WATER AT INTERFACES

A Molecular Approach

Jordi Fraxedas



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CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL 33487-2742

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International Standard Book Number-13: 978-1-4398-6105-9 (eBook - PDF)

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Dedication

Hay libros que no son de quien los escribe sino de quien los sufre Relato de un náufrago, G. García-Márquez

Dedicated to my wife Montse and my sons Roger and Marc

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Preface

Guárdate del agua mansa, the Spanish translation of the known proverb, *beware of still waters*, is a theater piece of the great Golden Age Spanish writer Pedro Calderón de la Barca based on a story of love and honor. This title is perfectly suited to any work devoted to the understanding of water, this vital, essential, fascinating, surprising, and eccentric small molecule that continues to preserve an aura of mystery around it, as if to remind us that without it, life (as we understand it) is not possible. The water molecule can be considered as a very simple one, given that it is constituted by only one oxygen and two custodian hydrogen atoms with a shape that recalls a very popular cartoon character, but we have to be aware when water molecules condense into liquid and solid states through hydrogen bonding because this simplicity is only apparent. Below such an apparent simplicity a complex and mysterious creature is hidden. It is a sort of complex simplicity fully justifying the term, *Guárdate del agua mansa*. We could find a parallelism between water and Fermat's last theorem, where no integer solution exists for the equation $x^n + y^n = z^n$, for n > 2. It appears to be a rather simple problem but it took more than 300 years to solve it!

Water is perhaps the only compound having a biography (P. Ball, Life's Matrix: A Biography of Water, University of California Press, 2001) and many books, articles, reviews, and so on, have been and continue to be published focused on diverse aspects. I strongly recommend M. Chaplin's and US Geological Survey webpages http://www.lsbu.ac.uk/water/ and http://www.usgs.gov/, respectively. However, an introductory book on interfacial water trying to reach a broad multidisciplinary audience was missing in my view, and this was the pivotal motivation, or excuse, that drove me to conceive the work you are now reading. Among the myriad published works devoted to water and interfacial water, only a partial selection of them emerge in this book, as the tip of an iceberg. The rest, those below the surface, indeed contribute to the general knowledge, but this book is not intended as a review of all published material. That would have little sense for a book because of its intrinsic static nature in printed version in a quite dynamic and active subject. I just mention that more than 1.5×10^6 articles have been published on water since 1900, according to online bibliographic research platforms, and that about 4 and 18% of them contain the terms "interface" and "surface", respectively. Water at interfaces is thus a visible part of the water iceberg (only about 10% of the volume of an iceberg emerges).

This book is conceived to go from basic simplified concepts toward more complex issues, increasing the degree of complexity. We start in Chapter 1 with isolated water molecules, because it is fundamental to know its properties in the absence of intermolecular interactions. Then we allow them to interact through van der Waals interactions, then through hydrogen bonding to build liquids and solids, and we submerge in Chapter 2 into the (pristine) interfaces built by water in a broad sense, including flat liquid/vapor, liquid/oil, and liquid/solid interfaces. Chapters 3 and 5 are devoted to interfaces involving both ideal and real surfaces, respectively, and Chapter 4 discusses the affinity of water to surfaces (hydrophobicity and hydrophilicity). Finally, Chapter 6 deals with the interaction of water with biomolecules. Interfaces are considered in a broad sense and at different length scales: the zero-dimensional case of water sequestering small molecules (clathrate hydrates), water surrounding macromolecules, liquid water wetting (or not) extended flat surfaces, and so on.

Finally, I would like to acknowledge many people who have participated to different extent during the preparation of this book, but to the tip of the iceberg I would first invite E. Canadell and C. Rovira for extended Hückel and DFT calculations, M. M. Conde and C. Vega for MD simulations, M. V. Fernández-Serra for discussions on DFT calculations, and T. Hernández and A. Santos for help on documentation. I would skip my family, my wife Montse and my sons Roger and Marc, from the uncomfortable, cold, and slippery honorary iceberg tip and reserve for them a more hospitable place for their warm permanent support.

Abbreviations and Symbols

٨	Acceptor		
	Acceptor Free Oscillation Amplitude		
A0 A	Critical Free Amplitude		
	Atomic Force Microscope		
AFD	Antifreeze Proteins		
AM-AFM	Annitude Modulation Atomic Force Microscope		
	Amplitude Modulation Atomic Force Microscope		
ASW	Aquaporine-1 Amorphous Solid Water		
AU	Astronomical Unit		
BALVP	Becke Three-Parameter Lee_Yang_Parr		
CERN	European Organization for Nuclear Research		
CNT	Carbon Nanotube		
CPMD	Carr–Parrinello Molecular Dynamics		
CVD	Chemical Vapor Deposition		
D	Donor		
DFT	Density Functional Theory		
DNA	Deoxyribonucleic Acid		
DOS	Density of States		
DPPC	Dipalmitovlphosphatidylcholine		
DWNT	Double-Walled Nanotube		
е	Electron Charge		
$E_{\rm ads}$	Adsorption Energy		
$E_{\rm coul}$	Coulomb Interaction Energy		
$E_{\rm F}$	Fermi Level		
E_{LJ}	Lennard–Jones Interaction Energy		
E_{LL}^{0}	Minimum of the Lennard–Jones Interaction Energy		
$E_{\rm vdW}^{\rm LJ}$	van der Waals Interaction Energy		
EELS	Electron Energy Loss Spectroscopy		
EH	Extended Hückel		
EWOD	Electrowetting on Dielectric		
EXAFS	Extended X-ray Absorption Fine Structure		
$F_{\rm cap}$	Capillary Force		
FIR-VRT	Far-Infrared Vibration-Rotation-Tunneling		
FWHM	Full Width at Half Maximum		
g	Gravity Constant		
G	Gibbs Free Energy		
GAXS	Glancing-Angle X-ray Scattering		
GGA	Generalized Gradient Approximation		
h	One-Electron Hamiltonian		
HAS	Helium Atom Scattering		
HDA	High-Density Amorphous		
HF	Hartree–Fock		
HGW	Hyperquenched Glassy Water		
номо	Highest Occupied Molecular Orbital		

