

# Quantum Mechanics of the Hydrogen Bond

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Hydrogen bonds are a fundamental force in chemistry, crucial for understanding the behavior of many biological molecules and materials, from water's anomalous properties to the structure of DNA. At their core, hydrogen bonds arise due to the interaction between protons and their associated electron clouds, which are governed by the principles of quantum mechanics. We will discuss the probabilistic behavior of protons and the wavefunction interactions that shape the bond's strength and geometry.

## The Schrödinger Equation for the Hydrogen Atom

A hydrogen atom consists of a single proton and a single electron. The proton, as the positively charged nucleus of the hydrogen atom, has a mass of approximately:

$$m_p \approx 1.67 \times 10^{-27} \text{ kg},$$

and a charge

$$e = 1.602 \times 10^{-19} \text{ C}.$$

The electron, with its opposite negative charge, orbits around the proton due to the electrostatic Coulomb attraction between the two particles. The proton's mass is much larger than the electron's, approximately 1836 times greater, but in most quantum mechanical treatments of hydrogen, the proton's motion is often neglected for simplicity, assuming the proton to be stationary relative to the electron. However, it is important to recognize that the proton, like all quantum mechanical particles, does not behave as a fixed point in space.

In fact, the proton's position is also described probabilistically through a quantum mechanical wavefunction. The proton's wavefunction is closely tied to that of the electron, particularly when considering systems like hydrogen bonds, where the interaction between hydrogen atoms is essential. The behavior of the proton, in combination with the electron, dictates many of the chemical and physical properties of the hydrogen atom and its interactions with other molecules.

In the case of the hydrogen atom, the electron and proton are bound together by the Coulomb force, and this two-particle system is described by the

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Schrödinger equation, which governs the quantum behavior of the system:

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}),$$

where  $\hat{H}$  is the Hamiltonian operator,  $\psi(\mathbf{r})$  is the wavefunction describing the quantum state of the system, and  $E$  is the energy eigenvalue associated with the state.

For the electron in a hydrogen atom, the Hamiltonian  $\hat{H}$  consists of two main parts: (1) Kinetic Energy of the Electron: This term accounts for the motion of the electron and is represented by the Laplacian operator  $\nabla^2$ , which acts on the spatial coordinates of the electron. (2) Potential Energy due to Coulomb Attraction: This term describes the electrostatic interaction between the electron and the proton. The potential energy is given by the Coulomb potential:

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

where  $r$  is the radial distance between the electron and the proton,  $e$  is the charge of the electron (and proton), and  $\epsilon$  is the permittivity of the medium. Thus, the Hamiltonian for the hydrogen atom is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon r},$$

where  $\hbar$  is the reduced Planck constant, and  $m_e$  is the mass of the electron.

Solving the Schrödinger equation for the hydrogen atom leads to a set of discrete energy eigenvalues that describe the possible energy states of the system. These energy levels are quantized and given by:

$$E_n = -\frac{13.6 \text{ eV}}{n^2},$$

where  $n$  is a positive integer, the principal quantum number. The ground state of the hydrogen atom corresponds to  $n = 1$ , and higher states correspond to  $n > 1$ .

The corresponding wavefunctions,  $\psi_{n\ell m}(\mathbf{r})$ , describe the probability distribution of the electron's position. For the ground state (where  $n = 1$ ), the radial wavefunction is:

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0},$$

where  $a_0$  is the Bohr radius, approximately  $5.29 \times 10^{-11} \text{ m}$ , which represents the characteristic scale of the hydrogen atom.

This wavefunction describes the spatial probability distribution of the electron. The probability density of finding the electron at a distance  $r$  from the proton is proportional to  $|\psi_{1s}(r)|^2$ , which is a decreasing exponential function of  $r$ . This means the electron is most likely to be found near the Bohr radius, but its position is not fixed; there is always a nonzero probability of finding the electron at any distance.

