

Molecular Quantum Modeling of Water

Purpose:

This paper was done to familiarize myself with some of the Quantitative Molecular Properties of water. This was a learning experience for me. This work provides **Quantitative Solutions and Simulations** for the molecular behavior of water. This material has been gathered from a number of books and papers on the theoretical and experimental work on water. A list of some the books and papers used in this analysis are given at the end of this work. This is not original work with regard to the discovery or descriptions of phenomena. This work is simply conventional Quantum Mechanics abstracted from various QM texts and organized into four major parts. (See the four parts listed below.) The goal was to aid my understanding by capturing the molecular, or Quantum Mechanical, structure of water with mathematical models implemented in the **Mathcad, Maple, and Mathematica** programming languages. We will use this methodology to mathematically simulate various molecular phenomena associated with water.

In Summary, water's properties are encoded in its molecular structure and energies.

This investigation has four major parts.

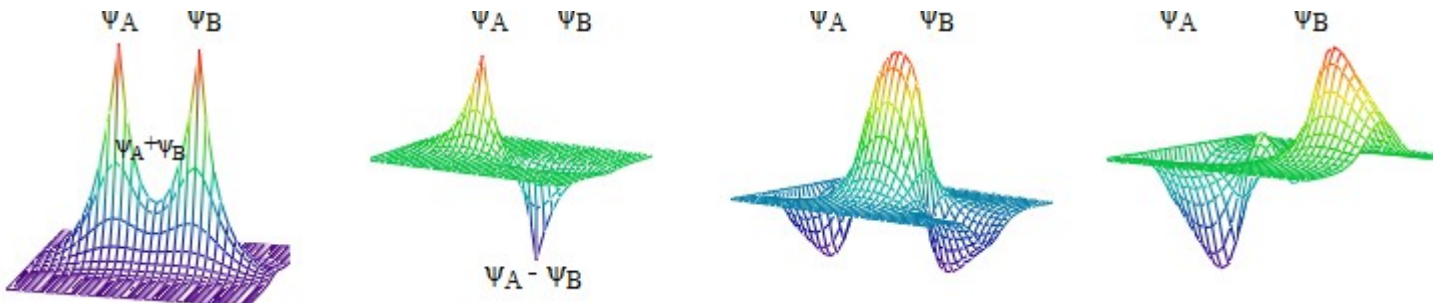
1. Define the Key Concepts of Quantum Mechanics (QM),
2. Develop a QM model for an electron,
3. Develop a QM model for a hydrogen ion, atom, and molecule,
4. Using a Linear Combination of Atomic Orbitals (LCAO), develop a QM model for the water molecule.

NOTE: *Mathcad operations are shown in purple italics.*

For example: $\sin\left(\frac{\pi}{2}\right) = 1$

[This Mathcad File is available at: VXPhysics.com/Mathcad](http://VXPhysics.com/Mathcad)

Mathcad 3D Perspective Plots of Hydrogenic Molecular Orbitals. See Section VIII.



Introduction

Water, a fundamental compound and the essence of life, is ubiquitous in our world. Its unique properties and crucial role in biological processes have captured the interest of scientists for centuries. While macroscopic properties of water have been extensively studied and utilized, understanding its behavior at the molecular level remains a complex and intriguing challenge. Molecular quantum modeling provides a powerful tool to explore the microscopic interactions and dynamics that govern the behavior of water molecules.

This paper embarks on a journey into the realm of molecular quantum mechanics, focusing on the fascinating properties of water and its enigmatic behavior in various environments. By employing key postulates of quantum mechanics, this study aims to shed light on the intricate nature of water through rigorous theoretical analysis and numerical simulations.

The paper is organized as follows:

I. Six Key Postulates of Quantum Mechanics:** This section provides a foundational basis for the subsequent discussions, introducing the core principles that underlie the quantum mechanical framework.

II. QM: Schrödinger Wavefunction, Matrix, and Wigner Phase Space:** Building upon the postulates, this section delves into the mathematical formalisms of quantum mechanics, including the Schrödinger wavefunction, matrix representation, and the Wigner phase space representation.

III. Solution of Schrödinger Wave Equation for Propagation of an Electron:** Here, the focus shifts to solving the Schrödinger wave equation, providing insight into the behavior of electrons in different environments.

IV. Numerical Schrödinger Equation Solutions: 3-D Harmonic Oscillator:** This section explores numerical solutions of the Schrödinger equation, with a specific emphasis on the 3-D harmonic oscillator, a fundamental model in quantum mechanics.

V. Basic Quantum Mechanics in Coordinate, Momentum & Phase Space:** Expanding further into quantum mechanics, this section investigates the behavior of systems in different spaces, including coordinate, momentum, and phase space.

VI. Molecular Quantum Mechanics: Hydrogen Molecule Orbits:** The focus now shifts to the application of quantum mechanics in molecular systems, with a particular focus on the orbits of hydrogen molecules.

VII. 3D Plots of sp^2 , dz^2 , d_{xy} , $3p_z$ Hydrogenic Hybrid Orbitals:** Building on the previous section, this part explores the three-dimensional plots of various hydrogenic hybrid orbitals, revealing their distinctive shapes and characteristics.

VIII. Linear Combination of Atomic Orbitals (LCAO):** This section introduces the concept of LCAO, a fundamental technique used in molecular quantum mechanics to describe molecular orbitals.

IX. Molecular Structure of Water:** Here, we transition to the central focus of this study, exploring the molecular structure of water and the intricacies of its intermolecular interactions.

X. Radial Distribution Functions of Water: Derived from Radiation Total Scattering:** Finally, this section presents a detailed analysis of radial distribution functions of water, derived from radiation total scattering data, providing valuable insights into the molecular arrangement of water molecules.

Through the comprehensive investigation of these topics, this paper aims to provide a deeper understanding of the molecular structure of water and how it establishes the macroscopic behavior of water.

I. Six Key Postulates of Quantum Mechanics

Physical Chemistry, Engel, Read, 3rd Ed 2014

Quantum mechanics can be formulated in terms of six postulates. Postulates cannot be proven, but they can be tested. The five postulates discussed in this chapter provide a framework for summarizing the basic concepts of QM.

POSTULATE 1

The state of a quantum mechanical particle is **completely specified by a wave function**. The state of a physical system is represented by a normalized ket in a Hilbert space H . To simplify the notation, only one spatial coordinate is considered. The probability that the particle will be found at time t_0 in a spatial interval of width centered at x_0 is given by

$$P(x_0, t_0) = \int \Psi^*(x_0, t_0) \Psi(x_0, t_0) dx = |\Psi(x_0, t_0)|^2 dx$$

The wave function must be a single-valued function of the spatial coordinates. If this were not the case, a particle would have more than one probability of being found in the same interval.

POSTULATE 2

For every measurable property of a system such as position, momentum, and energy, **there exists a corresponding operator in quantum mechanics**. An experiment in the laboratory to measure a value for such an observable is simulated in the theory by operating on the wave function of the system with the corresponding operator. All quantum mechanical operators belong to a mathematical class called Hermitian operators that have real eigenvalues. For a Hermitian operator \hat{A} , $\int \psi^*(x) [\hat{A}\psi(x)] dx = \int \psi(x) [\hat{A}\psi(x)]^* dx$

POSTULATE 3 (Born's Rule)

In any single measurement of the observable that corresponds to the operator, the **only** values that will ever be measured are the **eigenvalues** of that operator \hat{A}

POSTULATE 4

If the system is in a state described by the wave function, and the value of the observable a is measured once on each of many identically prepared systems, the average value (also called the expectation value) of all of these measurements is given by the normalized wave

$$\langle a \rangle = \int \Psi^*(x, t) \hat{A} \Psi(x, t) dx$$

As we know, two cases apply with regard to $\Psi(x, t)$: it either is or is not an eigenfunction of the operator \hat{A} .

These two cases need to be examined separately. The state space of a composite physical system is the **tensor product (See Section VI)** of the state spaces of the component physical systems. If we have systems number 1 to n , prepared in state $|\psi_i\rangle$, then the joint state is of the total system is: $|\psi_1\rangle \otimes |\psi_2\rangle \otimes \dots \otimes |\psi_n\rangle$

POSTULATE 5

The evolution in time of a quantum mechanical system is governed by the time-dependent Schrödinger equation:

$$\hat{H} \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$

POSTULATE 6 (See Section V)

Quantum superposition is a fundamental principle of quantum mechanics. In classical mechanics, things like position or momentum are always well-defined. We may not know what they are at any given time, but that is an issue of our understanding and not the physical system. In quantum mechanics, a particle can be **in a superposition of different states**. It can be in **two places at once** (see double-slit experiment). A measurement always finds it in one state, but before and after the measurement, it interacts in ways that **can only be explained by having a superposition of different states**. A simple demonstration of superposition can be made using a beam of light that passes through a polarizing filter.

II. QM: Schrödinger Wavefunction, Matrix, and Wigner Phase Space

We will model three Formulations of Quantum Mechanics:

Schrödinger Wavefunction, Matrix, and Wigner Phase Space

There are seven commonly used nonrelativistic formulations for quantum mechanics. These are the wavefunction, matrix, path integral, phase space, density matrix, second quantization, variational, formulations. Also mentioned are the many-worlds and transactional interpretations. The various formulations differ dramatically in mathematical and conceptual overview, yet each one makes identical predictions for all experimental results.

A. The matrix formulation (Heisenberg)

The matrix formulation of quantum mechanics, developed by Werner Heisenberg in June of 1925, was the first formulation to be uncovered. The wavefunction formulation, which enjoys wider currency today, was developed by Erwin Schrödinger about six months later.

B. The wavefunction formulation (Schrödinger)

Compared to the matrix formulation, the wavefunction formulation of quantum mechanics shifts the focus from “measurable quantity” to “state.” The state of a system with two particles ~ ignoring spin ! is represented mathematically by a complex function in six-dimensional configuration space.

C. Phase space formulation - See Section XXIV: The Wigner Quasiprobability Distribution)

For a single particle restricted to one dimension, the Wigner phase-space distribution function is

$$W(x,p,t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \psi^*(x - \frac{1}{2}y, t) \times \psi(x + \frac{1}{2}y, t) e^{-ipy/\hbar} dy$$

D. The path integral formulation (Feynman)

The path integral formulation (also called the sum-over-histories formulation) shifts the focus from “state” to “transition probability.”

E. Density matrix formulation

The density matrix corresponding to a pure state $|\psi\rangle$ is the outer product $\hat{\rho} = |\psi\rangle\langle\psi|$

Given the density matrix $\hat{\rho}$, the quantal state $|\psi\rangle$ can be found as follows: First select an arbitrary state $|\phi\rangle$.

The unnormalized ket $|\psi\rangle$ is $\hat{\rho}|\phi\rangle$ (as long as this quantity does not vanish).

F. Second quantization formulation This formulation features operators that create and destroy particles. It was developed in connection with quantum field theory, where such actions are physical effects ~ for example, an electron and a positron are destroyed and a photon is created ! .

G. Variational formulation

The “variational formulation” must not be confused with the more-commonly-encountered “variational method”, which provides a bound on the ground state energy. Instead the variational formulation provides a full picture describing any state—not just the ground state—and dictating its full time evolution—not just its energy. It is akin to Hamilton’s principle in classical mechanics.

