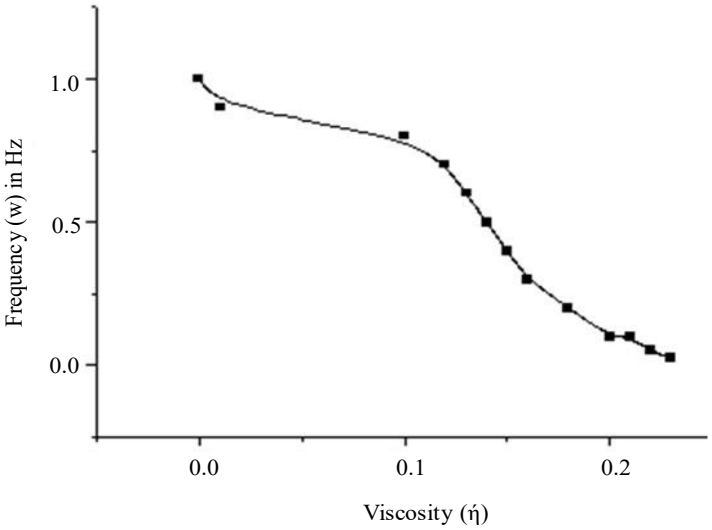


**Figure 7.** The changes in relaxation frequency with viscosity.

In Figure 7, it is noticed that, unlike the effect of the magnetic field, as the viscosity (η) increases, the spin relaxation frequency decreases. Consequently, it retards the rate of blood count and oxygen delivery to the body tissues. Thus, as the viscosity increases, magnetic interaction increases by slowing molecular motion.

In addition, the oxygen partial pressures can facilitate the phenomenon of spin transport by creating oxygen vacancies and improving the electronic and crystal structure of hemoglobin. Hence, oxygen

 

partial pressure enhances spin transport along the Fe-N symmetric easy axis. What is the best strategy to enhance such a spin transport? Modifying heme structure by doping with transition metals to increase the strength of oxygen affinity and decrease carbon monoxide affinity, and producing a concentration gradient. This is done by doping hemoglobin with elemental Cr and Ru. This kind of doping can alter a crystal's structures, spin states, and electronic configurations. The interaction of $Cr^{+3}$ with Heme, Fe changes its spin state by creating suitable conditions for transport. These mechanisms reinforce hemoglobin's ability to bind oxygen. The doping of hemoglobin with Cr and Ru can also minimize the toxicity of Carbon monoxide (CO). Increasing the concentration of hemoglobin and myoglobin also has a profound impact on spin diffusion. As per Lal *et al.*, viscosity changes associated with protein concentration can account for observed changes in translational diffusion [39].

As Xue *et al*. demonstrated, composites with high thermal conductivity nano-additives, such as carbon nanotube and graphene, may lead to protein-based materials with high thermal conductivity in the future [40]. Strictly speaking, the phenomenon of transport/conductivity of organic hemoglobin is determined by acidic solutions, ($-NH_3$, -COO-), Hydronium ions, (acidic water solutions) charge carriers, (e, $O^+$) where e is carried by electron charge and $O^+$ is holes. As Aminudin *et al.* described, the sensitivity of the GMR sensor increased with an increase in flow rate and concentration of hemoglobin [41].

Moreover, thermal effects can also impact the oxygen binding and transport. Raising the temperature decreases the oxygen saturation and breaks the bond between Fe-O. It also increases the dynamics of the energy landscape by decreasing oxygen affinity. Consequently, it increases the kinetic energy of hemoglobin molecules and hastens the rate of oxygen release.

The heating effect cannot facilitate the ballistic transport (free flow). Instead, it alters hemoglobin structure, protein conformations, and eventually denatures hemoglobin at high temperature. Consequently, increasing temperature decreases hemoglobin's affinity to oxygen but reinforces the release of oxygen by the Bohr Effect. Moreover, as Szczesny-Malysiak *et al.* revealed that changes in temperature can affect the spin polarization of electrons involved in oxygen binding [42].

The spin and the crystal field parameters of the iron ion were extracted by a spin Hamiltonian approach. Mayda *et al*. experimentally studied Human adult hemoglobin (HbA) from the magnetic susceptibility, Mossbauer Effect, and magnetic circular dichroism (MCD) measurements [17]. From this study, we can infer that the deoxygenated hemoglobin has unpaired spins exhibiting paramagnetism, while the oxygenated hemoglobin has spin pairs having lower spin energy. Hence, it exhibits antiferromagnetic coupling in the porphyrin layer.