HOPG	Highly Oriented Pyrolytic Graphite			
HREELS	High-Resolution Electron Energy Loss Spectroscopy			
Ih	Hexagonal Ice			
INP	Ice Nucleating Protein			
IR	Infrared			
IUPAC	International Union of Pure and Applied Chemistry			
Κ	Kinetic Energy			
k _B	Boltzmann Constant			
k _c	Force Constant			
$k_{\rm GT}$	Gibbs–Thomson Coefficient			
KPFM	Kelvin Probe Force Microscopy			
l _c	Capillary Length			
$l_{\rm v}$	Latent Heat of Vaporization			
LB	Langmuir–Blodgett			
LCAO	Linear Combination of Atomic Orbitals			
LDA	Low-Density Amorphous			
LEED	Low-Energy Electron Diffraction			
LJ	Lennard–Jones			
LUMO	Lowest Occupied Molecular Orbital			
MD	Molecular Dynamics			
MEMS	Microelectromechanical System			
ML	Monolayer			
MO	Molecular Orbital			
MP2	Moller–Plesset (second-order perturbation theory)			
NAPP	Near Ambient Pressure Photoemission			
NASA	National Aeronautics and Space Administration			
NEMS	Nanoelectromechanical System			
NEXAFS	Near-Edge X-Ray Absorption Fine Structure			
NMR	Nuclear Magnetic Resonance			
NP	Nanoparticle			
$p_{\rm v}$	Vapor Partial Pressure			
$p_{\rm v}^{\rm sat}$	Vapor Partial Pressure at Saturation			
PBE	Perdew-Burke-Ernzerhof			
PDOS	Partial Density of States			
PECVD	Plasma Enhanced Chemical Vapor Deposition			
Q	Q-Factor			
QLL	Quasiliquid Layer			
r	Radius			
R	Molar Gas Constant			
r^*	Critical Radius			
r _d	Droplet Radius			
r _{ion}	Ionic Radius			
r _{pore}	Pore Radius			
r_0	Intermolecular Distance at Minimum LJ Potential Energy			
r_{μ}	Dipole Radius			
RAIRS	Reflection Absorption Infrared Spectroscopy			
KH	Relative Humidity			
КГ	Room Temperature			

S	Entropy			
S_{jk}	Overlap Integral			
SAM	Self-Assembled Monolayer			
SEM	Scanning Electron Microscopy			
SFG	Sum-Frequency Generation			
SFM	Scanning Force Microscopy			
SPFM	Scanning Polarization Force Microscopy			
SPM	Scanning Probe Microscopy			
SR	Synchrotron Radiation			
STM	Scanning Tunneling Microscopy			
SWNT	Single-Walled Nanotube			
T_{g}	Glass Transition Temperature			
$T_{\rm m}$	Bulk Melting Point			
$T_{\rm s}$	Onset Temperature			
UHV	Ultra High Vacuum			
UN	United Nations			
UPS	Ultraviolet Photoemission Spectroscopy			
UV	Ultraviolet			
V	Potential Energy			
$V_{\rm m}$	Molar Volume			
vdW	van der Waals			
VHDA	Very-High-Density Amorphous			
VUV	Vacuum Ultraviolet			
W	Bandwidth			
$W_{\rm N}$	Weber Number			
XAS	X-Ray Absorption Spectroscopy			
XES	X-Ray Emission Spectroscopy			
XPS	X-Ray Photoemission Spectroscopy			
XRS	X-Ray Raman Spectroscopy			
$z_{\rm G}$	Position of the Gibbs Surface			
0D	Zero-dimensional			
1D	Two-dimensional			
2D	Two-dimensional			
3D	Three-dimensional			
α	Electronic Polarizability			
$\gamma_{\rm lv}$	Surface Tension			
ϵ	One-Electron Energy			
ε	Relative Permittivity			
ε_0	Dielectric Constant of Free Space			
ζ	Order Parameter			
Θ	Surface Coverage			
$\theta_{\rm c}$	Contact Angle			
$\theta_{\rm c}^{\rm a}$	Advancing Contact Angle			
$\theta_{\rm c}^{\rm r}$	Receding Contact Angle			
$\theta_{\rm CB}$	Cassie–Baxter's Contact Angle			
$\theta_{\rm W}$	Wenzel's Contact Angle			
$\Theta_{\rm D}$	Debye Temperature			
ĸ	Curvature			
$\kappa_{\rm D}^{-1}$	Debye Length			
λ_{K}	Kelvin Length			