## Wavefunction Overlap and Bond Strength

A hydrogen bond forms when a hydrogen atom, covalently bonded to an electronegative atom (such as oxygen or nitrogen), interacts with a lone pair of electrons from another electronegative atom. The strength and geometry of this interaction are governed by quantum mechanical principles. The interaction strength depends critically on the overlap between the wavefunctions of the involved particles: the proton ( $\text{H}^+$ ), the electron in the hydrogen atom, and the lone pair electrons on the electronegative atom.

In this context, the key interaction is between the proton ( $\text{H}^+$ ) of the hydrogen atom and the lone pair electrons of an electronegative atom. We can describe the strength of this interaction by evaluating the overlap of the relevant wavefunctions, particularly the wavefunction of the proton and the wavefunction of the lone pair.

Consider two interacting molecules: One molecule contains a proton ( $\text{H}^+$ ) covalently bonded to an electronegative atom, and The other contains a lone pair of electrons on an electronegative atom (such as oxygen or nitrogen). The wavefunctions associated with the proton, the hydrogen atom's electron, and the lone pair electrons can be described as follows: The proton's probabilistic position is captured by a wavefunction  $\psi_{\text{H}}(\mathbf{r}_1)$ , which is a description of the proton's quantum mechanical delocalization. The electron in the hydrogen atom is bound to the proton and has a wavefunction  $\psi_{\text{e}}(\mathbf{r}_1)$ , but it does not directly participate in the hydrogen bonding interaction. The focus is on the proton's interaction. The lone pair electrons on the electronegative atom are described by a wavefunction  $\psi_{\text{L}}(\mathbf{r}_2)$ , which captures the electron density of the lone pair.

The interaction between the proton ( $\text{H}^+$ ) and the lone pair electrons can be described by the potential  $\hat{V}$ , which represents the Coulomb interaction between the proton and the lone pair electrons. The interaction energy is given by the expectation value of the interaction potential:

$$E_{\text{int}} = - \int \psi_{\text{H}}^*(\mathbf{r}_1) \hat{V} \psi_{\text{L}}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2.$$

This integral represents the quantum mechanical interaction between the proton and the lone pair. The Coulomb potential is given by:

$$\hat{V} = \frac{e^2}{4\pi\epsilon|\mathbf{r}_1 - \mathbf{r}_2|},$$

where  $e$  is the charge of the proton,  $\epsilon$  is the permittivity of the medium, and  $|\mathbf{r}_1 - \mathbf{r}_2|$  is the distance between the proton and a point in the lone pair region. Thus, the interaction energy depends on the spatial overlap between the proton's wavefunction  $\psi_{\text{H}}(\mathbf{r}_1)$  and the lone pair's wavefunction  $\psi_{\text{L}}(\mathbf{r}_2)$ . The degree of overlap influences the strength of the interaction and, consequently, the strength of the hydrogen bond.

Several factors can influence the strength of the hydrogen bond: (1) Distance: A smaller distance between the proton and the lone pair increases the interaction energy, thereby strengthening the hydrogen bond. (2) Orientation: The relative

orientation of the lone pair’s wavefunction with respect to the proton affects the degree of overlap. A more favorable orientation increases the overlap, leading to a stronger bond. (3) Electronegativity: The relative electronegativity of the atoms involved affects the extent of the lone pair and the strength of the interaction.

The quantum mechanical description of the hydrogen bond reveals that its strength is determined by the interaction between the wavefunctions of the proton ( $\text{H}^+$ ) and the lone pair electrons. The interaction energy depends on both the spatial overlap of these wavefunctions and their relative orientation, as well as factors such as the distance between the interacting particles and the electronegativity of the atoms involved.

## The Impact of Quantum Tunneling in Hydrogen Bonding

Quantum tunneling is a fundamental phenomenon that arises due to the wave-like nature of particles in quantum mechanics. It refers to the ability of a particle to pass through a potential barrier that, according to classical mechanics, would be insurmountable. This concept has profound implications for the behavior of protons in hydrogen bonds, which distinguishes quantum mechanical interactions from purely classical ones.