Although there was no standard equipment for measuring the interaction energy of hemoglobin, like a hemoglobin meter, there are alternatives such as spectroscopic devices, electrospray ionization, and mass spectroscopy. A spectrophotometer can also be used to determine the hemoglobin concentration of a blood sample. Neutron spin Echo (NSE) spectroscopy and Muon Spin Relaxation (μSR) are permissible for measuring spin polarization. Neutron spin Echo (NSE) helps to explore magnetic dynamics and spin drag by using polarized neutrons, while the interaction of positive Muon with heme enables visualizing spin dynamics and energy difference between high and low energy states.

The antiferromagnetic coupling is due to the pairing of equal-sized up and down spin states. As Bren *et al*. determined from magnetic susceptibility measurements, the magnetic moment (μ) of the deoxy protein is $5.46\ \mu_B$ [19]. This value is slightly greater than the magnetic moment of hemoglobin, which is $4.9\ \mu_B$. This has four unpaired spins per Fe (II). The electronic fine structure measurements give low-temperature magnetic susceptibility data for heme exposed to light. Although the result had a major impact on the subject of hemoglobin and oxygen transport, the Pauling-Coryell interpretation proved incorrect.

 

**Search for Ballistic Transport**

Hemoglobin exhibits different electrical properties, namely permanent dipole moment, dielectric constant, and conductivity. Frustration leads to degeneracy; finite degeneracy allows splitting of magnetic energy and moments into d/t energy states. The hemoglobin's primary function is oxygen transport.

It is not an easy task to achieve ballistic transport in hemoglobin due to diffusive and conformational properties. In the case of ballistic transport, the electrons do not undergo scattering; instead, they undergo diffusion. Ballistic transport is the unimpeded flow or transport of charge carriers and energy over relatively long distances in bulk materials. It is a quantum phenomenon. In order to establish ballistic transport in hemoglobin, correcting protein-specific structures, producing a concentration gradient, and oxygen binding based on pH are important. However, external agents such as fields, heat, and photon energy have a weak contribution in enhancing ballistic transport. As Mairbäurl and Weber clarified, ballistic transport is an efficient and direct path oxygen takes when interacting with the protein's binding site [43].

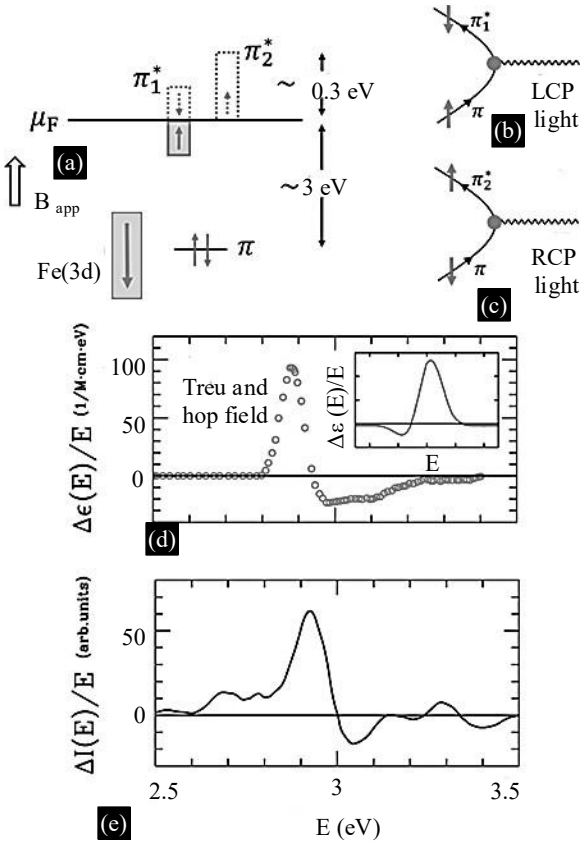


**Figure 8.** Anomalous MCD Spectrum of deoxy-HbA in the UV region. (a) Illustration of the spin polarization for Fe (3d) and bonding $\boldsymbol{\pi}$ and anti-bonding $\boldsymbol{\pi_1^*}$ and $\boldsymbol{\pi_2^*}$ host states in applied magnetic fields, $\vec{B}_a$ For deoxy heme. (b) Feynman diagram representing the absorption of LCP light in the optical transition $\pi \rightarrow \pi_1^*$. (c) The $\pi \rightarrow \pi_1^*$ Transition is shown for RCP light. (d) Anomalous MCD line shape in the UV-region for deoxy-HbA from the experiment Treu and Hopfield. (e) MCD spectrum for Deoxy-Heme cluster [17].

In hemoglobin, the spin transport is very weak. In turn, it does not significantly exhibit giant magnetoresistance since hemoglobin has no layered magnetic and non-magnetic structures. However, it can serve as a circuit element and analytics for biosensors for spin-dependent phenomena. Primary, as Jo *et al*. demonstrated, a hemoglobin-DNA conjugated biosensor can be used for detecting $H_2O_2$ [44].

 

Moreover, Yuan *et al*. revealed that Hb concentrated in magnetic molecular imprinted (MMIP) can enhance the sensitivity of biosensors [45].