μ	Electrical Dipole
χs	Surface Potential
$ \chi^{at}\rangle$	Atomic Orbitals
ρ	Density
$\rho_{\rm ch}(x)$	Spatial Charge Density
Q	Roughness Factor
ϕ	Phase
ϕ	Work Function
φ	Electrostatic Potential
$ \psi angle$	One-Electron Wave Function
ħ	Normalized Planck Constant
$\omega_{\rm red}$	Reduced Normalized Frequency

1 An Introduction to Water

que las aguas mansas son de las que hay que fiar menos P. Calderón de la Barca, Guárdate del agua mansa

From our everyday life experience we all know that water vapor from the air condenses in droplets upon decrease of temperature on distinct surfaces such as windows, leaves, and the like, and that a further decrease of temperature leads to the formation of solid water (ice) below 273 K (0° C) at about standard atmospheric pressure (1013 hPa). Up in the troposphere, the clouds have no large surfaces to condense on and for this reason they can stay there as huge wandering shape-changing beings with a milk-white appearance. Their characteristic color arises from the scattering of visible (white) light with water droplets whose sizes are comparable to the wavelength of such light (\sim 500 nm). Such droplets, if pure, can be cooled down to about 233 K $(-40^{\circ}C)$ without the formation of ice (Schaefer 1946). Water is then said to be in a supercooled state. But ice in the clouds can be formed at higher temperatures (or not that low) as a result of the presence of foreign bodies such as dust particles, contaminants, nanoparticles, and so on, both from natural and anthropogenic origin, which act as nucleation agents (Langmuir 1950), in a process known in the crystal growth community as heterogeneous nucleation. This is one aspect of the watersurface interactions that is discussed at length in this book. The surface of ice plays a relevant role for atmospheric phenomena because it is able to catalyze chemical reactions such as those involved in polar ozone depletion, and those who love skiing should be grateful for the presence of a thin film of liquid water at the surface of snow below 273 K, where water would be expected to be in the solid state (again a supercooled liquid but this time on top of solid water). When the liquid water film is too thick (above 273 K) the resulting (spring) snow makes skiing a difficult task.

In this book we consider interfaces in a broad sense and at different length scales: water sequestering small molecules, which may lead to burning ice when the kidnapped molecule is methane, surrounding macromolecules such as proteins actively participating in their biological function, wetting or not extended flat surfaces, and the like. In this chapter a general introduction to water is given, describing the basic concepts needed for the rest of the book. Among the many books specifically devoted to water, I make a personal choice of:

- The Structure and Properties of Water, by D. Eisenberg and W. Kauzmann (1969)
- Water: A Matrix of Life, by F. Franks (2000)

- Life's Matrix: A Biography of Water, by P. Ball (2001)
- *Physics of Ice*, by V. Petrenko and R. W. Whitworth (2006)
- The Hydrogen Bonding and the Water Molecule, by Y. Maréchal (2007)
- Interfacial and Confined Water, by I. Brovchenko and A. Oleinova (2008)

In addition, there are books where water benefits from a privileged although not pivotal position as in *Intermolecular and Surface Forces* of J. Israelachvili (1991; 2011), and in *Physics and Chemistry of Interfaces* of Butt, Graf and Kappl (2013) and a plethora of excellent review articles that are referred to in this book. But before going into detail, just refer to the recent accurate determination of the Avogadro constant, which links the atomic and macroscopic properties of matter (Andreas et al. 2011). Thus, 18.0152 g of water (one mole) has $6.02214078(18) \times 10^{23}$ molecules and lots of surprises.

1.1 WHERE DOES WATER COME FROM?

Water is one of the most abundant constituents of the universe and of our solar system and is composed of hydrogen and oxygen, the first and third most abundant elements in the universe, respectively. It was A. Lavoisier (1743-1794) who gave the name to hydrogen and oxygen, before losing his head. They mean water and acid formed, respectively, from Greek roots. But before they could combine into the magic 2:1 proportion both elements had to be produced and in order to see how they came on the scene we have to go back to the very origin of the universe, when and where it all started. Matter was formed after the Big Bang, the most solid model describing the origin of the universe, when the incipient universe was cooling upon expansion. Hydrogen was generated when the temperature was sufficiently low in order to allow the young protons and electrons to combine, but oxygen had to wait much longer. It had to wait for the formation of stars, the veritable alchemists of the universe, which was made possible thanks to the gravitational force that started to aggregate the existing matter, mostly in the form of gas, up to a point where the increasingly denser matter collapsed, becoming heated up and starting ignition. The fuel was hydrogen and the final product helium (⁴He), the second most abundant element in the universe, plus energy in the form of radiation. But the production, nucleosynthesis is the correct word, of heavier elements such as boron (⁸B), carbon (¹²C), oxygen (¹⁶O), neon (²⁰Ne), magnesium (²⁴Mg), silicon (²⁸Si), and beyond needed the burning of helium after the gravitational collapse of the stars (Burbridge et al. 1957). So hydrogen had to wait quite some time for the successful alliance with oxygen, one of its great-grandsons.