III. Solution of Schrödinger Wave Equation for Propagation of an Electron

Given an electron of mass, m_e , velocity, v_e , kinetic energy of 1 eV

By Quantum Mechanics. it has an associated de Broglie wavelength, λ_e , and wavenumber k_0

Planck's Constant: $h := 6.626 \cdot 10^{-34} \text{ J}\cdot\text{s}$

Given: $m_e := 9.10938 \cdot 10^{-31} \text{ kg}$ $v := 1 \cdot 10^3 \frac{\text{m}}{\text{s}}$ $T_{\text{mw}} := 1 \text{ eV}$ $\lambda_e := \frac{h}{\sqrt{2 \cdot m_e \cdot T}} = 1.226 \times 10^{-9} \frac{\text{m}}{\text{Å}}$

Consider a monochromatic E Field plane wave associated with an electron which propagates in an isotropic and homogeneous medium: $E(r, t) = E_0 \cdot e^{[i \cdot (k \cdot r - \omega \cdot t)]}$

Associated with this electron is a wavenumber, k_e , amplitude, A

$$k_e := 8.637 \cdot 10^6 \cdot \frac{1}{\text{m}} \quad A_{\text{mw}} := \frac{1}{\sqrt{a \cdot \sqrt{\pi}}} \quad h_{\text{bar}} := \frac{h}{2 \cdot \pi} \quad A_m := A \cdot \sqrt{m}$$

$$eV_{\text{mw}} := 1.602 \cdot 10^{-19} \text{ J}$$

The electron has Kinetic Energy: $E_{\text{mw}} := \frac{h_{\text{bar}}^2 \cdot k_e^2}{2 \cdot m_e} \quad E = 4.554 \times 10^{-25} \text{ J} \quad \text{Electron Frequency: } \omega = 2 \pi \cdot f$

Equation of Traveling Wave:

$$\psi(x) = A \cdot e^{i \cdot (k \cdot x - \omega t)} + B \cdot e^{-i \cdot (k \cdot x + \omega t)}$$

To solve the one-dimensional Schrödinger equation for a free particle of mass m moving with velocity v , we can proceed as follows:

Solve Schrödinger's Wave Equation for the Quantum Wavefunction, $\Psi(x, t)$

$$\frac{-\hbar^2}{2 \cdot m_e} \cdot \frac{\partial^2}{\partial x^2} \Psi = i \cdot \hbar \cdot \frac{\partial}{\partial t} \Psi$$

$$\Psi(x, t) = \int_{-\infty}^{\infty} \psi(k, x, t) dk$$

$$\Psi(x, t) = \frac{A \cdot a}{\sqrt{2 \pi}} \cdot \int_{-\infty}^{\infty} \exp \left[\frac{-1}{2} a^2 \cdot (k - k_0)^2 + i \cdot k \cdot x - \frac{i \cdot h_{\text{bar}} \cdot t}{2 \cdot m_e} \cdot k^2 \right] dk$$

Evaluate the Wavefunction over the Space and Time Region:

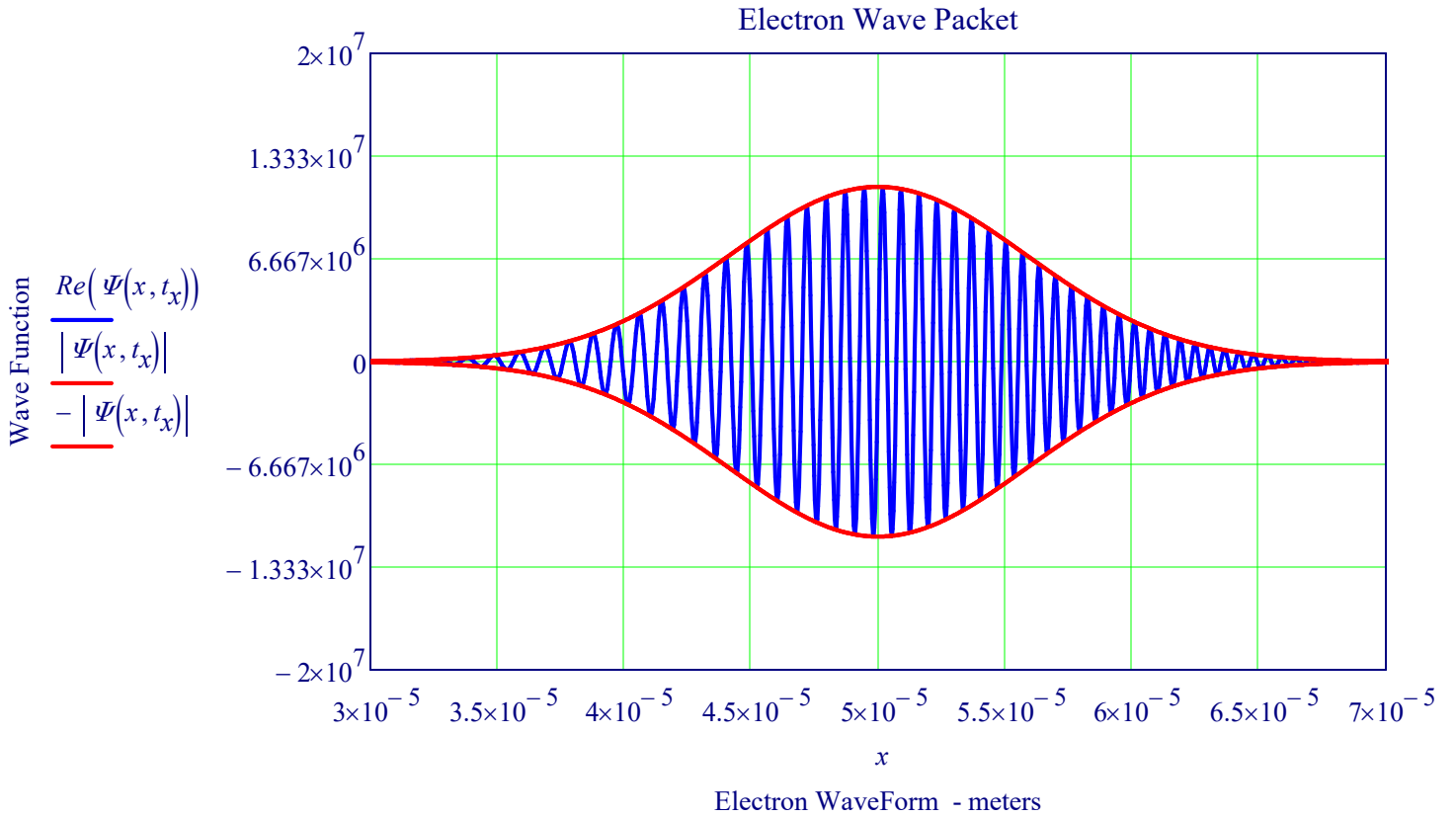
$$a_{\text{mw}} := 1 \cdot \mu\text{m} \quad t_x := 50 \text{ ns}$$

Solution for $\Psi(x, t)$:

$$\Psi(x, t) := \frac{A_m}{\sqrt{1 + \frac{i \cdot h_{\text{bar}} \cdot t}{m_e \cdot a^2}}} \cdot \exp \left[\frac{- \left(x^2 - 2 \cdot i \cdot a^2 \cdot k_e \cdot x + \frac{i \cdot h_{\text{bar}} \cdot t}{2 \cdot m_e} \cdot k_e^2 \cdot a^2 \right)}{2 \cdot a^2 \cdot \left(1 + \frac{i \cdot h_{\text{bar}} \cdot t}{m_e \cdot a^2} \right)} \right]$$

Plot Wavefunction $\Psi(x,t)$ over Distance Range, x

Distance Range: $x := 10^{-5} \cdot 2m, 10^{-5} \cdot 2m + \left(\frac{10^{-5} \cdot 8 \cdot m - 10^{-5} \cdot 2m}{2000} \right) .. 10^{-5} \cdot 8m$



IV. Numerical Schrödinger Equation Solutions: 3-D Harmonic Oscillator

Parameters:

Reduced mass: $\mu := 1$ Angular momentum: $L := 0$ Integration limit: $r_{max} := 6$ $E := 7.5$ $L := 0$
 $r := 0, 0.01 \dots r_{max}$
 Force constant: $k := 1$

Solve Schrödinger's equation numerically. Use Mathcad's ODE solve block:

Given

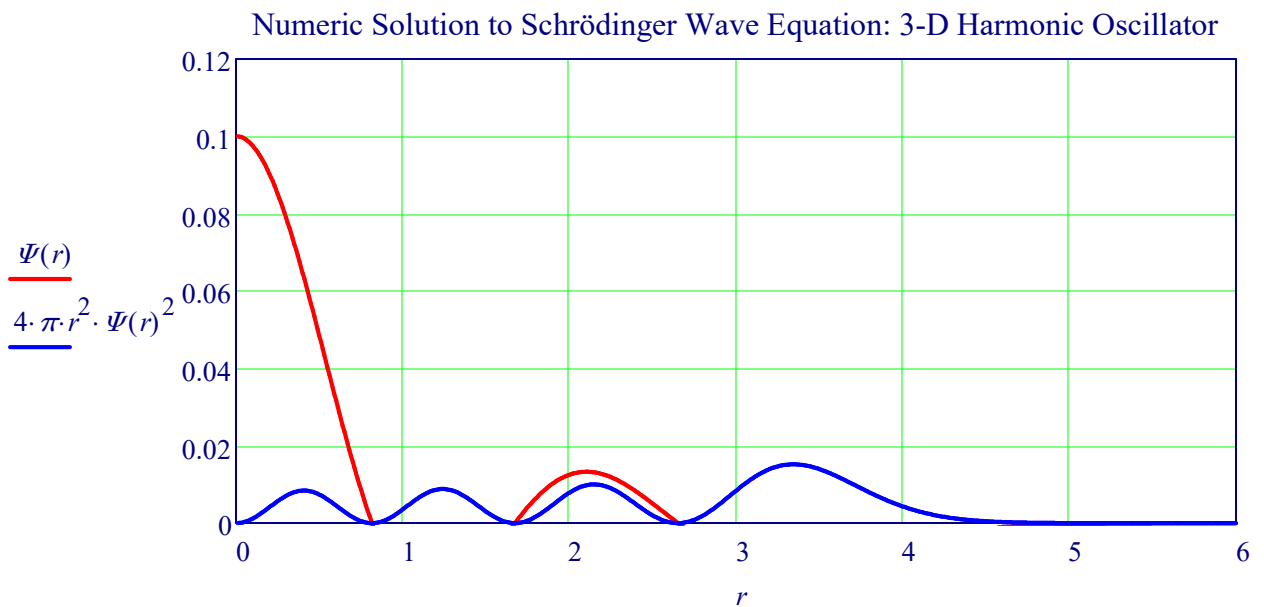
$$\frac{-1}{2 \cdot \mu} \cdot \frac{d^2}{dr^2} \Psi(r) - \frac{1}{r \cdot \mu} \cdot \frac{d}{dr} \Psi(r) + \left[\frac{L \cdot (L + 1)}{2 \cdot \mu \cdot r^2} + \frac{1}{2} \cdot k \cdot r^2 \right] \cdot \Psi(r) = E \cdot \Psi(r)$$

$$\Psi(.001) = .1 \quad \Psi'(.001) = .1$$

$$\Psi := \text{Odesolve}(r, r_{max})$$

Energy guess: $E \equiv 7.5$

$$\text{Normalize the wavefunction: } \Psi(r) := \left(\int_0^{r_{max}} \Psi(r)^2 \cdot 4 \cdot \pi \cdot r^2 \, dr \right)^{\frac{-1}{2}} \cdot \Psi(r)$$



V. Basic Quantum Mechanics in Coordinate, Momentum & Phase Space

Tutorial: *The Wigner Quasiprobability Distribution*, Wikipedia

The Wigner quasiprobability distribution (also called the Wigner function or the Wigner–Ville distribution, after Eugene Wigner and Jean-André Ville) is a quasiprobability distribution. It was introduced by Eugene Wigner in 1932 to study quantum corrections to classical statistical mechanics. The goal was to link the wavefunction that appears in Schrödinger's equation to a probability distribution in phase space.

It is a generating function for all spatial autocorrelation functions of a given quantum-mechanical wavefunction $\psi(x)$. Thus, it maps on the quantum density matrix in the map between real phase-space functions and Hermitian operators introduced by Hermann Weyl in 1927, in a context related to representation theory in mathematics (see Weyl quantization). In effect, it is the Wigner–Weyl transform of the density matrix, so the realization of that operator in phase space.

In 1949, José Enrique Moyal, who had derived it independently, recognized it as the quantum moment-generating functional, and thus as the basis of an elegant encoding of all quantum expectation values, and hence quantum mechanics, in phase space.

Relation to classical mechanics

A classical particle has a definite position and momentum, and **hence it is represented by a point in phase space**. Given a collection (ensemble) of particles, the probability of finding a particle at a certain position in phase space is specified by a probability distribution, the Liouville density. **This strict interpretation fails for a quantum particle, due to the uncertainty principle**. Instead, the above quasiprobability Wigner distribution plays an analogous role, but does not satisfy all the properties of a conventional probability distribution; and, conversely, satisfies boundedness properties unavailable to classical distributions.

For instance, the Wigner distribution can and normally does take on negative values for states which have no classical model—and is a **convenient indicator of quantum-mechanical interference**. (See below for a characterization of pure states whose Wigner functions are non-negative.) Smoothing the Wigner distribution through a filter of size larger than \hbar (e.g., convolving with a phase-space Gaussian, a Weierstrass transform, to yield the Husimi representation, below), results in a positive-semidefinite function, i.e., it may be thought to have been coarsened to a semi-classical one.

Regions of such negative value are provable (by convolving them with a small Gaussian) to be "small": they cannot extend to compact regions larger than a few \hbar , and hence disappear in the classical limit. They are shielded by the uncertainty principle, which does not allow precise location within phase-space regions smaller than \hbar , and thus renders such "negative probabilities" less paradoxical.

Definition and meaning

The Wigner distribution $W(x,p)$ of a pure state is defined as

$$W(x, p) \stackrel{\text{def}}{=} \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \psi^*(x+y)\psi(x-y)e^{2ipy/\hbar} dy,$$

where ψ is the wavefunction, and x and p are position and momentum, but could be any conjugate variable pair (e.g. real and imaginary parts of the electric field or frequency and time of a signal). Note that it may have support in x even in regions where ψ has no support in x ("beats"). It is symmetric in x and p : See the Phase Space Distribution of the Wigner Function Expressed in Dirac Notation shown on the following page.