As Tian and Xie revealed, organic semiconductors have weak spin-orbital coupling and hyperfine interaction [46]. Consequently, the spin diffusion length of electrons can be very long, which makes them preferred materials in spintronics. Long spin coherence length enables the development of devices that are reliable and efficient, that can carry a spin current and signal over long distances. As Panda *et al*. noted, carrier transport in bio-inspired materials, including proteins, has drawn functional electric properties [47].

Hill coefficient describes the cooperativity or sensitivity of heme-heme interaction. The value of affinity depends on the value of the Hill coefficient. If the Hill coefficient is greater than 1, the affinity of hemoglobin increases, while if the Hill coefficient is less than 1, its affinity decreases, and vice versa. Exceptionally, if the Hill coefficient is equal to 1, the oxygen-hemoglobin binding is independent of it. As Buxbaum noted, a drop in pH lowers the affinity but not the Hill coefficient of hemoglobin [48].

Hoping conductivity, i.e., tunneling between individual and sequential bridge states in the hemoglobin protein crystal structure, is enhanced due to the existence of electron transfer between multi-set states. The spin configuration of the spin in the hemoglobin molecule at the heme or iron center can change electronic energy levels. This energy level, in conjunction with temperature, can influence the mechanism of charge transport. It also impacts its electrical conductivity, which decreases exponentially as a function of temperature.

$$\sigma(\Delta E,\ T) = 1.0x10^{-5}e^{\frac{\Delta E}{k_B T}}$$

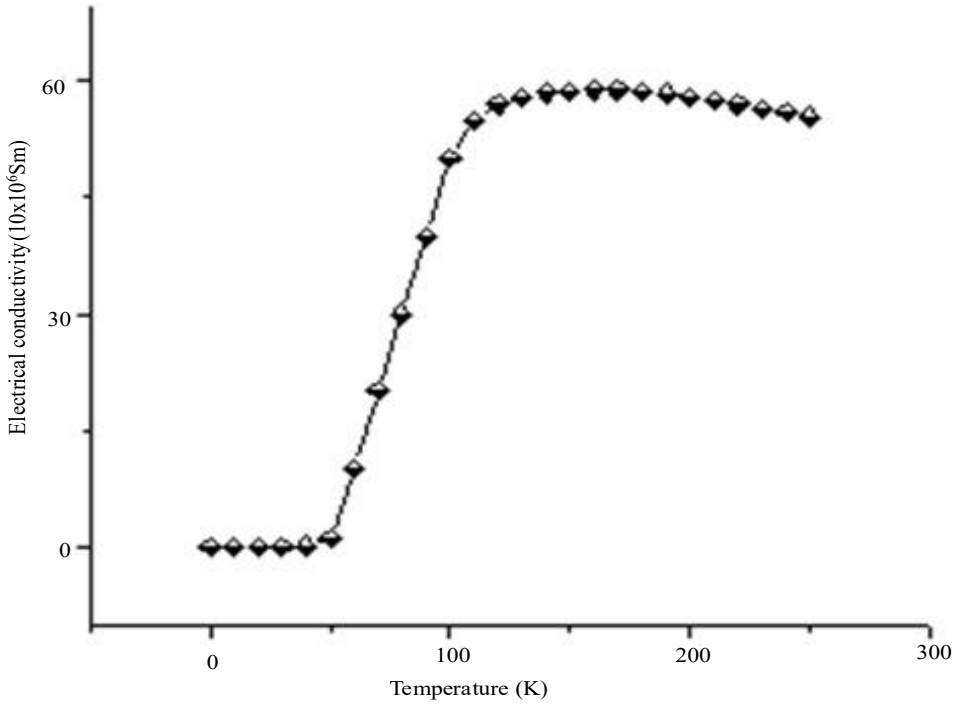


**Figure 9.** The change in electrical conductivity as a function of temperature (T).

As Figure 9 and the equation above demonstrate, the electric conductivity increases exponentially as a function of temperature. It shows a gradual increase at the beginning and increases rapidly in the middle. Although it increases as temperature rises, it decreases gradually at extremely high temperatures since it denatures the protein (Hemoglobin). Moreover, higher body temperature decreases hemoglobin's affinity and oxygen loading capacity to deliver oxygen to tissues.

 

Hirsch *et al*. had shown that the electrical conductivity of blood can be used to measure red cell concentration [49]. However, the resistance and thus the resistivity of semiconductors decrease as the thickness increases. Therefore, the Hall coefficient increases as the thickness increases.

To sum up, dry solid-state hemoglobin has no mobile electrons. However, its conductivity is associated with spin magnetic susceptibility and spin transition or flipping. As a solid protein, it experiences relatively very low electrical conductivity, of less than $10\times10^{-6}$ Sm, which shares semiconducting electrical behavior. Although it exhibits electrical behavior of semiconductors, its electrical properties are induced by electron-electron interaction or heme-heme interaction within the hemoglobin.