The next question is that of how water was incorporated to the Earth, our beloved planet. It is assumed that such a process took place both during the formation of the Earth, by the accretion of planetary embryos, also called planetesimals, bringing both absorbed and adsorbed water with them, as well as at a later stage, which includes the late impact of external bodies after the formation of the moon (which would have vaporized the pre-existing water), such as carbonaceous chondrites, meteorites, asteroids, and comets which brought lattice water, that is, water molecules incorporated in their chemical structure, and external ice (Mottl et al. 2007; Hartogh et al. 2011). While writing this book, the journal *Nature* published the detection of water ice on the surface of an asteroid (24 Themis) by spectroscopic methods (Campins et al. 2010; Rivkin and Emery 2010). The observed absorption line at 3.1 μ m, in the infrared (IR) region, has been ascribed to water ice in the form of thin films, with a thickness ranging from 10 to 100 nm. Such a finding provides a further example, fallen from heaven, of the importance of interfacial water, in this case as water supply. About 3.8–3.9 billion years ago the conditions on Earth were clement enough to become the scenario for the most important performance, the emergence of life (Luisi 2006; Lynden-Bell et al. 2010).

The search for extraterrestrial life in the solar system goes hand in hand with the detection of water, the well-known *follow the water* principle, hence the efforts mainly coordinated by the National Aeronautics and Space Administration (NASA) to look for water in planets and in their satellites. The Phoenix Mission was sent to Mars to verify the presence of subsurface water ice. It landed on May 25, 2008 in a northern arctic region and has provided evidence of the existence of both ice and atmospheric water (Smith et al. 2009). Water ice has also been observed on the moon, in the south pole crater Cabeus, after impact of a rocket and analysis of the ejected material (Colaprete et al. 2010), but its existence was predicted earlier by Hergé, Tintin's father, in *Explorers on the Moon*. This story was published in 1954, well before the Apollo 11 landing in 1969. On the other hand, Europa, a moon of Jupiter, is believed to host a deep ocean of liquid water beneath an icy shell (Carr et al. 1998).

But water has also been detected in the atmosphere of extrasolar planets (Seager and Deming, 2010). The atmosphere of the exoplanet with the nonmythological given name HD 189733b possesses water vapor, as observed with the powerful NASA Spitzer Space Telescope using an IR array camera (Tinetti et al. 2007). HD 189733b is an enormous gas giant with temperatures around 1,000 K, not the most indicated place for water-based life. Life as we know it needs the presence of liquid water and, for a given solar system, this imposes some constraints in terms of the starplanet distance. If the distance is too small the temperature becomes too high and vice versa. The *habitable zone* is defined as the distance that permits water to be in the liquid state. In our solar system this distance is about 1 astronomical unit (AU), the distance between the sun and the Earth. The GJ 1214b exoplanet has a water ice core surrounded by hydrogen and helium (Charbonneau et al. 2009). It is more massive than the Earth (6.55 times) and larger with a radius 2.68 times Earth's radius and the estimated temperatures lie around 475 K, still too high for liquid water but encouraging further research. Recently, the first confirmed exoplanet orbiting in the middle of the habitable zone of a star similar to our sun, initially termed Kepler-22b, has been discovered. It has a radius about 2.4 times that of the Earth and is about 600 light years away with a 290-day year (Borucki et al. 2012). The growing interest in exoplanets will bring in the forthcoming years a less Earth-centric vision of the universe. But let us come back to Earth after such a short journey to distant parallel worlds and explore what we know about the fascinating H₂O molecule.



FIGURE 1.1 Ball-and-stick model of a water molecule. Oxygen and hydrogen atoms are represented by dark gray and white balls, respectively.

1.2 MOLECULAR STRUCTURE OF ISOLATED WATER MOLECULES

1.2.1 A NONLINEAR POLAR MOLECULE

Let us now start the study of the molecular structure of individual (isolated) water molecules. In Chapter 3 we discuss the experimental visualization of single molecules (monomers) and of small clusters on surfaces but here we consider the case of non-interacting molecules as in the gas phase. Understanding the properties of isolated molecules is essential. When the intermolecular interactions are much weaker than the intramolecular interactions the electronic and vibrational properties of the condensed phases can be rationalized in terms of free molecules, a strategy that has been successfully applied to molecular organic materials (Fraxedas 2006). In the limit of weak intermolecular interactions physicists like to describe a solid in terms of a weakly interacting gas whereas chemists prefer a supramolecular description.

The isolated water molecule has a V-shape (see Figure 1.1), with an H–O–H angle of 104.52 \pm 0.05° and an O–H distance of 0.9572 \pm 0.0003 Å (Benedict, Gailer, and Plyler 1956). Given the different electron affinities of oxygen and hydrogen, the molecule is polarized with a permanent dipole $\mu = 1.8546$ D (Clough et al. 1973), where 1 D (Debye) = 3.336×10^{-30} C m, but is only slightly polarizable, with an electronic polarizability $\alpha = 1.64 \times 10^{-40}$ C² m² J⁻¹ arising mostly from the oxygen atom (Murphy 1977; Tsiper 2005). We interchangeably use the term atom or ion (hydrogen atoms or protons) throughout the book.