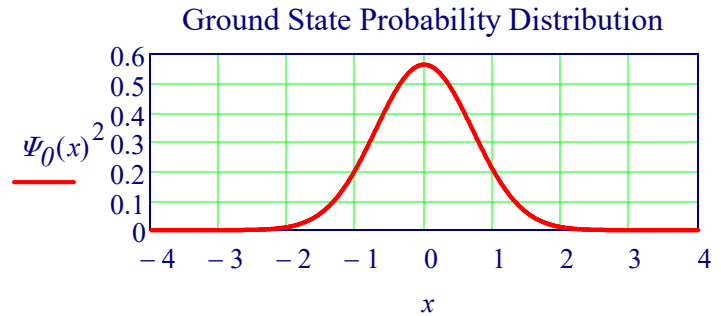
Ground State Probability Distribution for a Harmonic Oscillator: Math

We will use calculations on the harmonic oscillator to illustrate the relationship between the coordinate, momentum and phase space representations of quantum mechanics.

The first (ground state) oscillator eigenfunction is given below.

$$\Psi_0(x) := \pi^{-\frac{1}{4}} \cdot \exp\left(\frac{-x^2}{2}\right) \quad x := -4, -3.99 \dots 4$$

As is well-known, in coordinate space the position operator is multiplicative and the momentum operator is differential. In momentum space it is the reverse, while in phase space, both position and momentum are multiplicative operators.



$$\int_{-\infty}^{\infty} \Psi_0(x)^2 dx = 1 \quad x_{\text{ave}} = \int_{-\infty}^{\infty} x \cdot \Psi_0(x)^2 dx \rightarrow 0 \quad x^2_{\text{ave}} := \int_{-\infty}^{\infty} x^2 \cdot \Psi_0(x)^2 dx \rightarrow \frac{1}{2}$$

$$p_{\text{ave}} := \int_{-\infty}^{\infty} \Psi_0(x) \cdot \frac{1}{i} \cdot \frac{d}{dx} \Psi_0(x) dx \rightarrow 0 \quad p^2_{\text{ave}} := \int_{-\infty}^{\infty} \Psi_0(x) \cdot \frac{d^2}{dx^2} \Psi_0(x) dx \rightarrow \frac{1}{2}$$

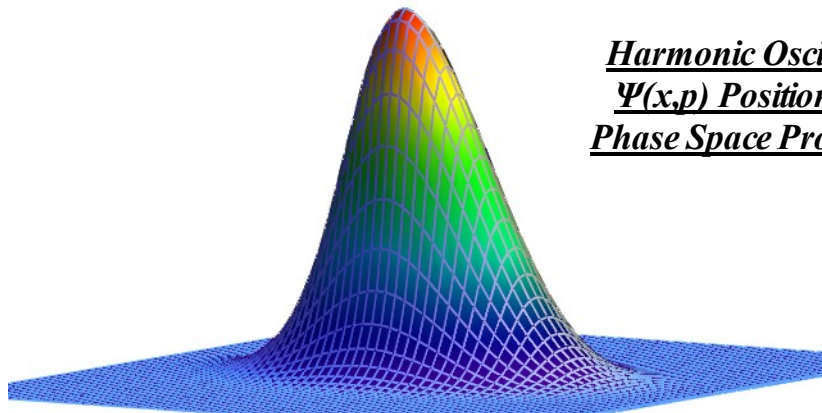
Phase Space Distribution Calculations: The Wigner Quasiprobability Distribution for a Harmonic Oscillator

Phase-space calculations require a Phase-Space Distribution, such as the Wigner function. Because this approach to quantum mechanics is not as familiar as the Schrödinger formulation, several important equations will be deconstructed using Dirac notation. **Expressed in Dirac Notation, the Wigner Function resembles a classical trajectory.**

$$W(x, p) = \int_{-\infty}^{\infty} \left\langle \Psi \left| x + \frac{s}{2} \right\rangle \left\langle x + \frac{s}{2} \right| p \right\rangle \left\langle p \left| x - \frac{s}{2} \right\rangle \left\langle x - \frac{s}{2} \right| \Psi \right\rangle ds \quad W_0(x, p) := \frac{1}{\pi} \cdot e^{-\left(\frac{x^2}{2} + p^2\right)}$$

The four Dirac brackets are read from right to left as follows: (1) is the amplitude that a particle state Ψ has at position $(x - s/2)$; 2 is the amplitude that a particle position $(x - s/2)$ has momentum p ; 3 is the amplitude that a particle has the momentum p has position $(x + s/2)$; (4) is the amplitude that a particle with position $(x + s/2)$

$$N := 60 \quad i := 0..N \quad x_i := -3 + \frac{6 \cdot i}{N} \quad j := 0..N \quad p_j := -5 + \frac{10 \cdot j}{N} \quad Wigner_{i,j} := W_0(x_i, p_j)$$



Harmonic Oscillator Ground State $\Psi(x,p)$ Position - Momentum 3-D Phase Space Probability Distribution

Wigner

In these phase-space calculations $W(x,p)$ appears to behave like a classical probability function. By eliminating the need for differential operators, it seems to have removed some of the weirdness from quantum mechanics. The Wigner function, phase-space approach only temporarily hides the weirdness generated using a Schrödinger wave function.

To see how the weirdness is hidden we generate the Wigner function for the $v=2$ harmonic oscillator state.

$$W_1(x, p) := \frac{1}{2\pi} \int_{-\infty}^{\infty} \Psi_1 \left(x + \frac{s}{2} \right) \cdot \exp(i \cdot s \cdot p) \cdot \Psi_1 \left(x - \frac{s}{2} \right) ds \text{ simplify}$$

$$W_1(x, p) := e^{-\left(x^2\right)-p^2} \cdot \frac{\left(2 \cdot x^2 + 2 \cdot p^2\right) - 1}{\pi}$$

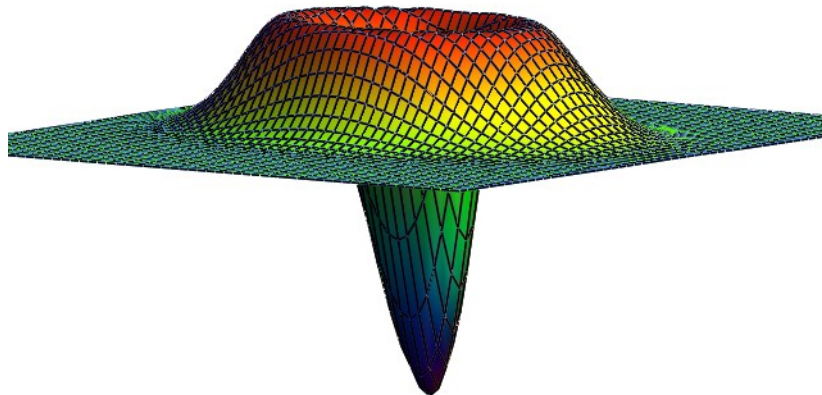
Next, it is demonstrate that the Wigner functions for the ground and excited harmonic oscillator states are orthogonal over phase space.

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_0(x, p) \cdot W_1(x, p) dx dp \rightarrow 0$$

This result indicates that $W_1(x,p)$ must be negative over some part of phase space, because the graph of $W_0(x,p)$ shows that it is positive for all values of position and momentum. To explore further we display the Wigner distribution for the $v=1$ harmonic oscillator state.

$$Wigner_{i,j} := W_1(x_i, p_j)$$

Harmonic Oscillator $v=1$ State
 $\Psi(x,p)$ Position - Momentum 3-D Phase Space
Probability Distribution



Wigner, Wigner

Quantum Numbers for Orbitals for Hydrogen and Oxygen

The principal quantum number is denoted by the letter "n" and is one of the four quantum numbers that describe the energy levels of electrons in an atom. It represents the main energy level or shell in which the electron resides.

Hydrogen Atom (H): The electron configuration of hydrogen is simply one electron in its lone electron shell. Therefore, the principal quantum number (n) for hydrogen is 1.

Hydrogen molecule (H₂)

Each hydrogen atom contributes one electron to form a covalent bond. The electron configuration of a hydrogen molecule can be represented as $(\sigma 1s)^2$, where $\sigma 1s$ is the molecular orbital formed by the combination of the two 1s atomic orbitals from each hydrogen atom. In a hydrogen molecule (H₂), the principal quantum number refers to the quantum number of the molecular orbitals that result from the combination of the atomic orbitals of the two hydrogen atoms.

The molecular orbitals in a **hydrogen molecule** can be classified as **sigma (σ) and pi (π) orbitals**.

Sigma (σ) molecular orbital: formed by the **constructive overlap** of the two 1s atomic orbitals from each H atom,

The pi (π) molecular orbitals: formed by the **sideways overlap** of the 1s atomic orbitals.

The principal quantum numbers for the molecular orbitals are as follows:

Sigma (σ) molecular orbitals: The electrons in sigma orbitals have a principal quantum number (n) of 1, as they arise from the overlap of the 1s atomic orbitals.

Pi (π) molecular orbitals: The electrons in pi orbitals also have a principal quantum number (n) of 1, as they also originate from the overlap of the 1s atomic orbitals.

Oxygen Atom, (O):

The atomic number of oxygen is 8, it has 8 electrons. **The electron configuration of oxygen is: $1s^2 2s^2 2p^4$** . Here, there are two electrons in the first energy level (n=1) and six electrons in the second energy level (n=2). So, the principal quantum number (n) for oxygen's valence electrons (outermost electrons) is 2.

An oxygen molecule (O₂)

Each oxygen atom has its set of quantum numbers for its electrons. The quantum numbers describe the properties of the electrons in the atom or molecule, including their energy levels, angular momentum, magnetic orientation, and spin.

Each oxygen atom in O₂ has the following quantum numbers:

1. Principal Quantum Number (n): The principal quantum number determines the main energy level or shell of the electron. In oxygen atoms, the electrons are distributed in different electron shells, so they have different values of n. For oxygen, the possible principal quantum numbers are 1, 2, 3, and so on.
2. Azimuthal Quantum Number (l): The azimuthal quantum number defines the subshell or orbital type. In oxygen atoms, the electrons can have l values of 0 to (n-1) for each value of n. For example, if n = 2, l can be 0 or 1.
3. Magnetic Quantum Number (m_l): The magnetic quantum number specifies the orientation of the orbital in space. For each value of l, there are (2l + 1) possible values of m_l. So, for l = 0, there is only one possible value of m_l, and for l = 1, there are three possible values of m_l.
4. Spin Quantum Number (m_s): The spin quantum number determines the spin state of the electron, either +1/2 (spin-up) or -1/2 (spin-down).

In a water molecule (H₂O), the electrons from the hydrogen atoms and the oxygen atom combine to form molecular orbitals. The specific quantum numbers for the electrons in these molecular orbitals will depend on the electron configuration and bonding of the water molecule. The interactions between the hydrogen and oxygen atoms will determine the distribution of the electrons in the molecular orbitals.

There is a mix of different types of hybrid orbitals and atomic orbitals for H₂O. Let's clarify each one:

1. **sp² Hybrid Orbitals:**

The sp² hybrid orbitals are formed when one s orbital and two p orbitals from the same atom combine to create three equivalent hybrid orbitals. These hybrid orbitals are used to explain the molecular geometry in molecules with trigonal planar geometry, like in the case of boron trifluoride (BF₃) or the double bonds in molecules like ethene (C₂H₄) and formaldehyde (CH₂O).

2. **dz² Atomic Orbital:**

The dz² orbital is one of the five d orbitals (d_{xy}, d_{yz}, d_{xz}, dz², and d_{x²-y²}) present in atoms with d orbitals. The dz² orbital has a lobed shape along the z-axis (a set of lobes above and below the xy plane) and is often associated with the d-block elements in the periodic table.

3. **d¹ Configuration:**

The term "d¹" refers to the electron configuration of an atom or ion that has one electron in its d orbital. For example, "3d¹" represents an atom/ion with one electron in the 3d orbital.

4. **3p_z Atomic Orbital:**

The 3p_z orbital is one of the three p orbitals (3p_x, 3p_y, and 3p_z) present in atoms with p orbitals. The 3p_z orbital has a dumbbell shape along the z-axis and is oriented along the z-axis.

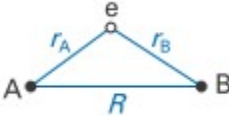
It's important to note that "Hydrogenic" typically refers to orbitals for hydrogen-like atoms, where there is **only one electron** (e.g., H, He⁺, Li²⁺). When considering atoms other than hydrogen, the term "hybrid orbitals" is more appropriate.