In classical physics, a proton in a hydrogen bond would be restricted to specific locations dictated by the potential energy of the bond, and its motion would be confined to a well-defined region between the two interacting molecules. However, quantum mechanics allows the proton to exhibit non-classical behavior, such as tunneling, where it can “leap” across energy barriers that would normally prevent its passage.

To understand how quantum tunneling impacts hydrogen bonding, we need to consider the wavefunction,  $\psi(x)$ , of a proton in a potential energy landscape. The energy eigenvalue equation governing the proton’s behavior in one dimension is given by:

$$\hat{H}\psi(x) = E\psi(x),$$

where  $\hat{H}$  is the Hamiltonian operator,  $E$  is the energy eigenvalue, and  $\psi(x)$  is the wavefunction. The Hamiltonian in the region of interest (such as between two hydrogen atoms in the bond) is:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x),$$

where  $\hbar$  is the reduced Planck’s constant,  $m$  is the mass of the proton, and  $V(x)$  is the potential energy.

For a hydrogen bond, the potential  $V(x)$  typically exhibits a well or barrier where the proton is localized in one region but faces a potential barrier between two interacting molecules. Classically, the proton would be confined to the well, but quantum mechanically, the wavefunction  $\psi(x)$  can extend into or even pass through the potential barrier.

In regions where the potential energy is higher than the proton’s total energy,  $\psi(x)$  does not represent a propagating wave but rather an exponentially decaying or growing function. This is known as *tunneling*, and the wavefunction’s behavior in the tunneling region can be approximated as:

$$\psi(x) \sim e^{-\kappa x},$$

where  $\kappa = \sqrt{2m[V(x) - E]/\hbar^2}$  is the decay constant, and  $V(x) - E$  is the difference between the potential and the proton’s energy.

The probability of tunneling, or the transmission coefficient  $T$ , is related to the exponential decay of the wavefunction. For a barrier of width  $d$ , the probability  $T$  that the proton tunnels through the barrier is roughly:

$$T \sim e^{-2\kappa d}.$$

For short barriers or low masses (as with protons), tunneling is often a significant effect, meaning that the proton is not fully confined to one molecule but may “leak” into the region of the other molecule, effectively blurring the boundaries between the two interacting species.

In the context of hydrogen bonding, the tunneling phenomenon has important consequences: (1) Proton Delocalization: Quantum tunneling allows the proton to be delocalized across the bond, meaning that it is no longer confined to one specific position between two atoms but can occupy multiple sites with a certain probability. This delocalization enhances the strength and flexibility of the hydrogen bond, as the proton is not fixed in a single position, but its effective position is smeared out over the potential energy surface. (2) Bond Dynamics: The proton’s tunneling behavior modifies the dynamics of the bond, potentially leading to faster reactivity or the ability for the bond to “switch” between different configurations. This makes hydrogen bonds more dynamic compared to classical bonds, where the proton’s position would be fixed. (3) Energy Barrier Reduction: Quantum tunneling lowers the effective energy barrier for proton transfer in a hydrogen bond. As a result, processes like proton transfer in enzymes or proton conduction in water can occur much more easily at lower temperatures than would be predicted by classical thermodynamics alone. (4) Temperature Dependence: Quantum tunneling becomes more significant at lower temperatures, where classical thermal energy is insufficient to overcome potential barriers. In this regime, tunneling is responsible for much of the hydrogen bond’s reactivity, even when classical thermal activation is not available.

In conclusion, quantum tunneling introduces a key quantum mechanical effect into the dynamics of hydrogen bonding, blurring the classical boundaries of the interaction by allowing protons to explore multiple positions along the bond. This quantum feature sets hydrogen bonding apart from purely classical interactions, contributing to its unique physical properties and behavior in various chemical and biological systems.