Figure 1.2 shows a water molecule oriented in a Cartesian coordinate system, where the origin is arbitrarily set at the oxygen atom and both hydrogen atoms are contained in the yz-plane (z > 0). With this convention, that is kept throughout the book, the water dipole is defined along the positive z-axis. The water molecule remains invariant under the symmetry operations:

$$E, C_2(z), \sigma_v(xz), \sigma_v(yz)$$



FIGURE 1.2 Symmetry operations for the water molecule corresponding to the C_{2v} point group.

TABLE 1.1Character Table of the $C_{2\nu}$ Point Group				
C_{2v}	Ε	<i>C</i> ₂	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

where *E* represents the identity operator (from German *Einheit*), $C_2(z)$ stands for a proper rotation of π degrees (rotation of order 2) with respect to the *z*-axis, and $\sigma_v(xz)$, $\sigma_v(yz)$ are planes of symmetry with respect to the *xz* and *yz* planes, respectively (from German *Spiegel*). The full set of such symmetry operations leads to the C_{2v} point group, using Schönflies symbols. Symmetry is a very important parameter when characterizing molecules (and solids) because it helps in simplifying the resolution of the Schrödinger equation, as discussed later in this chapter.

Table 1.1 shows the character table corresponding to the C_{2v} point group, where every row corresponds to an irreducible representation. Cotton's book *Chemical Applications of Group Theory* is a must for those interested in learning more about group theory applied to chemistry (Cotton 1990).

We are interested in the electronic and vibrational structures of the water molecule but before going into detail let us start first with a simple physical water model consisting of three point charges, -2q for the oxygen ion and +q for both hydrogen ions (q > 0) and see what we can learn from it. The model is shown in Figure 1.3a. The total interaction energy $E_{coul}(r)$ is given by the sum of the two O–H and one H–H Coulomb contributions:

$$E_{\text{coul}}(r) = \frac{1}{4\pi\varepsilon\varepsilon_0} \left\{ -\frac{4q^2}{r} + \frac{q^2}{2r\sin\theta} \right\}$$
(1.1)

where ε and ε_0 represent the relative permittivity and the dielectric constant of free space ($\varepsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$), respectively, *r* the O–H distance, and θ half the angle between both O–H pairs. The angle that minimizes the total energy is $\theta = \pi/2$, as can be analytically obtained and initially guessed without any calculation; inasmuch as both +*q* charges repel each other, hence they will tend to stay as far away as possible. This model is clearly unable to describe the known V-shape and thus additional conditions have to be considered.

If we allow, for instance, the oxygen ion to be polarized, then the total interaction energy becomes:

$$E_{\text{coul}}(r) = \frac{1}{4\pi\varepsilon\varepsilon_0} \left\{ -\frac{4q^2}{r} + \frac{q^2}{2r\sin\theta} \right\} - \frac{1}{(4\pi\varepsilon\varepsilon_0)^2} \frac{4\alpha q^2}{2r^4} \cos^2\theta \qquad (1.2)$$

This improved model is represented in Figure 1.3b. The second term of this expression corresponds to the interaction between an ion and an uncharged polarizable atom or molecule. Minimization of (1.2) gives rise to two solutions: $\cos \theta = 0$ and



FIGURE 1.3 (a) Unpolarized and (b) polarized point charge model of a water molecule. The O–H distance and half the H–O–H angle are represented by r and θ , respectively.

sin³ θ = 4πεε₀r³/8α. The former corresponds to the solution found from (1.1) and the latter implies that $\alpha > 4\pi εε_0 r^3/8$ and that the angle θ becomes more acute when α increases, which can intuitively be understood as caused by the induced positive charge in the oxygen ion which exerts a repulsion in both hydrogen ions. Indeed, with r = 0.9572 Å, as mentioned earlier, we obtain $\alpha > 0.12 \times 10^{40}$ C² J⁻¹ m⁻¹, a condition that is fulfilled because the experimental value is $\alpha = 1.64 \times 10^{-40}$ C² m² J⁻¹. With this simple model we cannot know much about the electronic structure of the water molecule but it provides us a hint of the importance of the charge distribution opposite the hydrogen ions as discussed later. To go further we need some basic concepts of quantum chemistry and this is exactly what we introduce next. Many introductory textbooks on quantum chemistry can be found in the literature and interested readers are referred to them. Among them I would suggest that from I. N. Levine (2008).

1.2.2 ELECTRONIC STRUCTURE

In what follows we describe the electronic structure of the water molecule or equivalently its molecular orbitals (MOs). Physicists prefer the former term and chemists the latter, although they are referring to the very same concept. A detailed discussion on MOs and their interactions can be found in the book by Albright, Burdett, and Whangbo (1985). Let us start by considering the general many-electron problem of N_e electrons contributing to chemical bonding, and N_{ion} ions, which contain the nuclei and the tightly bound core electrons. This problem can be described quantum-mechanically, in the absence of external fields and ignoring atomic vibrations (we consider the latter in the next section), by the 0-order Hamilton operator:

$$H_0 = H_{\rm ee} + H_{\rm ion-ion} + H_{\rm e-ion} \tag{1.3}$$

where H_{ee} , $H_{ion-ion}$, and H_{e-ion} correspond to the Hamilton operators concerning electron–electron, ion–ion, and electron–ion interactions, respectively. Thus, the Schrödinger equation to be solved is:

$$H_0|\Psi\rangle = E_0|\Psi\rangle \tag{1.4}$$

where $|\Psi\rangle$ and E_0 represent the N_e-electron wave (eigen)function and energy, respectively. In the vast majority of cases (1.4) cannot be solved exactly and approximations

are needed. A successful strategy consists of assuming that every electron is subject to an effective interaction potential, the so-called one-electron approximation. Ideally we would like to express H_0 in the form:

$$H_0 \simeq \sum_{i=1}^{N_e} \left\{ -\frac{\hbar^2}{2m_e} \nabla_i^2 + V_i \right\} = \sum_{i=1}^{N_e} h_i$$
(1.5)

where the Hamiltonian H_0 of an N_e -electron system can be expressed as the sum of N_e one-electron Hamiltonians h_i where $h_i = -\hbar^2/2m_e\nabla_i^2 + V_i$, the first and second terms accounting for the kinetic energy and the mean interaction potential, respectively, where \hbar represents the normalized Planck constant (1.054 × 10⁻³⁴ J s = 6.582 × 10⁻¹⁶ eV s), m_e the electron mass, and the ∇^2 operator is given by $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

Within the one-electron approximation, we can obviate the i index and the Schrödinger equation to be solved becomes:

$$h|\psi\rangle = \epsilon|\psi\rangle \tag{1.6}$$

where h, ϵ , and $|\psi\rangle$ stand for the one-electron Hamiltonian, energy, and wave function, respectively. In the case of molecules $|\psi\rangle$ represents the MOs and can be simply expressed as a linear combination of N_{at} atomic orbitals $|\chi^{at}\rangle$ (LCAO) of the different atoms forming the molecule:

$$|\psi_j\rangle = \sum_{k=1}^{N_{\text{at}}} c_{jk} |\chi_k^{\text{at}}\rangle$$
(1.7)

where *j* runs from 1 to N_{at} and the c_{jk} coefficients have to be determined. For most purposes these atomic orbitals can be assumed to be real functions and normalized such that the probability of finding an electron in $|\chi_j^{at}\rangle$ when integrated over all space is one: $\langle \chi_j^{at} | \chi_j^{at} \rangle = 1$. On the other hand the MOs should be orthonormal, that is, orthogonal and normalized: $\langle \psi_j | \psi_k \rangle = \delta_{jk}$, where $\delta_{jk} = 1$ if j = k and $\delta_{jk} = 0$ if $j \neq k$.

Introducing (1.7) into (1.6) we obtain:

$$\sum_{k=1}^{N_{\text{at}}} c_{jk} \left\{ h | \chi_k^{\text{at}} \rangle - \epsilon | \chi_k^{\text{at}} \rangle \right\} = 0$$
(1.8)

and multiplying (1.8) to the left by $\langle \chi_i^{at} |$, the complex conjugate of $|\chi_i^{at} \rangle$, we obtain:

$$\sum_{k=1}^{N_{\text{at}}} c_{jk} \left\{ \langle \chi_j^{\text{at}} | h | \chi_k^{\text{at}} \rangle - \epsilon \langle \chi_j^{\text{at}} | \chi_k^{\text{at}} \rangle \right\} = 0$$
(1.9)

By defining $h_{jk} = \langle \chi_j^{\text{at}} | h | \chi_k^{\text{at}} \rangle$, the interaction energy, and $s_{jk} = \langle \chi_j^{\text{at}} | \chi_k^{\text{at}} \rangle$, the overlap integral, where $j, k = 1, ..., N_{\text{at}}$, (1.9) is simplified to the expression:

$$\sum_{k=1}^{N_{\rm at}} c_{jk} \left\{ h_{jk} - \epsilon s_{jk} \right\} = 0 \tag{1.10}$$

Therefore, within the LCAO approximation, (1.6) transforms into a system of N_{at} equations with N_{at} unknown parameters c_{jk} . The resolution of (1.10) implies that the determinant of the $\{h_{jk} - \epsilon s_{jk}\}$ matrix has to be zero:

$$\begin{vmatrix} h_{11} - \epsilon s_{11} & h_{12} - \epsilon s_{12} & \dots & h_{1N_{at}} - \epsilon s_{1N_{at}} \\ h_{21} - \epsilon s_{21} & h_{22} - \epsilon s_{22} & \dots & h_{2N_{at}} - \epsilon s_{2N_{at}} \\ \vdots & \vdots & \vdots & \vdots \\ h_{N_{at}1} - \epsilon s_{N_{at}1} & h_{N_{at}2} - \epsilon s_{N_{at}2} & \dots & h_{N_{at}N_{at}} - \epsilon s_{N_{at}N_{at}} \end{vmatrix} = 0$$
(1.11)

In conclusion, the energies that satisfy (1.11) are associated with molecular electronic states. Because (1.11) is an equation of N_{at} order, we obtain N_{at} energy values ϵ_j ($j = 1, ..., N_{at}$), that is, as many molecular levels as atomic orbitals.