VI. Molecular Quantum Mechanics: Hydrogen Molecular Orbits

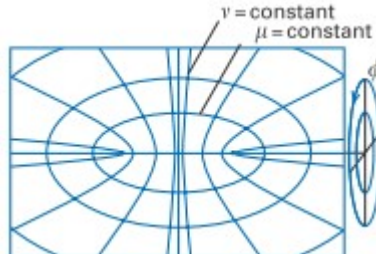
Molecular Quantum Mechanics, Peter Akins, Ronald Friedman, Oxford University Press

8.2 The hydrogen molecule-ion

Even within the Born–Oppenheimer approximation there is only one molecular species for which the Schrödinger equation can be solved exactly: the hydrogen molecule-ion, H_2^+ . The hamiltonian (H) for this species is

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R}$$


The first term represents the repulsive interaction between the two nuclei, and within the Born–Oppenheimer approximation is a constant for a given relative location of the nuclei. As H_2^+ has only one electron, it has a status in valence theory analogous to the hydrogen atom in the theory of atomic structure. Just as the Schrödinger equation for the hydrogen atom is **separable and solvable** when expressed in **spherical polar coordinates**, so the equation for H_2^+ is **separable and solvable** when expressed in ‘**ellipsoidal coordinates**’ (μ, ν, ϕ), where

$$\mu = \frac{r_A + r_B}{R} \quad \nu = \frac{r_A - r_B}{R}$$


and ϕ is the azimuthal angle around the internuclear axis. In these coordinates, the **two nuclei lie at the foci of ellipses of constant μ** . The resulting solutions are called molecular orbitals and resemble atomic orbitals but spread over both nuclei.

Molecular Orbital Theory (MO)

Even the simplest molecule, H_2^+ , consists of three particles, and its **Schrödinger equation cannot be solved analytically**. We are forced to make **an approximation**, but use the exact solutions for H_2^+ as a guide. Another reason why making a further approximation is quite sensible is that we **already have available quite good atomic orbitals** for many-electron atoms, and it seems appropriate to try to use them as a starting point for the description of many-electron molecules built from those atoms.

8.3 Linear combinations of atomic orbitals

Inspection of the form of the wavefunctions for H_2^+ suggests that they can be simulated by forming **linear combinations** of hydrogen atomic orbitals: $\psi_+ \approx \phi_a + \phi_b$ $\psi_- \approx \phi_a - \phi_b$

where ϕ_a is a $1s$ -orbital on nucleus A and ϕ_b its analogue on nucleus B. In the first case, the **accumulation of electron density** in the internuclear region is **simulated by the constructive interference** that takes place between the two waves centered on neighboring atoms. **The nodal plane** in the true wavefunction is recreated by the **destructive interference** between waves superimposed with **opposite signs**.

The partial justification for simulating molecular orbitals as an LCAO, a linear combination of atomic orbitals, can be appreciated by examining the Hamiltonian. When the electron is close to nucleus A, $r_A \ll r_B$, and the hamiltonian is approximately

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} + \frac{e^2}{4\pi\epsilon_0 R}$$

Apart from the final, constant term, this hamiltonian is the same as that for a hydrogen atom. **Therefore, close to nucleus A, the wavefunction of the electron will resemble a hydrogen atomic orbital**. The same is true close to B, and this form of the solution is captured by the two linear combinations constructed above.

8.4 The hydrogen molecule H₂

We model the electronic structure of the hydrogen molecule, H₂, by the addition of a second electron to the 1σ_g orbital, to give the configuration 1σ_g². The orbital description is therefore ψ₊(1)ψ₊(2), where the 1 and 2 in parentheses are short for r₁ and r₂, respectively, the locations of the two electrons. Writing the true wavefunction ψ(1,2) as a product is an approximation that is valid only if electron–electron interactions are ignored or replaced by some kind of average one-electron potential energy (as in the central-field approximation, Section 7.12) so that the true hamiltonian

$$H = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}} - \frac{e^2}{4\pi\epsilon_0 r_{A2}} - \frac{e^2}{4\pi\epsilon_0 r_{B2}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R}$$

is replaced by an expression of the form

$$H = H_1 + H_2 + \frac{e^2}{4\pi\epsilon_0 R}$$

where each H_i is expressed in terms of the coordinates of the **electron i alone**. The approximate spatial wavefunction ψ₊(1)ψ₊(2) is symmetric under particle interchange, so **the spin component** must be proportional to μ(1)β(2) - μ(1)α(2) to guarantee that the **overall wavefunction is anti-symmetrical**. Therefore, when the two electrons enter a single molecular orbital, they do so with paired spins (↑↓). Spin-pairing is thus seen not to be an end in itself, but the way that electrons **must arrange themselves** in order to **pack into the lowest energy orbital**.

Molecular orbital theory of Polyatomic Molecules

The molecular orbitals of polyatomic species are LCAOs just like those above:

$$\psi = \sum_r (c_r \cdot \varphi_r) \quad 8.35$$

The main difference is that now the **sum extends over all the atomic orbitals** of the atoms in the molecule. However, as for diatomic molecules, **only** atomic orbitals that have the **appropriate symmetry make a contribution**, because only they **have net overlap** with one another. When a molecule lacks any symmetry elements (other than the identity), there is no way of avoiding assembling each molecular orbital from the entire basis set. However, when the molecule has elements of **symmetry, group theory** can be particularly helpful in deciding which orbitals can contribute to each molecular orbital, and in **classifying** the resulting orbitals according to their **symmetry species**.

8.8 Symmetry-adapted linear combinations

The concept behind the construction of a **symmetry-adapted linear combination (SALC)** is to **identify two or more equivalent atoms** in a molecule, such as the two H atoms in H₂O, and to **form linear combinations** of the atomic orbitals they provide that belong to specific symmetry species. Then molecular orbitals are constructed by forming linear combinations of each SALC with an atomic orbital of the same symmetry species on the central atom (the O atom in H₂O).

Symmetry Analysis for H₂O

Water belongs to the C_{2v} symmetry group and has the following four symmetry elements: E, C₂^z, σ_{xz}, and σ_{yz}. Its character table is shown below.

It can be thought of as a four dimensional space with the A₁, A₂, B₁, and B₂ irreducible representations playing the **role of unit vectors of vector algebra**.

C _{2v}	E	C ₂ ^z	σ _{xz}	σ _{yz}	h = 4
A ₁	1	1	1	1	z, x ² , y ² , z ²
A ₂	1	1	-1	-1	xy, R _z
B ₁	1	-1	1	-1	x, xz, R _y
B ₂	1	-1	-1	1	y, yz, R _x
Γ _{tot}	-9	-1	1	3	

Orbital Angular Momentum

Molecular Physical Chemistry, José Teixeira-Dias, **Section 3.4**

3.4 Angular Momentum

In classical mechanics, the motion of one particle around a center of force can be characterized by two kinds of momenta, linear and angular momenta. Let \mathbf{r} be the vector from the center of force to the particle position,

$$\mathbf{r} = i\mathbf{x} + j\mathbf{y} + k\mathbf{z}$$

and \mathbf{v} the corresponding velocity vector,

$$\mathbf{v} \equiv \frac{d\mathbf{r}}{dt} = i\frac{dx}{dt} + j\frac{dy}{dt} + k\frac{dz}{dt}$$

The classical definitions of the linear and angular momenta are given by

$$\mathbf{p} \equiv m\mathbf{v} \quad \text{and} \quad \mathbf{L} = \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

where the components of \mathbf{L} along the x , y , and z axes are

$$L_x = yp_z - zp_y \quad L_y = zp_x - xp_z \quad L_z = xp_y - yp_x$$

3.4.1 Orbital Angular Momentum

The quantum-mechanical operators of the linear momentum are given by

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \quad \hat{p}_y = -i\hbar\frac{\partial}{\partial y} \quad \hat{p}_z = -i\hbar\frac{\partial}{\partial z}$$

The angular momentum associated with one-electron motion around a center of force is called orbital angular momentum. Substitute the above p_x into L_x leads to the expressions for the orbital angular momentum operators:

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \quad \hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \quad \hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

This operator commutes with each angular momentum component,

$$[\hat{L}^2, \hat{L}_x] = 0 \quad [\hat{L}^2, \hat{L}_y] = 0 \quad [\hat{L}^2, \hat{L}_z] = 0$$

The square of the angular momentum operator of an isolated atom commutes with each of its components.

However, no two components commute with each other. Therefore, the square of the angular momentum operator and only one of its angular momentum components, for example the z -component, have a common complete set of eigenfunctions. In spherical coordinates, the angular momentum operators involve only the variables θ and ϕ .

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \quad \hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

the last expression suggests a separation of the variables θ and ϕ in the eigenfunctions. The one-electron eigenvalue equations and quantum numbers for the square and the z -component of the angular momentum operators are given

$$\hat{L}^2 Y_\ell^m(\theta, \phi) = \ell(\ell+1)\hbar^2 Y_\ell^m(\theta, \phi) \quad \ell = 0, 1, 2, \dots$$

$$\hat{L}_z Y_\ell^m(\theta, \phi) = m\hbar Y_\ell^m(\theta, \phi) \quad m = -\ell, -\ell+1, \dots, 0, \dots, \ell-1, \ell$$

where the eigenfunctions

$$Y_\ell^m(\theta, \phi) = \sqrt{\frac{2\ell+1(\ell-m)!}{4\pi(\ell+m)!}} P_\ell^m(\cos\theta) e^{im\phi}$$

are called spherical harmonics and P_ℓ^m are the associated Legendre polynomials. See the Section below: **VII. 3D Plots.**

VII. 3D Plots of sp^2 , dz^2 , d^1 , $3p^z$ Hydrogenic Hybrid Orbitals

Molecular Quantum Mechanics, Atkins Chapter 3: Rotational Motion - Spherical Harmonics
Quantum Chemistry, Levine, Chapter 6: The Hydrogen Atom

3D Plots of three sp^2 Hydrogenic Hybrid Orbitals

Generate the three sp^2 Spherical Harmonic Hybrid Orbitals and represent them graphically

$$i := 0..30 \quad \theta_i := \frac{\pi \cdot i}{30} \quad j := 0..40 \quad \phi_j := \frac{2\pi \cdot j}{40}$$

The two p orbitals are represented by the corresponding spherical harmonics The s orbital can be represented simply by a constant:

$$px_{i,j} := \sin(\theta_i) \cdot \cos(\phi_j) \quad py_{i,j} := \sin(\theta_i) \cdot \sin(\phi_j)$$

Define the three hybrid orbitals, using the s orbital radius to be 1/3

$$\text{The first hybrid orbital, } sp^2(1) \quad sp21_{i,j} := \left| \frac{0.333}{\sqrt{3}} + \sqrt{\frac{2}{3}} \cdot px_{i,j} \right|$$

$$\text{The second hybrid orbital, } sp^2(2) \quad sp22_{i,j} := \left| \frac{0.333}{\sqrt{3}} - \frac{1}{\sqrt{6}} \cdot px_{i,j} - \frac{1}{\sqrt{2}} \cdot py_{i,j} \right|$$

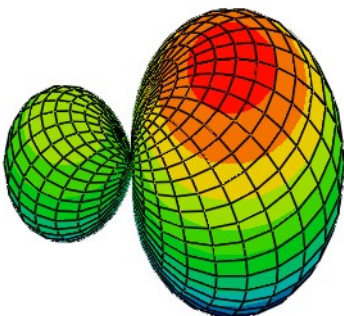
$$\text{The third hybrid orbital, } sp^2(3) \quad sp23_{i,j} := \left| \frac{0.333}{\sqrt{3}} - \frac{1}{\sqrt{6}} \cdot px_{i,j} + \frac{1}{\sqrt{2}} \cdot py_{i,j} \right|$$

Define the x, y, z coordinates for the parametric plots:

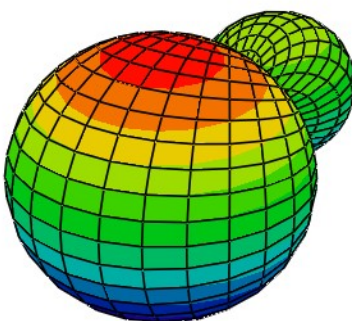
$$x1_{i,j} := sp21_{i,j} \cdot \sin(\theta_i) \cdot \cos(\phi_j) \quad x2_{i,j} := sp22_{i,j} \cdot \sin(\theta_i) \cdot \cos(\phi_j) \quad x3_{i,j} := sp23_{i,j} \cdot \sin(\theta_i) \cdot \cos(\phi_j)$$

$$y1_{i,j} := sp21_{i,j} \cdot \sin(\theta_i) \cdot \sin(\phi_j) \quad y2_{i,j} := sp22_{i,j} \cdot \sin(\theta_i) \cdot \sin(\phi_j) \quad y3_{i,j} := sp23_{i,j} \cdot \sin(\theta_i) \cdot \sin(\phi_j)$$

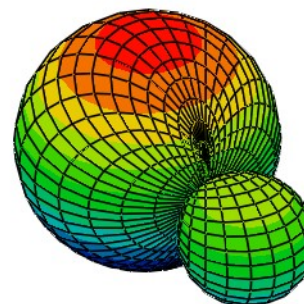
$$z1_{i,j} := sp21_{i,j} \cdot \cos(\theta_i) \quad z2_{i,j} := sp22_{i,j} \cdot \cos(\theta_i) \quad z3_{i,j} := sp23_{i,j} \cdot \cos(\theta_i)$$