## Quantum Mechanical Calculations and the Geometry of Hydrogen Bonds

The geometry of hydrogen bonds, specifically the bond length and bond angle, is determined by the quantum mechanical interactions between the wavefunctions of the participating atoms or molecules. At equilibrium, the bond geometry corresponds to the configuration that minimizes the total potential energy of the system. This total energy arises from several contributions, most notably the electrostatic Coulomb interaction, the Pauli exclusion principle, and the repulsive forces due to the overlap of electron clouds of the atoms involved.

To describe this rigorously, the system of interacting protons and electrons is treated quantum mechanically. The total energy  $E_{\text{total}}$  of the system is a functional of both the electron wavefunctions and the positions of the protons, denoted as  $\psi(\mathbf{r}, \mathbf{R})$ , where  $\mathbf{r}$  represents the electron coordinates and  $\mathbf{R}$  the proton coordinates. In the absence of time dependence, the electron wavefunctions  $\psi(\mathbf{r})$  depend only on spatial coordinates. The total energy can be expressed as:

$$E_{\text{total}}(\psi, \mathbf{R}) = \langle \psi(\mathbf{r}, \mathbf{R}) | \hat{H} | \psi(\mathbf{r}, \mathbf{R}) \rangle,$$

where  $\hat{H}$  is the Hamiltonian operator for the system, which includes the kinetic energy of the protons and electrons, as well as the interaction terms. The Hamiltonian is generally written as:

$$\hat{H} = \hat{T}_{\text{proton}} + \hat{T}_{\text{electron}} + \hat{V}_{\text{int}},$$

where  $\hat{T}_{\text{proton}}$  and  $\hat{T}_{\text{electron}}$  are the kinetic energy operators for the protons and the electrons, respectively, and  $\hat{V}_{\text{int}}$  is the interaction potential, which includes both the Coulomb interaction between the protons and electrons, and the Pauli exclusion repulsion due to the overlap of electron wavefunctions.

### Potential Energy Surface (PES) and Bond Geometry

The potential energy surface (PES) is a representation of the total energy  $E_{\text{total}}$  as a function of the positions of the protons  $\mathbf{R}$ , specifically the positions of the donor and acceptor protons in the case of a hydrogen bond. The PES is obtained by solving the Schrödinger equation for the electron wavefunctions  $\psi(\mathbf{r})$  at each fixed configuration of the protons  $\mathbf{R}$ :

$$E_{\text{total}}(\mathbf{R}) = \min_{\psi} \langle \psi(\mathbf{r}, \mathbf{R}) | \hat{H} | \psi(\mathbf{r}, \mathbf{R}) \rangle.$$

To determine the equilibrium bond geometry, we minimize the PES with respect to the proton coordinates, typically the bond length  $r_{\text{bond}}$  and bond angle  $\theta$ , by solving the following condition for energy minimization:

$$\frac{\partial E_{\text{total}}(\mathbf{R})}{\partial \mathbf{R}} = 0.$$

This condition ensures that the total energy is at a local minimum with respect to the bond length and bond angle, corresponding to the equilibrium configuration. The equilibrium geometry is the set of protonic positions where the forces acting on the protons, defined by the gradient of the total energy, vanish.

The total energy consists of several terms. The most significant contributions are the Coulomb interaction and the Pauli repulsion. The Coulomb interaction arises from the electrostatic attraction between the partial charges on the donor proton and the acceptor atom, and it favors a shorter bond length. This electrostatic attraction can be expressed as:

$$V_{\text{Coulomb}}(r_{\text{bond}}) = \frac{q_{\text{donor}}q_{\text{acceptor}}}{4\pi\epsilon r_{\text{bond}}},$$

where  $q_{\text{donor}}$  and  $q_{\text{acceptor}}$  are the partial charges of the donor proton and the acceptor atom, respectively, and  $r_{\text{bond}}$  is the distance between the donor and acceptor protons. This term decreases with increasing bond length, thereby encouraging the protons to approach each other.