Although we are fortunate to establish ballistic and billiard transport in hemoglobin, the possibility of attaining such transports and conductivity is quite challenging due to the growth of native magnetism, spin drag caused by viscosity, and collisions with neighboring ions. However, by producing a concentration gradation, it is possible to establish such spin transport in one direction. In addition, introducing an external magnetic field can alter spin diffusion in a unidirectional path.

In general, the existence of heme, at the center of hemoglobin, changes its valence states from ferrous iron, $Fe^{2+}$, to Ferric iron, $Fe^{3+}$. This shows that hemoglobin can act as a source of nanomagnetism, though the strength of the magnetic moment of hemoglobin is much less than the magnetic moment of Mafic lava. This behavior can be used in biomedical engineering for separating red blood cells from other blood components by magnetic separation. This research has laid the ground and insights on the impact of spin transport on human health. At different stages of transport, electron-electron or heme-heme interaction leading to spin-spin interaction encounters internal friction or spin drag. The spin drag is caused by a chaotic effect, which can greatly influence the transport of minerals, air, and water. It is responsible for common health problems, including breathing disorders, respiratory hypertension, and sickle cell anemia.

This research has great significance in detecting, preventing, and monitoring such health defects. Biosensors, magneto sensors, biomarkers, and magnetic relaxometers can perform such tasks. These devices enable imaging, cell labeling, and cell separation more easily. Moreover, the flow directions can be detected and monitored by magnetic sensors.

Hemoglobin can serve as a circuit analytics for noninvasive blood analysis and diagnosis of blood-borne disease. Due to its pigment and capacity to absorb red and infrared radiation, it can be used in optical medicine. Hemoglobin also helps to determine oxygen concentration and level for a health survey. As Protopapas revealed, RBCs, comprising a substantial portion (45%) of human blood, serve as crucial biomarkers in medical diagnostics such as MRI, MEG, and Nuclear Magnetic Resonance (NMR) [50]. As a primary example, micro nuclear magnetic resonance relaxometer spectroscopy enables early-stage and rapid diagnosis of malaria and anemia by using the target parasite.

Moreover, slowly rising temperatures enable shifting the oxyhemoglobin dissociation curve to the right, which promotes oxygen delivery to cells and tissues, for heat therapy. On the other hand, due to 3D conformations, the transport in hemoglobin (Protein) is subjected to several challenges. Thus, an in-depth study of spin transport in the hemoglobin molecule has a potential role in preventing hematopathologic disease.

## CONCLUSION

In this study, the nature of spin transport is studied by enumerating the magnetic, structural, and electrical behavior of hemoglobin. This transport is weak due to chaotic dynamics and the high viscosity of blood. As the research revealed, the nature of spin transport is caused by transitions of spin from deoxyhemoglobin to oxyhemoglobin. This transport is influenced by various factors such as concentration, spin drag, pH value, and oxygen and carbon monoxide affinity. The transport is caused

 

by electron-electron coupling or heme-heme interactions. Associated with this coupling is magneto resistance, which grows quadratically with the applied magnetic field. The resulting spin transport depends on the concentrations of electrons, sedimentations, temperature, and conformations. The spin transport observed in hemoglobin does not resemble either ballistic or billiard-like transport. This is because spin diffusion is dominant in hemoglobin rather than ballistic or billiard transport due to chaotic effects and spin drag. Hemoglobin bears Fe at the center of Heme, and the spin-orbit coupling of these states results in antiferromagnetic ordering. The antiferromagnetic coupling is due to the pairing of equal-sized up and down spin states. The existence of unpaired electrons at the heme structure exhibits ferromagnetism. Other constituents, like Fe-N, Fe-O, and Fe, result in paramagnetic states. Not only transport but also the presence of magnetic states with different phases indicated that hemoglobin exhibits magnetic moments much less than the magnetic moment of the Earth's mafic lava. Studying the magnetic properties of hemoglobin has a potential application in biomedical engineering for separating red blood cells from other blood components using magnetic techniques. It is also seen that not only the natural transport of oxygen but also producing a concentration gradient enables efficient spin transport, which might be useful in blood flow measurement. Hence, this study provides a possibility of visualizing both oxygen and pin transport mechanisms in hemoglobin. As the result indicates, by carefully controlling the biophysical properties of hemoglobin and the mechanism of spin transport, it is possible to diagnose blood-related diseases such as anemia, blood clotting, solid tumors, cardiovascular disease (CVD), etc., caused by defects in the mechanism of transport in hemoglobin.

**Statement of Author**

I declare that this manuscript is my own and original work, while suitable concepts, ideas, and theorems that are reviewed from others' work are properly cited.

**Conflict of Interest**

There is no conflict of interest in the area of study.

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