$(x1, y1, z1)$



$(x2, y2, z2)$



$(x3, y3, z3)$

3D Plot of dz^2 Hydrogenic Hybrid Orbital

Generate the dz^2 hybrid orbital and represent it graphically

$$i := 0..31 \quad \theta_i := \frac{\pi \cdot i}{31} \quad j := 0..41 \quad \phi_j := \frac{2\pi \cdot j}{41}$$

Thus, θ goes from 0 to π , and ϕ goes from 0 to 2π . Now, define the spherical harmonic corresponding to the desired orbital (the angular part) Y_{lm} as a function of θ and ϕ , using the definitions of the angular parts for the atomic orbitals. Let us examine the $3d_z^2$ orbital, for which Y_{lm} is defined as:

Create a Parametric Plot of (x,y,z)

Spherical Harmonic Functions, Y_{lm}

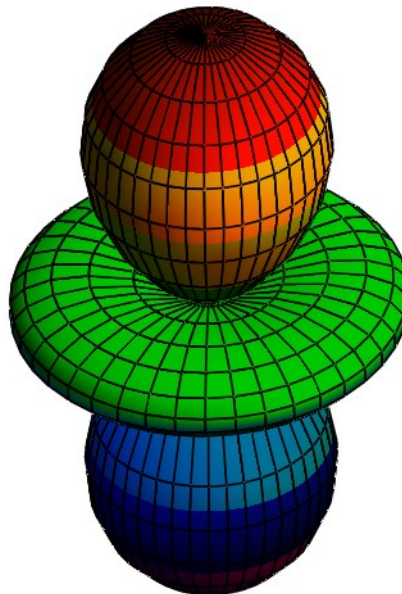
$$Y_{lm_{i,j}} := \left| 3 \cos(\theta_i)^2 - 1 \right|$$

$$x_{i,j} := Y_{lm_{i,j}} \cdot \sin(\theta_i) \cos(\phi_j)$$

$$y_{i,j} := Y_{lm_{i,j}} \cdot \sin(\theta_i) \sin(\phi_j)$$

$$z_{i,j} := Y_{lm_{i,j}} \cdot \cos(\theta_i)$$

The dz^2 Orbital



(x, y, z)

Generalized Plots of 3D Plots of Hydrogenic Hybrid Orbitals

We will plot hydrogen orbitals given the orbital quantum numbers conventional parameters: n, l, m

$Y(l, m, \theta, \phi)$ is the spherical harmonic or angular part of an orbital, where l is the angular momentum (azimuthal) quantum number and m is the magnetic quantum number. θ is the angle with the z axis in spherical coordinates and ϕ is the angle around the z axis in spherical coordinates.

$Y(l, m, \theta, \phi)$ Spherical Harmonics

Radial Component 3p (S is Slater Orbital)

d_{z^2} Orbital Quantum Numbers

$n=1$
 $l=2$
 $m=0$
 θ Angle with z -axis
 ϕ Azimuthal z -axis

Electron Constants:

$$a_0 := \frac{\epsilon_0 \cdot h^2}{\pi \cdot m \cdot e^2 \cdot q_e^2}$$

$$R_{3p}(r) := \frac{1}{81} \cdot \sqrt{2} \cdot \sqrt{3} \cdot r \cdot e^{-\frac{1}{3}r} \cdot \left(4 - \frac{2}{3}r\right)$$

$$R_{3pS}(r) := \frac{2}{1215} \cdot \sqrt{2} \cdot \sqrt{15} \cdot r^2 \cdot e^{-\frac{1}{3}r}$$

$$\zeta(\theta, \phi, l, m) := \sum_{i=0}^{l-|m|} \left[\frac{(l!)^2 \cdot (\cos(\theta) - 1)^{l-|m|-i} \cdot (\cos(\theta) + 1)^i}{(l-i)! \cdot i! \cdot (l-|m|-i)! \cdot (|m|+i)!} \right] \cdot e^{i \cdot m \cdot \phi} \quad \zeta(\pi, 2\pi, 1, 1) = 1$$

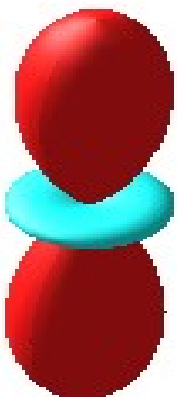
$$\xi(\theta, l, m) := \sqrt{(2l+1) \cdot (l-|m|)! \cdot (l+|m|)!} \cdot \sin(\theta)^{|m|} \quad \xi(\pi, 2, 0) = 4.472$$

$$\chi(r, \theta, \phi, n, l, m) := \sum_{i=0}^{n-l-1} \left[\frac{(-1)^i \cdot (n+l)! \cdot \left(\frac{2r}{n \cdot a_0}\right)^i}{(n-l-1-i)! \cdot (2l+1+i)! \cdot i!} \right] \cdot \xi(\theta, l, m) \cdot \zeta(\theta, \phi, l, m)$$

$$\Psi(r, \theta, \phi, n, l, m) := \frac{1}{\sqrt{\pi \cdot l!}} \cdot \left[\frac{\sqrt{(n-l-1)!}}{n \cdot [(n+l)!]^3} \cdot \left(\frac{1}{n \cdot a_0}\right)^{\frac{3}{2}} \cdot \left(\frac{r}{n \cdot a_0}\right)^l \cdot e^{-\frac{r}{n \cdot a_0}} \cdot (n+l)! \cdot \chi(r, \theta, \phi, n, l, m) \right]$$

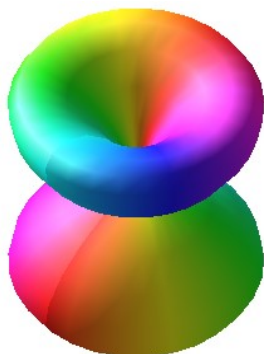
Ψ Plot Orbital d_{z^2}

$l=2, m=0$



Ψ Plot Orbital d_{xy}

$l=2, m=1$



Ψ Plot Orbital $3p_z$

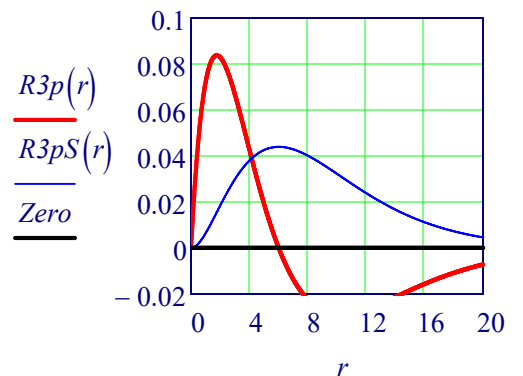
$l=1, m=0$



Radial 3p Component

$Y(2, 1, \theta, \phi)$

Radial Distribution



Note: The above orbitals were plotted with Maple Version 2020

VIII. Linear Combination of Atomic Orbitals (LCAO)

Molecular Quantum Mechanics, Atkins Chapter 8: An Introduction to Molecular Structure

A molecular orbital is a **one-electron wavefunction** for an electron that spreads throughout the molecule. The mathematical forms of such orbitals are highly complicated, even for such a simple species as H_2 , and they are unknown in general. All modern work builds approximations to the **true molecular orbital** by building them **from the atomic orbitals** of the atoms present in the molecule.

$$\text{Molecular Orbital: } \psi = a \psi_1 + b \psi_2$$

ψ_1 and ψ_2 are wavefunctions for molecules with different electron distributions and the same nuclear locations

The quantum mechanical treatment of bonding in molecules, including water (H_2O), is often based on the Linear Combination of Atomic Orbitals - Molecular Orbital (LCAO-MO) approach. This method provides a theoretical framework for describing the electronic structure and bonding in molecules. In the LCAO-MO approach, the wave function (Ψ) of a molecule is expressed as a linear combination of atomic orbitals (AOs) belonging to the constituent atoms. The molecular orbitals (MOs) are formed by combining these atomic orbitals **with appropriate coefficients** (expansion coefficients). **The coefficients** represent the **contributions of each atomic orbital** to the molecular orbital, and they are determined through quantum mechanical calculations.

For water, the LCAO-MO approach involves combining the atomic orbitals of the two hydrogen atoms and the oxygen atom to generate a set of molecular orbitals. The molecular orbitals are **classified as bonding, antibonding, and nonbonding orbitals**, depending on their **energy levels** and **symmetry properties**.

In a simplified description, the LCAO-MO treatment of water considers the **1s** atomic orbitals of the **hydrogen atoms** and the **2s** and **2p** atomic orbitals of the **oxygen atom**. These atomic orbitals combine to form a series of molecular orbitals. **The two lowest-energy** molecular orbitals are typically the **bonding orbitals**, where **electrons are more likely to be found**, promoting the formation of the covalent O-H bonds. **The antibonding orbital is higher in energy** and has a **node between** the hydrogen atoms, which **destabilizes the molecule**. The **nonbonding orbital** has **no significant contribution to bonding** and contains a **lone pair** of electrons **localized on the oxygen atom**.

The LCAO-MO approach **provides valuable insights** into the **electronic structure and bonding of water**, helping to **explain its bent molecular geometry**, the nature of covalent and noncovalent bonds, as well as its overall chemical behavior. Although it involves simplifications and approximations, it is a powerful tool for understanding the quantum mechanics of molecular systems, including water.

Some Methods of Application of LCAO to QM Analysis of Water Orbitals

Ab initio calculations for water: "Ab initio" refers to methods that rely on basic and established laws of nature without additional approximations. In this context, it would refer to calculations done from the basic principles of QM.

Hartree-Fock calculations: A specific form of ab initio calculation that is often performed using LCAO. This method accounts for electron-electron repulsion in a simplified way, which makes it computationally tractable for small molecules.

Density Functional Theory (DFT): DFT is another method for calculating the electronic structure of molecules, which can also be done using LCAO. It's more approximate than Hartree-Fock, but often more accurate for certain properties.

Basis sets for water: The "basis set" is the **set of functions (usually atomic orbitals)** that are combined in the LCAO method. Different basis sets can lead to different results, so the choice of basis set is a major topic of study in Q chemistry.

Electron correlation in water: Electron correlation refers to the ways in which the motions of electrons in a molecule are linked to each other. This is another major topic of study in quantum chemistry that often involves the use of LCAO.

Generating Molecular Orbitals by Linear Combination of Atomic Orbitals (LCAO-MO)

This problem can be very easily solved using the Variational Method. The most sensible trial function to use is one made up of a linear combination of **1s orbitals** centered on each of the two nuclei. The **nuclei themselves** are at a fixed **distance R** from each other (Born-Oppenheimer approximation). Let us assume that **R** corresponds to the **minimum energy configuration** (or equilibrium bond length) of the two nuclei. Let us further assume that this is **approximately twice** the H-H distance in the **neutral H₂ molecule**. Define our constants. Distances are measured in Angstroms.