In contrast, the Pauli repulsion arises from the Pauli exclusion principle, which asserts that no two fermions (such as electrons) can occupy the same quantum state simultaneously. As the donor and acceptor atoms approach one another, the electron clouds of these atoms begin to overlap, leading to a repulsive interaction that prevents them from coming too close. The Pauli repulsion can be approximated by a potential of the form:

$$V_{\text{repulsion}}(r_{\text{bond}}) = \frac{A}{r_{\text{bond}}^{12}} - \frac{B}{r_{\text{bond}}^6},$$

where  $A$  and  $B$  are constants specific to the atom types involved. The  $1/r^{12}$  term represents a very strong repulsion at short distances, while the  $1/r^6$  term represents a weaker, longer-range repulsion.

In more complex scenarios, such as those involving highly polarizable atoms or solvent effects, additional terms may be required to account for polarization effects. These interactions can be modeled using a polarization potential, which depends on the polarizabilities of the donor and acceptor atoms and the bond angle  $\theta$ . The polarization energy can be written as:

$$V_{\text{polar}}(r_{\text{bond}}, \theta) = -\frac{\alpha_{\text{donor}}\alpha_{\text{acceptor}}}{r_{\text{bond}}^6} \cos^2(\theta),$$

where  $\alpha_{\text{donor}}$  and  $\alpha_{\text{acceptor}}$  are the polarizabilities of the donor and acceptor atoms, respectively, and  $\theta$  is the bond angle between the donor, proton, and acceptor atoms.

By minimizing the total energy  $E_{\text{total}}$  with respect to both  $r_{\text{bond}}$  and  $\theta$ , the equilibrium bond geometry can be determined. In typical hydrogen bonds, the bond length generally ranges from 1.5 to 2.5 Å, with bond angles near 180° for linear hydrogen bonds and smaller deviations for nonlinear geometries. These values result from the balance between the attractive Coulomb interaction and the repulsive Pauli forces, along with any additional terms accounting for polarization effects or solvent interactions.

In conclusion, the geometry of hydrogen bonds is determined by minimizing the total potential energy of the system, which includes contributions from the Coulomb interaction, Pauli repulsion, and potentially polarization effects. The equilibrium bond length and bond angle correspond to the configuration that minimizes the total energy, and these values can be obtained by solving the Schrödinger equation and applying the minimization condition to the potential energy surface.

## Zero-Point Energy in Hydrogen Bond Models

Zero-point energy (ZPE) refers to the lowest possible energy a quantum mechanical system can possess, even when it is in its ground state. In a classical system, one might assume that the minimum energy configuration is at rest, with particles having no motion. However, quantum systems, due to the uncertainty principle, cannot have zero motion; there is always residual vibrational motion even in the ground state, leading to non-zero energy. This residual energy plays a significant role in various physical properties of molecular systems, including hydrogen bonds.

### Quantum Mechanical Foundation

Consider a simplified model of a hydrogen bond as an interaction between two molecules, where the bonding interaction primarily arises from the electrostatic attraction between a proton (hydrogen) and a lone pair of electrons on an electronegative atom (e.g., oxygen or nitrogen). These interactions can be described using quantum mechanics, where the system’s total energy consists of contributions from the electronic, vibrational, rotational, and translational modes.

The zero-point energy is rooted in the quantum harmonic oscillator model. For simplicity, assume that the bond can be approximated as a harmonic potential, which describes the vibrational modes of the hydrogen bond. The energy levels for a quantum harmonic oscillator are given by:

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega$$

where  $n$  is a non-negative integer representing the vibrational quantum number ( $n = 0, 1, 2, \dots$ ),  $\hbar$  is the reduced Planck constant, and  $\omega$  is the angular frequency of the oscillation.