[See Illustration Below: Examine the Molecular Orbitals of the Hydrogen molecular Ion H₂⁺](#)

$$\underset{\text{Angstroms}}{R} := 2 \quad \underset{\text{Angstroms}}{a_0} := 0.52917 \quad Z := 1$$

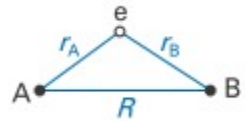
Define the overlap integral (which depends mainly on the distance between the nuclei):

$$\underset{\text{Angstroms}}{S} := \left(1 + R + \frac{R^2}{3} \right) \cdot \exp(-R) \quad S = 0.586$$

Now, for plotting purposes, we need to establish a GLOBAL coordinate system applicable to the entire molecular orbital. The atomic orbitals themselves are defined with respect to the respective nuclei. Let us establish the **origin** for the GLOBAL coordinate system **midway between the two nuclei**, and assume that the molecule is oriented along the **X-axis**. So, nucleus A is at (x, y) = (-R/2, 0), and nucleus B is at (x, y) = (+R/2, 0).

$$\underset{\text{Angstroms}}{N} := 30 \quad \underset{\text{Angstroms}}{a} := 3 \quad b := 6 \quad i := 1..N \quad j := 1..N$$

$$\text{Distances: } x_i := -a + 2 \cdot \frac{i}{N} \cdot a \quad y_j := -b + \frac{2 \cdot j}{N} \cdot b$$



$$r_{A_{i,j}} := \sqrt{\left(x_i + \frac{R}{2}\right)^2 + (y_j)^2}$$

$$r_{B_{i,j}} := \sqrt{\left(x_i - \frac{R}{2}\right)^2 + (y_j)^2}$$

$$\phi_{1sA_{i,j}} := 2 \cdot \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \exp\left(\frac{-Z}{a_0} r_{A_{i,j}}\right)$$

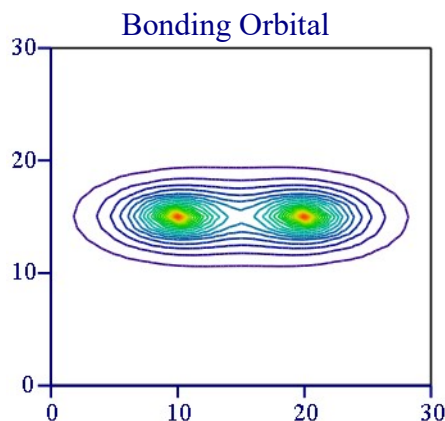
$$\phi_{1sB_{i,j}} := 2 \cdot \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \exp\left(\frac{-Z}{a_0} r_{B_{i,j}}\right)$$

$$\text{Bonding Orbital: } \sigma_{g1s_{i,j}} := \frac{1}{\sqrt{2 \cdot (1 + S)}} \cdot (\phi_{1sA_{i,j}} + \phi_{1sB_{i,j}})$$

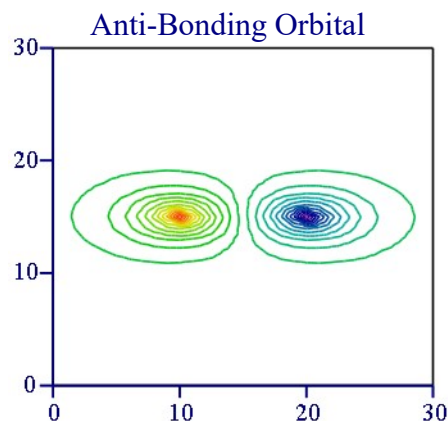
$$\text{Anti-Bonding Orbital: } \sigma_{u1s_{i,j}} := \frac{1}{\sqrt{2 \cdot (1 - S)}} \cdot (\phi_{1sA_{i,j}} - \phi_{1sB_{i,j}})$$

If the atomic orbitals are combined with different phases, they interfere destructively and an **antibonding molecular orbital** is formed.

Antibonding molecular orbitals have a higher energy than the atomic orbitals from which they were formed.



σ_{g1s}



σ_{u1s}

Defining and Plotting Molecular Orbitals from 2p orbitals:

Molecular orbitals formed by the 2px orbitals on nuclei A and B. Assume that the overlap integral S has the same value as before, even though this is will not really be the case. The angular part of the 2px orbital can be converted to cartesian coordinates to give $\sim x/r$. Define x for atomic orbitals centered at each nucleus:

$$xA_i := x_i + \frac{R}{2} \quad xB_i := x_i - \frac{R}{2} \quad Z := 1.5$$

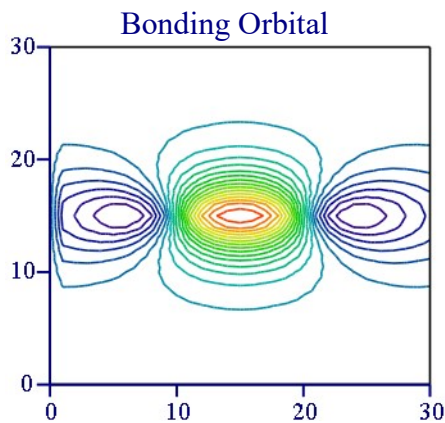
Redefine Z to make the more diffuse p orbitals fit in the range of x and y we have chosen above. Since Z is now treated as a parameter, it can take on ANY value, not just integers.

$$\phi_{2pA_{i,j}} := \frac{1}{\sqrt{3}} \cdot \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} xA_i \cdot \exp\left(\frac{-Z rA_{i,j}}{a_0}\right) \quad \phi_{2pB_{i,j}} := \frac{1}{\sqrt{3}} \cdot \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} xB_i \cdot \exp\left(\frac{-Z rB_{i,j}}{a_0}\right)$$

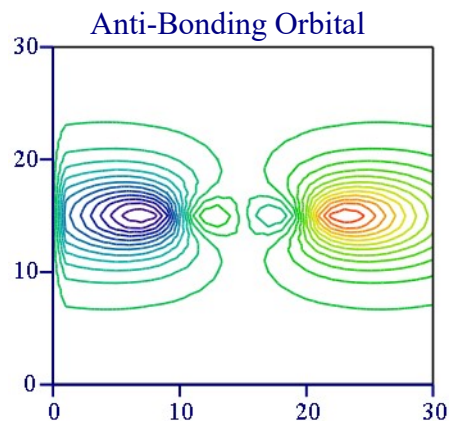
The σ bonding and anti-bonding orbitals:

Bonding Orbital: $\sigma_{g2p_{i,j}} := \frac{1}{\sqrt{2 \cdot (1 - S)}} \cdot (\phi_{2pA_{i,j}} - \phi_{2pB_{i,j}})$

Anti-Bonding Orbital: $\sigma_{u2p_{i,j}} := \frac{1}{\sqrt{2 \cdot (1 + S)}} \cdot (\phi_{2pA_{i,j}} + \phi_{2pB_{i,j}})$

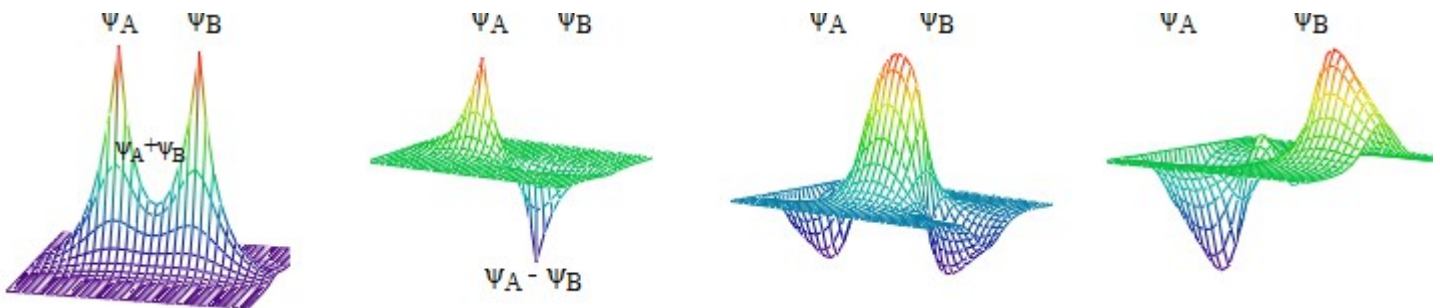


σ_{g2p}



σ_{u2p}

Mathcad 3D Perspective Plots of Hydrogenic Molecular Orbitals: Waveforms ψ_A and ψ_B are shown below



IX. Molecular Structure of Water

Physical Chemistry for the Biosciences, Chang, Chapter 13

Table 13.4
Interactions Between Molecules

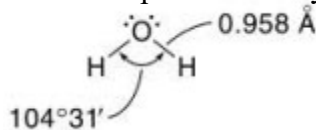
Type of Interaction	Distance Dependence	Example	Order of Magnitude (kJ mol ⁻¹) ^a
Covalent bond ^b	No simple expression	H–H	200–800
Ion–ion	$\frac{q_A q_B}{4\pi\epsilon_0 r}$	Na ⁺ Cl ⁻	40–400
Ion–dipole	$\frac{q\mu}{4\pi\epsilon_0 r^2}$	Na ⁺ (H ₂ O) _n	5–60
Dipole–dipole	$\frac{2}{3} \frac{\mu_A^2 \mu_B^2}{(4\pi\epsilon_0)^2 r^6} \frac{1}{k_B T}$	SO ₂ SO ₂	0.5–15
Ion–induced dipole	$\frac{1}{2} \frac{\alpha q^2}{4\pi\epsilon_0 r^4}$	Na ⁺ C ₆ H ₆	0.4–4
Dipole–induced dipole	$\frac{\alpha\mu^2}{4\pi\epsilon_0 r^6}$	HCl C ₆ H ₆	0.4–4
Dispersion	$\frac{3}{4} \frac{\alpha^2 I}{r^6}$	CH ₄ CH ₄	4–40
Hydrogen bond	No simple expression	H ₂ O···H ₂ O	4–40

13.5 The Structure and Properties of Water

Water is so common a substance that we often overlook its unique properties. For example, given its molar mass, water should be a gas at room temperature, but due to hydrogen bonding, it has a boiling point of 373.15 K at 1 atm. In this section, we shall study the structure of ice and liquid water and consider some biologically significant aspects of water.

The Structure of Ice

To understand the behavior of water, we must first investigate the structure of ice. There are nine known crystalline forms of ice; most of them stable only at high pressures. Ice I, the familiar form, has been studied thoroughly. It has a density of 0.924 g mL⁻¹ at 273 K and 1 atm pressure. There is a significant difference between H₂O and other polar molecules, such as NH₃ and HF. The number of hydrogen atoms in a water molecule that can form the positive ends of hydrogen bonds is equal to the number of lone pairs on the oxygen atom that can form the negative ends:



The result is an extensive three-dimensional network in which each oxygen atom is bonded tetrahedrally to four hydrogen atoms by means of two covalent bonds and two hydrogen bonds. This equality in number of protons and lone pairs is not characteristic of NH₃ and HF. Consequently, NH₃ and HF can form only rings or chains and not an extensive three-dimensional structure. Figure 13.10 shows the structure of ice I. The distance between adjacent oxygen atoms is 2.76 Å. The O–H distance is between 0.96 Å and 1.02 Å, and the O···H distance is between 1.74 Å and 1.80 Å. Because of its open lattice, ice has a lower density than water. Water reaches its maximum density at 277.15 K (4 K above freezing). Cooling below 277.15 K decreases the density of water and allows it to rise to the surface, where freezing occurs. An ice layer formed on the surface does not sink; just as

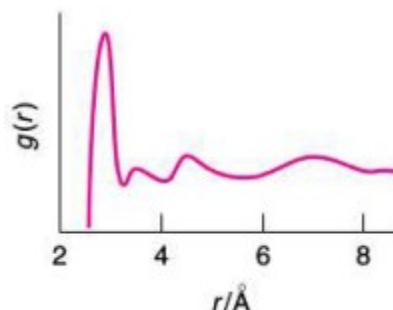
important, it acts as a thermal insulator to protect the biological environment beneath it.

The Structure of Water

Although using the word structure may seem strange when discussing liquids, most liquids possess short-range order. A convenient way to study the structure of liquids is to use the **radial distribution function, $g(r)$** . This function is defined so that $4\pi r^2 g(r) dr$ gives the probability that a molecule will be found in a spherical shell of width dr at distance r from the center of another molecule. For a crystalline solid, a plot of $g(r)$ versus r gives a series of sharp lines because crystals have long-range order. In contrast, as Figure 13.11 shows, the radial distribution curve for liquid water at 4°C produces a major peak at 2.90 Å, with weaker peaks at 3.50 Å, 4.50 Å, and 7.00 Å.

Figure 13.11

Experimental radial distribution curve for water at 4°C. The peaks become broader at higher temperatures.



Beyond 7.00 Å, the function is essentially zero, meaning that the local order does not extend beyond this distance. X-ray diffraction studies of ice shows that the O-O distance is 2.76 Å. The strong peak at 2.90 Å suggests a very similar tetrahedral arrangement in the liquid. The peak at 3.50 Å does not correspond to any bond distance in ice I, which does, however, have interstitial sites at a distance of 3.50 Å from each O atom. Therefore, when ice melts, some of the water molecules break loose and become trapped in these interstitial sites, which are responsible for the peak at 3.50 Å. The peaks at 4.50 Å and 7.00 Å are also consistent with the tetrahedral arrangement.

The above discussion suggests that the extensive three-dimensional hydrogen-bonded structure that characterizes ice I is largely intact in water, although the bonds may become bent and distorted. On melting, monomeric water molecules occupy holes in the remaining "icelike" lattice, causing the density of water to be greater than that of ice. As temperature increases, more hydrogen bonds are broken, but at the same time the kinetic energy of molecules increases. Consequently, more water molecules are trapped, but the elevated kinetic energy decreases the density of water because the molecules occupy a greater volume. Initially, the trapping of monomeric water molecules outweighs the expansion in volume due to the increase in kinetic energy, so the density rises from 0°C to 4°C. Beyond this temperature, the expansion predominates, so the density decreases with increasing temperature (Figure 13.12).