The zero-point energy corresponds to the case  $n = 0$ , which is:

$$E_0 = \frac{1}{2} \hbar\omega$$

Thus, the minimum vibrational energy of the hydrogen bond (when  $n = 0$ ) is given by the zero-point energy  $E_0$ , which arises even in the absence of thermal excitation.



## Zero-Point Energy and Hydrogen Bond Strength

The zero-point energy affects the strength of the hydrogen bond by modifying the potential energy landscape of the bonding interaction. The vibrational motion of the bond, due to the zero-point energy, leads to fluctuations in the bond length and angle. These fluctuations are typically small but have measurable effects on the bond's behavior.

In the context of a hydrogen bond, the potential energy surface  $V(r, \theta)$  can be described as a function of the bond length  $r$  and bond angle  $\theta$ . Due to zero-point motion, the bond length and angle are not fixed, but instead, fluctuate around the equilibrium positions. These fluctuations influence the overall binding energy and thermal stability of the hydrogen-bonded system.

If we model the bond as a simple harmonic oscillator, then the bond strength  $D$  (which is the dissociation energy) can be affected by the zero-point energy. For a bond described by a potential of the form  $V(r)$ , the equilibrium bond length is determined by the minimum of the potential, but quantum fluctuations due to zero-point energy lead to slight deviations from the classical equilibrium position.

Mathematically, these deviations can be quantified using the harmonic approximation to the potential. In this approximation, the potential is expanded around the equilibrium bond length  $r_0$  as:

$$V(r) \approx V(r_0) + \frac{1}{2}k(r - r_0)^2$$

where  $k$  is the force constant, and  $r_0$  is the equilibrium bond length. The vibrational frequency  $\omega$  is related to the force constant by:

$$\omega = \sqrt{\frac{k}{\mu}}$$

where  $\mu$  is the reduced mass of the system.

## Thermal Properties and Zero-Point Energy

The zero-point energy also influences the thermal properties of hydrogen-bonded systems. At finite temperatures, the hydrogen bond will undergo additional thermal vibrations, but the zero-point energy will shift the vibrational spectrum. This results in small but important corrections to the heat capacity, entropy, and other thermodynamic properties of the system.

In particular, the vibrational partition function  $Z_v$  for a single harmonic oscillator at temperature  $T$  is given by:

$$Z_v = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

where  $\beta = 1/k_B T$ , with  $k_B$  being the Boltzmann constant and  $T$  the temperature.

At low temperatures, the contribution of zero-point energy is significant. The vibrational energy at low temperatures can be approximated by:

$$E_v = \frac{\hbar\omega}{2} \left( 1 + \frac{1}{e^{\beta\hbar\omega} - 1} \right)$$

At high temperatures, the system behaves classically, and the energy contribution becomes approximately  $k_B T$ . However, at low temperatures, the zero-point energy dominates, and the system's vibrational behavior will be influenced by this residual energy even in the absence of thermal excitations.

Zero-point energy plays a crucial role in hydrogen-bonded systems, influencing both the bond strength and the thermal properties. The quantum mechanical effects due to zero-point motion lead to slight fluctuations in bond length and angle, altering the binding energy and thermal stability of the system. Furthermore, zero-point energy contributes to the vibrational properties and the thermal behavior of hydrogen-bonded systems, particularly at low temperatures. Understanding these effects is essential for accurately modeling and predicting the behavior of materials and biomolecules that rely on hydrogen bonding.

## Conclusion

The hydrogen bond is an inherently quantum mechanical phenomenon, with its strength, geometry, and behavior rooted in the probabilistic nature of protons and electrons. The formation of a hydrogen bond depends critically on the overlap of wavefunctions, the probabilistic distribution of the proton's position, and the quantum mechanical interactions between electron clouds. As such, understanding hydrogen bonding requires not just classical models but a full quantum mechanical treatment, including considerations of wavefunction overlap, delocalization, zero-point energy, and tunneling. These quantum effects are what make the hydrogen bond both unique and indispensable in chemistry and biology.