Hydrophobic Interaction

Oil and water do not mix. The reason seems to be that the dipole-induced dipole and dispersion forces between water and nonpolar oil molecules are weak. From this observation, we might conclude that the enthalpy of mixing (ΔH) is positive, which causes ΔG to be positive ($\Delta G = \Delta H - T\Delta S$). Thus, the solubility of oil in water is very low. But this explanation is incorrect. The unfavorable interaction is primarily due to the hydrophobic interaction (also called the hydrophobic effect or hydrophobic bond). The thermodynamic quantities for the transfer of small non-polar molecules from nonpolar solvents to water: ΔS is negative for all of the compounds. When nonpolar molecules enter the aqueous medium, some hydrogen bonds must be broken to make room or create a cavity for the solutes. This part of the interaction is endothermic because the broken hydrogen bonds are much stronger than the dipole-induced dipole and dispersion interactions. Each solute molecule is now trapped in an icelike cage structure, referred to as the clathrate cage model, which consists of a specific number of water molecules held together by hydrogen bonds (Figure 13.13). The formation of the clathrate has two important consequences. First, the newly formed hydrogen bonds (an exothermic process) can partly or totally compensate for the hydrogen bonds that were broken initially to make the cavity. This explains why ΔH could be negative, zero, or positive for the overall process. Furthermore, because the cage structure is highly ordered (a decrease in the number of

microstates), there is **an appreciable decrease in entropy**, which far outweighs the increase in entropy due to the mixing of solute and water molecules, so that ΔS is **negative**. Thus, the immiscibility of non-polar molecules and water, or the hydrophobic interaction, is entropy driven rather than enthalpy driven.*

Hydrophobic interaction has a profound effect on the structure of proteins. When the polypeptide chain of a protein folds into a three-dimensional structure in solution, the nonpolar amino acids (for example, alanine, phenylalanine, proline, tryptophan, and valine) are in the interior of the macromolecule and have little or no contact with water, while the polar amino acid residues (such as arginine, aspartic acid, glutamic acid, and lysine) are on the exterior. An insight into this entropy-driven process can be gained by considering just two nonpolar molecules in aqueous solution (Figure 13.14). The hydrophobic interaction causes the nonpolar molecules to come together into a single cavity to reduce the unfavorable interactions with water by decreasing the surface area. This response destroys part of the cage structure, resulting in an increase in ΔS and hence a decrease in ΔG . Moreover, enthalpy increases ($\Delta H > 0$) because some of the hydrogen bonds in the original cage structures are broken. Similarly, the folding of a protein is an example of this phenomenon because it minimizes the exposure of nonpolar surfaces to water.

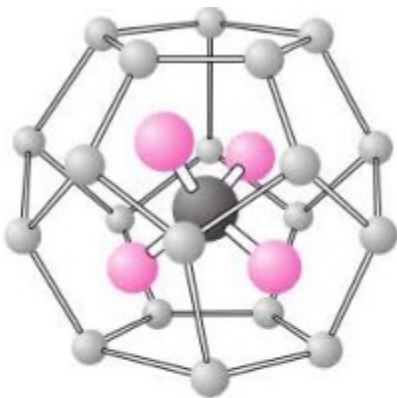
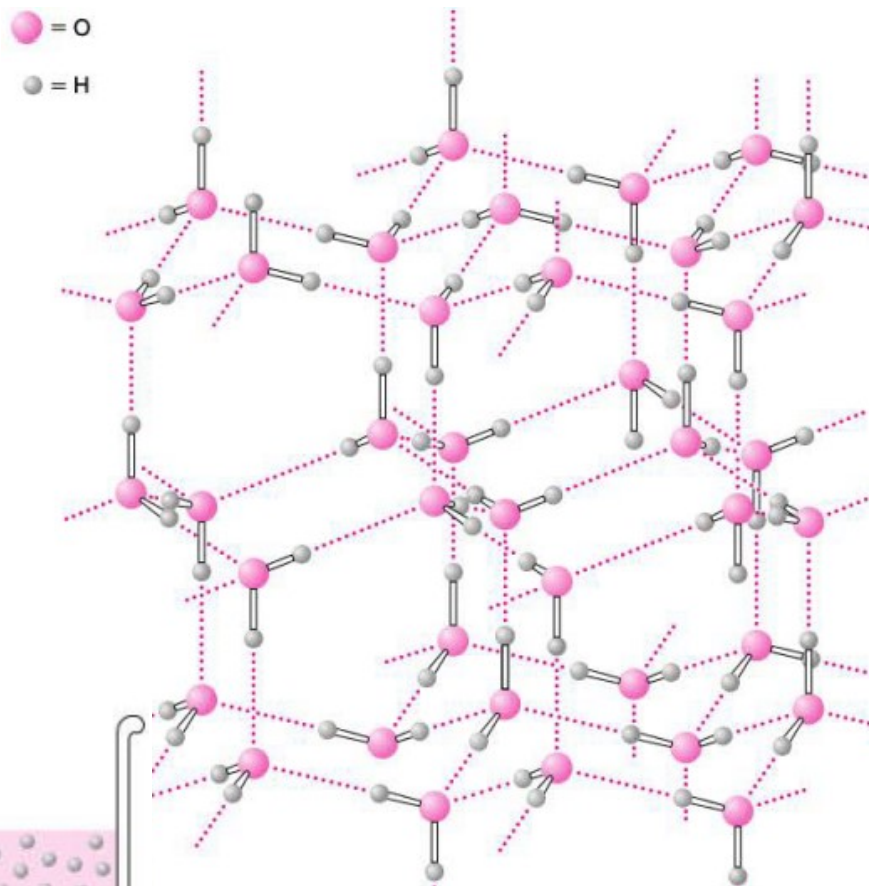


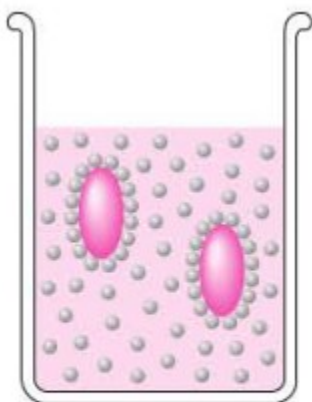
Figure 13.13
A probable structure for methane in water, called methane hydrate. The methane molecule is trapped in a cage of water molecules (gray spheres) held together by hydrogen bonds.

Figure 13.10
Structure of ice. The red dotted lines represent hydrogen bonds.

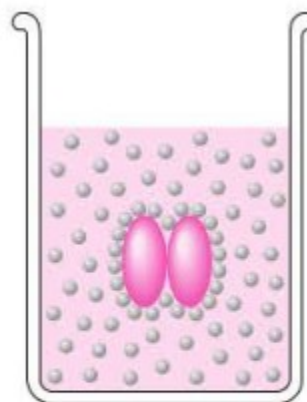


Left: The dissolution of nonpolar molecules in water is unfavorable because of the large decrease in entropy resulting from clathrate formation, even though the process is exothermic ($\Delta H < 0$). Consequently, $\Delta G > 0$.

Right: As a result of hydrophobic interaction, the nonpolar molecules come together, releasing some of the ordered water molecules in the clathrate structure and thus increasing entropy. This is a thermodynamically favorable process ($\Delta S > 0$), even though it is endothermic ($\Delta H > 0$) because more hydrogen bonds are broken than are made.



Nonpolar solutes
 $\Delta H < 0$
 $\Delta S < 0$
 $\Delta G > 0$



Hydrophobic interaction
 $\Delta H > 0$
 $\Delta S > 0$
 $\Delta G < 0$

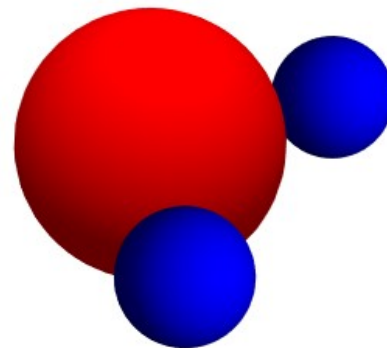
Plotting the Structure of a Water Molecule Using Mathematica 12.1

See for example: *Molecular Physical Chemistry*, José Teixeira-Dias, Section 3.4

Below is the Mathematica Code that was used to Generate the 3D Water Plots

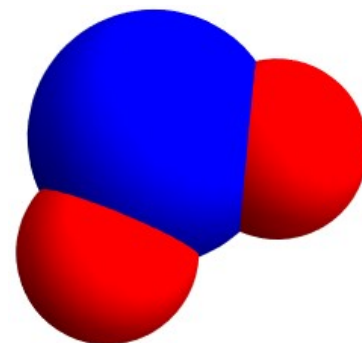
(*Hybridization of Water: Define the Mathematica Molecular Parameters for Water, e.g. radii*)

```
radiusO=0.66;(*Oxygen*)radiusH=0.31;(*Hydrogen*)(*Define the atoms*)
oxygen={radiusO,{0,0,0}};
hydrogen1={radiusH,{Cos[104.5/2 Degree],Sin[104.5/2 Degree],0}};
hydrogen2={radiusH,{Cos[104.5/2 Degree],-Sin[104.5/2 Degree],0}};
(*Define the bonds*)
bond1=Line[{oxygen[[2]],hydrogen1[[2]]};
bond2=Line[{oxygen[[2]],hydrogen2[[2]]};
(*Define the spheres for the atoms*)
sphereO={Red,Sphere[oxygen[[2]],oxygen[[1]]];
sphereH1={Blue,Sphere[hydrogen1[[2]],hydrogen1[[1]]};
sphereH2={Blue,Sphere[hydrogen2[[2]],hydrogen2[[1]]};
(*Create the 3D plot*)
Graphics3D[{sphereO,sphereH1,sphereH2,bond1,bond2},Boxed->False]
```



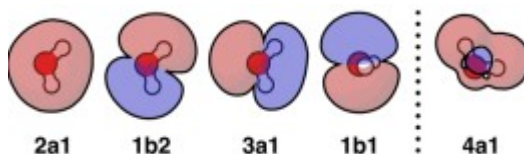
(*Plot a 3D Representation of a Water Molecule with ROR= 0.9611 Angstrom*)

```
Graphics3D[{Red,Sphere[{0,0.760117,-0.470585},0.7],
Sphere[{0,-0.760117,-0.470585},0.7],Blue,Sphere[{0,0,0.117646}],
Lighting->"Neutral",Boxed->False,ViewPoint->Right]
```



The molecular orbitals (MOs) of water are shown in the figure below.

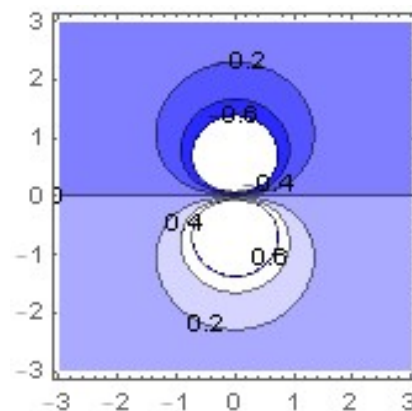
The four orbitals to the left of the dashed line each contain two electrons. To the right of the dashed line is the first empty orbital (lowest unoccupied molecular orbital, or LUMO); this plays a role in water hydrogen bonding.



Electrostatic Potential Contours for a Dipole

The following Mathematica code generates contour plots in the xy-plane for the electrostatic potential of a distribution of two charges (-1 and 1), located on the y-axis, at y=0.5 and y=-0.5.

```
Clear[f]
f[q_p_r]:=Sum[q[[i]]/Norm[r-p[[i]]],{i,Length[q]}]
q={-1,1}
Length[q]
q[[1]],q[[2]],p={{0,0.5},{0,-0.5}},p[[1]],p[[2]]
c=Table[Lighter[Blue,i],{i,0,1,1/6}]
ContourPlot[f[q,p,{x,y}],{x,-3,3},{y,-3,3},
ContourShading->c,ContourLabels->True,PlotPoints->{150,150},ImageSize->{300,300}]
```



Hybridization of Water

<https://byjus.com/jee/hybridization-of-h2o/#:~:text=So%20if%20we%20observe%20the,are%20occupied%20by%20lone%20pairs>

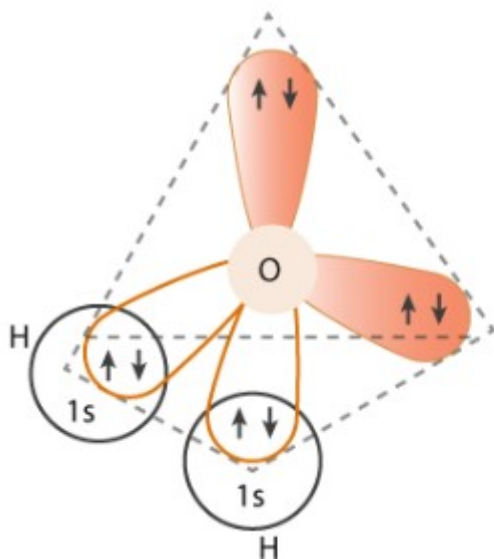
The formation of water on the basis of hybridization.

The central atom here is oxygen which is hybridized.

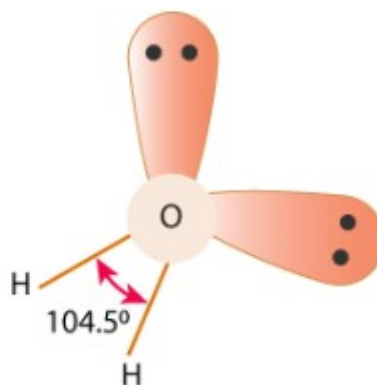
So if we observe the formation of the water molecule there are three 2p orbitals and one 2s orbital.

Hybridization: These combine to create the four sp³ hybrid orbitals.

Hybridization of Water: Four sp³ hybrid orbitals



Orbital Overlap in H₂O



Bent Shape

Two hybrid orbitals form covalent bonds with each hydrogen atom and two hybrid orbitals are occupied by lone pairs.

Structure

- * In H₂O hybridization orbitals having the same energy level will combine to form hybrid orbitals.
- * The water molecule has two lone pairs and two bond pairs.
- * Each O–H covalent bond is called a sigma (σ) bond.
- * H₂O Molecular Geometry and Bond Angles

H₂O Molecular Geometry and Bond Angles

H₂O has a tetrahedral arrangement of molecules or an angular geometry.

This is mainly because the **repulsion from the lone pair combination is more** than bond-pair repulsion.

Additionally, the existing pairs do not lie in the same plane.

One pair is below the plane and the other one is above.

This bond geometry is commonly known as a **distorted tetrahedron**.

Geometry of the water molecule

Distorted tetrahedral is the geometry of a water molecule.

As a result, the angle in a water molecule is 104.5° which again falls short of the true tetrahedral angle of 109°.

10.2 Polyatomic molecules

The ideas we have introduced so far are easily extended to polyatomic molecules. Each σ bond in a polyatomic molecule is formed by the merging of orbitals with cylindrical symmetry about the internuclear axis and the pairing of the spins of the electrons they contain. Likewise, each π bond (if there is one) is formed by pairing electrons that occupy atomic orbitals of the appropriate symmetry. The description of the electronic structure of H_2O will make this clear, but also bring to light a deficiency of the theory. The valence electron configuration of an O atom is $2s^2 2p_x^2 2p_y^1 2p_z^1$. Two unpaired electrons in the $\text{O}2p$ orbitals can each pair with an electron in a $\text{H}1s$ orbital, and each combination results in the formation of a σ bond (each bond has cylindrical symmetry about the respective O–H internuclear axis, Fig. 10.6). Because the $2p_y$ and $2p_z$ orbitals lie at 90° to each other, the two σ bonds they form also lie at 90° to each other. We predict, therefore, that H_2O should be an angular ('bent') molecule, which it is. However, the model predicts a bond angle of 90° , whereas the actual bond angle is 104° . Clearly, the VB model needs to be improved.

10.6 The structures of polyatomic molecules

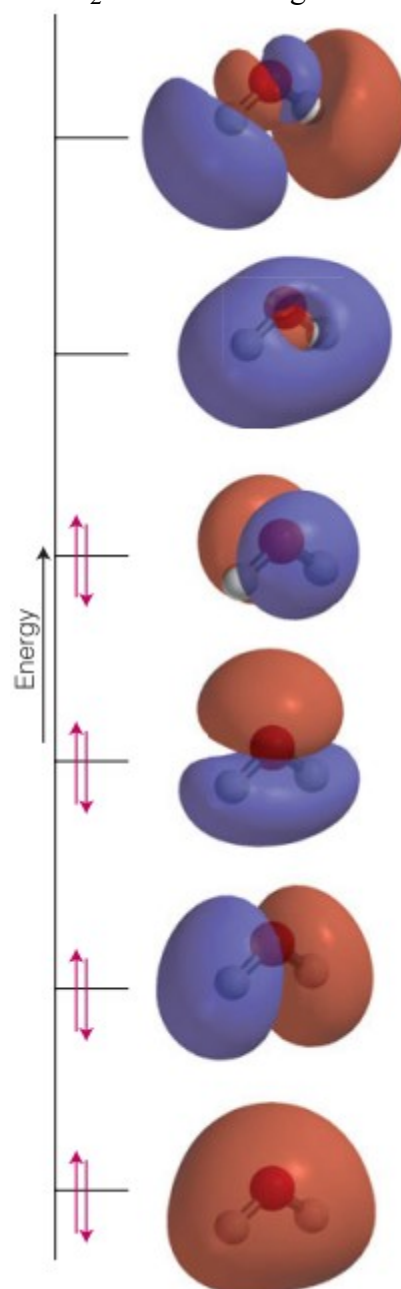
Polyatomic molecules are the building blocks of living organisms, and to understand their electronic structures we need to use MO theory; by doing so, we shall come to understand the unique role of carbon. The bonds in polyatomic molecules are built in the same way as in diatomic molecules, the only differences being that we use more atomic orbitals to construct the molecular orbitals and these molecular orbitals spread over the entire molecule, not just the adjacent atoms of the bond. In general, a molecular orbital is a linear combination of all the atomic orbitals of all the atoms in the molecule.

In H_2O , for instance, the atomic orbitals are the two $\text{H}1s$ orbitals, the $\text{O}2s$ orbital, and the three $\text{O}2p$ orbitals (if we consider only the valence shell). From these six atomic orbitals we can construct six molecular orbitals that differ in energy. The lowest-energy, most strongly bonding orbital has the least number of nodes between adjacent atoms. The highest-energy, most strongly antibonding orbital has the greatest numbers of nodes between neighboring atoms (Fig. 10.36). According to MO theory, the bonding influence of a single electron pair is distributed over all the atoms, and each electron pair (the maximum number of electrons that can occupy any single molecular orbital) helps to bind all the atoms together. In the LCAO approximation, each molecular orbital is modeled as a linear combination of atomic orbitals of matching symmetry, with atomic orbitals contributed by all the atoms in the molecule. Thus, a typical molecular orbital in H_2O constructed from $\text{H}1s$ orbitals (denoted ψ_A and ψ_B) and $\text{O}2s$ and $\text{O}2p_y$ and $\text{O}2p_z$ orbitals will have the composition

$$\psi = c_1\psi_A + c_2\psi_B + c_3\psi_{\text{O}2s} + c_4\psi_{\text{O}2p_y} + c_5\psi_{\text{O}2p_z}$$

The $\text{O}2p_x$ orbital (with x perpendicular to the molecular frame) does not contribute because it has the wrong symmetry to overlap with the $\text{H}1s$ orbitals. Because five atomic orbitals are being used to form the LCAO, there are five molecular orbitals of this kind: the lowest-energy (most bonding) orbital will have no inter-nuclear nodes and the highest-energy (most antibonding) orbital will have a node between each pair of neighboring nuclei.

Fig. 10.36 Schematic form of the molecular orbitals of H_2O and their energies.



X. Radial Distribution Functions of Water: Derived Radiation Total Scattering

TWK's Quantitative Approach to Modeling the Radial Behavior of Water

The Radial Distribution Functions of Water as Derived from Radiation Total Scattering Experiments,
ISRN Physical Chemistry, Volume 2013, Article ID 279463

This is a state-of-the-art determination of water structure using radiation, mostly X-ray and neutron, scattering methods to measure the radial distribution functions of water, $g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$. These three functions collectively describe the way atoms are arranged in the liquid and, therefore, form the bedrock for studying the statistical mechanical basis for water.

The $g_{OH}(r)$ function for water is arguably our only real chance of “seeing” a hydrogen bond in the flesh. The intramolecular version of this function gives the OH bond within the water molecule, but the intermolecular version shows clearly the way hydrogen atoms on one water molecule cluster around the oxygen atom of another water molecule. Although hydrogen bonding can exist between a variety of molecules, only in water (or perhaps hydrogen fluoride—but hydrogen fluoride is a really nasty chemical to investigate experimentally) do you see this clustering so vividly. Emanating from the hydrogen bond between water molecules comes a quite unique molecular arrangement, compared to most other known liquid materials. The $g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$ functions carry the information about that structure, which on one hand wants to be ordered and tetrahedral like ice but at the same time wants to be disordered like “normal” liquids such as mercury or liquid gold.

The Radial Distribution Function, $G(r,t)$. Unlike in a crystal, the atoms and molecules in a liquid are in a state of rapid and diffusive motion. There will, as a result, be a local density of atoms and molecules which fluctuates rapidly with time:

$$n(\mathbf{r}, t) = \sum_i \delta(\mathbf{r} - \mathbf{R}_i(t))$$

where $\mathbf{R}_i(t)$ is the position of atom i at time t . Hence, even if we could find some probe that would capture these density fluctuations that would not by itself be particularly useful, since it would be difficult to identify any clear features or trends in these seemingly randomly changing density fluctuations. Instead, to capture useful information, it is necessary to **perform an autocorrelation on the density fluctuations**, to see how they vary, depending on the (relative) positions of the atoms, \mathbf{r} , and the relative difference in time, t , between samplings of the density

X-ray atom pair correlation functions $G(r,t)$:

$$G_{rt}(r, t) = \int \int n(r_p + r) \cdot n(t_p + t) dt_p dr_p = \sum_j \sum_i \delta(r + R_j(t) - R_i(0))$$

In effect, we are sitting on an atom and counting all the atoms that we find at a given displacement, \mathbf{r} , from that atom, converting that number to a local density. This local density is then averaged over all the atoms in the system and compared with the density of atoms in the system as a whole.

Radial Distribution Function, $g(r)$

is a convenient way of keeping track of how the local number density varies with displacement from an average atom and with respect to the average number density.

For the water molecules used in the present simulations, the average OH bond distance was 0.976 with RMS deviation 0.066 Å, and the average HH distance was 1.55 Å with RMS deviation 0.103 Å

X-Ray Diffraction from Compton Scattering Experimental Results for RDF

Read Experimental G Calculation Function into Mathcad

$G_{\text{CalculationFunction}} := \text{READPRN}(\text{"Radial Distribution Function.txt"})$

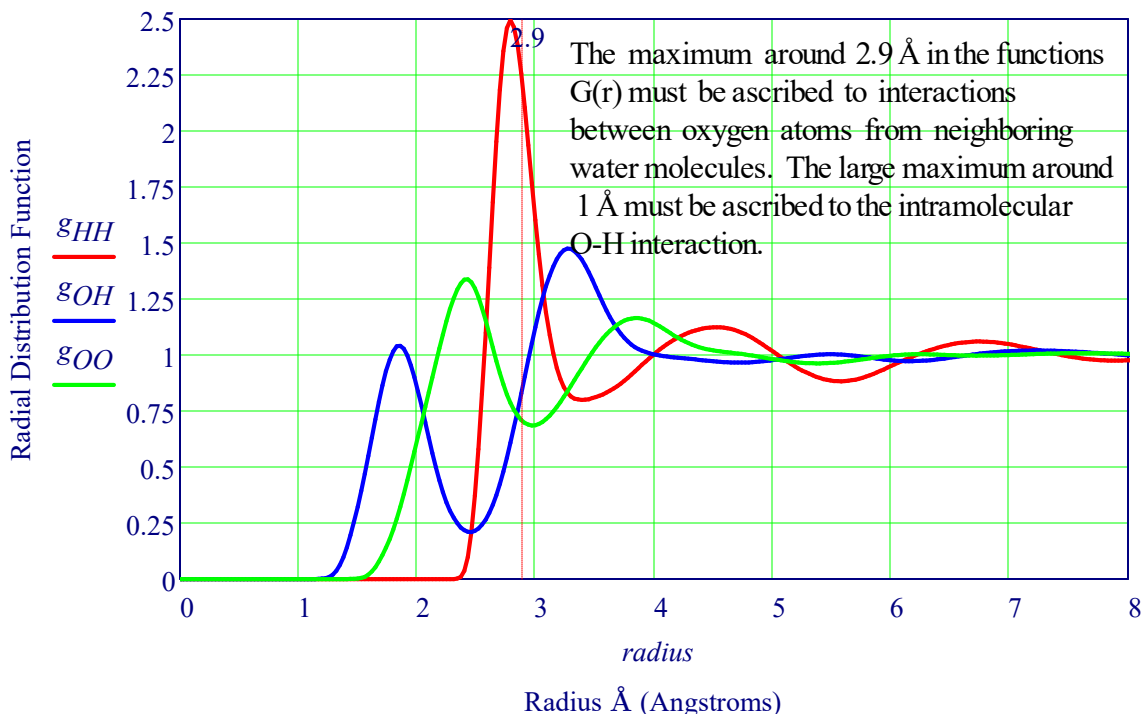
$$G_{rt}(r, t) = \int \int n(r_p + r) \cdot n(t_p + t) dt_p dr_p = \sum_j \sum_i \delta(r + R_j(t) - R_i(0))$$

$$G_{rt} := G_{\text{CalculationFunction}} \quad \text{rows}(G_{rt}) = 815$$
$$\text{radius} := G_{rt}^{\langle 0 \rangle} \quad g_{HH} := G_{rt}^{\langle 1 \rangle} \quad g_{OH} := G_{rt}^{\langle 3 \rangle} \quad g_{OO} := G_{rt}^{\langle 5 \rangle}$$

Plot the Experimental Data

Curves represent a superposition of modified atom pair correlation functions $g(r)$ descriptive of O-O, O-H, and H-H interactions.

The Radial Distribution Functions for Water at 300K



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