In the case of the H₂O molecule, the hydrogen atoms contribute with two 1s atomic orbitals (one each) and the oxygen atom with 1s, 2s, and 2p orbitals. The participation of O1s in the bonding is negligible (we later show the large energy difference between O1s and O2s), hence we concentrate on two atomic orbitals from hydrogen and four from oxygen, namely 2s, $2p_x$, $2p_y$, and $2p_z$. Thus $N_{\text{at}} = 6$ and our task consists in determining the corresponding 6 MOs. But before trying to solve the full 6 MOs problem, it is illustrative to start with the H–H subsystem, that is, ignoring the oxygen atom, as shown in Figure 1.4. In this case $N_{\text{at}} = 2$ and we have:

$$|\psi_1\rangle = c_{11}|\chi_1^{\rm at}\rangle + c_{12}|\chi_2^{\rm at}\rangle$$
 (1.12a)

$$|\psi_2\rangle = c_{21}|\chi_1^{\text{at}}\rangle + c_{22}|\chi_2^{\text{at}}\rangle \tag{1.12b}$$

where $|\chi_j^{\text{at}}\rangle \equiv |1s_j\rangle$ with j = 1, 2. We thus have to solve the following expression:

$$(h_{11} - \epsilon s_{11})c_{11} + (h_{12} - \epsilon s_{12})c_{12} = 0$$
(1.13a)

$$(h_{21} - \epsilon s_{21})c_{21} + (h_{22} - \epsilon s_{22})c_{22} = 0$$
(1.13b)

Because the atomic orbitals are normalized, then $s_{11} = s_{22} = 1$ and the interatomic overlap $s_{12} = s_{21} = 0.2261$, computed at a H–H distance of 1.514 Å (McGlynn et al. 1972). On the other hand $h_{11} = h_{22} = -13.6$ eV, the ionization potential of hydrogen,



FIGURE 1.4 Orbital interaction diagram for H-H. Energies in eV.

and $h_{12} = h_{21} = K_{\text{WH}} s_{12} h_{11}$ by virtue of the Wolfsberg–Helmholtz approximation, where $h_{jk} = K_{\text{WH}} s_{jk} (h_{jj} + h_{kk})/2$ and $K_{\text{WH}} = 1.75$. We are simply calculating orbital energies following the extended Hückel (EH) approximation, as developed by R. Hoffmann (1963).

From the determinant:

$$\begin{vmatrix} -13.6 - \epsilon & 0.2261(-23.8 - \epsilon) \\ 0.2261(-23.8 - \epsilon) & -13.6 - \epsilon \end{vmatrix} = 0$$
(1.14)

we obtain the two solutions for the MO energies, $\epsilon_1 = -15.48 \text{ eV}$ and $\epsilon_2 = -10.62 \text{ eV}$, and from (1.13) and the normalization of the MOs, $\langle \psi_1 | \psi_1 \rangle = \langle \psi_2 | \psi_2 \rangle = 1$, we obtain the coefficients $c_{11} = c_{12} = (\sqrt{2(1+s_{12})})^{-1} = 0.6385$ and $c_{21} = -c_{22} = (\sqrt{2(1-s_{12})})^{-1} = 0.8038$. Thus,

$$|\psi_1\rangle = 0.6385\{|1s_1\rangle + |1s_2\rangle\}$$
(1.15a)

$$|\psi_2\rangle = 0.8038\{|1s_1\rangle - |1s_2\rangle\}$$
 (1.15b)

Applying the symmetry operations of the C_{2v} point group to both $|\psi_1\rangle$ and $|\psi_2\rangle$ we find out that $|\psi_1\rangle$ and $|\psi_2\rangle$ transform according to the A_1 and B_2 irreducible representations, respectively (see Table 1.1). Accordingly, the symmetric/antisymmetric combination of atomic orbitals is labeled a_1 and b_2 , respectively, as shown in Figure 1.4.

Let us now proceed with the calculation of the energy diagram for the water molecule by allowing the interaction between the two MOs from the H-H molecule and the oxygen atomic orbitals. If we apply the symmetry operations to the oxygen s and p atomic orbitals, we find that s and p_z transform according to the A_1 irreducible representation, and p_x and p_y according to the B_1 and B_2 irreducible representations, respectively, hence the labels $a_1(s, p_z)$, $b_1(p_x)$, and $b_2(p_y)$. Before trying to generate the corresponding secular 6×6 determinant we should have in mind that symmetry is of great help because according to group theory, two orbitals will not interact unless they are of the same symmetry. This strongly reduces the number of nonzero s_{ik} terms. With the convention $a_1(H1s) \equiv 1, b_2(H1s) \equiv 2$, $a_1(O1s) \equiv 3$, $b_1(O2p_x) \equiv 4$, $b_2(O2p_y) \equiv 5$, and $a_1(O2p_z) \equiv 6$ the nonzero s_{ik} terms are $s_{13} = 0.5885$, $s_{16} = 0.3074$, and $s_{25} = 0.4993$, again taken from tabulated values according to the water molecular structure, and $s_{ii} = 1$ for j = 1, ..., 6. In addition, $h_{11} = -15.48 \text{ eV}, h_{22} = -10.62 \text{ eV}$, as previously obtained for the H–H case (Figure 1.4), and $h_{33} = -32.30$ eV and $h_{44} = h_{55} = h_{66} = -14.80$ eV, where -32.30and -14.80 eV correspond to the O1s and degenerate O2p ionization energies, respectively $(h_{13} = h_{31}, h_{16} = h_{61}$ and $h_{25} = h_{52}$ are obtained using the Wolfsberg-Helmholtz approximation mentioned earlier). From the corresponding determinant:

$$\begin{vmatrix} -15.48-\epsilon & 0 & 0.59(-41.81-\epsilon) & 0 & 0 & 0.31(-26.49-\epsilon) \\ 0 & -10.62-\epsilon & 0 & 0 & 0.50(-22.24-\epsilon) & 0 \\ 0.59(-41.81-\epsilon) & 0 & -32.30-\epsilon & 0 & 0 & 0 \\ 0 & 0 & 0 & -14.80-\epsilon & 0 & 0 \\ 0 & 0.50(-22.24-\epsilon) & 0 & 0 & -14.80-\epsilon & 0 \\ 0.31(-26.49-\epsilon) & 0 & 0 & 0 & 0 & -14.80-\epsilon \\ \end{vmatrix} = 0$$

$$(1.16)$$

the following energies (in eV) are obtained:

$$\epsilon_1 = -34.02, \epsilon_2 = -17.11, \epsilon_3 = -15.33, \epsilon_4 = -14.80, \epsilon_5 = -0.22, \epsilon_6 = 14.35$$

Figure 1.5 summarizes the orbital interaction diagram with the corresponding energies as calculated with the EH method. The resulting symmetry adapted water MOs are labeled according to the irreducible representation they belong to and to an integer number that just indicates a sequence. Note that the lowest MO is labeled $2a_1$ because $1a_1$ would correspond to the O1s core level, which participates negligibly in the molecular bonding.

Each MO can allocate two electrons, so that because oxygen participates with 6 electrons to the bonding (atomic number 8 minus the 2 from the 1s level) and



FIGURE 1.5 Orbital interaction diagram for H₂O. Energies (eV) obtained from an EH calculation are indicated and scaled. The orbital mixing is: $2a_1 \rightarrow 81\%$ O2s, 19% H1s, $1b_2 \rightarrow 66\%$ O2 p_y , 34% H1s, $3a_1 \rightarrow 93\%$ O2 p_z , 1% O2s, 6% H1s, $1b_1 \rightarrow 100\%$ O2 p_x , $4a_1 \rightarrow 17\%$ O2s, 7% O2 p_z , 76% H1s. $2b_2 \rightarrow 34\%$ O2 p_y , 66% H1s. (Courtesy of E. Canadell.)

each hydrogen gives one, we have 8 electrons to distribute. These 8 electrons fill the $2a_1$, $1b_2$, $3a_1$, and $1b_1$ MOs and leave the rest, $4a_1$ and $2b_2$, empty. $1b_1$ and $4a_1$ are termed the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO), respectively. $2a_1$ and $1b_2$ have bonding and $4a_1$ and $2b_2$ antibonding character, respectively, and $3a_1$ and $1b_1$ are nonbonding, also known as lone-pairs. The fact that the water molecule has two such lone-pairs makes it rather unique, allowing versatile interaction with other molecules, as we show in Section 1.4, through hydrogen bonding (H-bonding). This enables the water molecule to adapt to many configurations and here lies precisely the core of the complexity.

We now compare the relatively simple EH calculation with a state of the art (at the time this text is being written) density functional theory (DFT) calculation using the Gaussian code with the Becke three-parameter Lee–Yang–Parr (B3LYP) hybrid functional (Stephens et al. 1994) and the 6-311++G(2d,2p) basis. The obtained energies (in eV) are:

$$\epsilon_1 = -27.72, \quad \epsilon_2 = -14.97, \quad \epsilon_3 = -10.64, \quad \epsilon_4 = -8.77, \\ \epsilon_5 = -0.59, \quad \epsilon_6 = 0.79$$

Many simulations of the MO structure of water can be found in the literature but it is beyond the scope of the present book to summarize them. The point here is to be able to compare a simplified vis à vis a complex calculation. The energies obtained from both simulations are compared in Figure 1.6 to available photoemission data from Winter et al. (2004) on water vapor using synchrotron radiation (SR) in the vacuum ultraviolet (VUV) region. According to Koopmans' theorem, the molecular ionization energies correspond to orbital energies, hence the photoelectron spectrum of a molecule should be a direct representation of the MO energy diagram. This is true if the vibrational structure is ignored as it is in the present case. Figure 1.6 proves such an assessment illustrating the correctness of the MO approach. The calculated energies have been rigidly shifted (-3.83 and +2.2 eV for the DFT and EH)calculations, respectively) so as to bring the $1b_1$ MO to the well-known experimental -12.6 eV value. The figure is completed with available X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) from Guo and Luo (2010) taken from liquid water. Table 1.2 compares both calculated and measured MO energies and includes a self-consistent Hartree-Fock (HF) calculation from Ellison and Shull (1955) as well as X-ray photoemission spectroscopy (XPS) results of water vapor taken with 1486.6 eV photons (Siegbahn 1974). We observe an overall agreement for the occupied MOs, and the accuracy of the powerful DFT method, which correctly predicts the experimental values. In the case of the $1a_1$ MO, the corrected DFT value is -524.2 eV, quite far from the experimental -540.0 eV (Lundholm et al. 1986). A major prediction difference involves the unoccupied, also termed virtual, states. DFT provides the best approximation but both the EH and HF methods fail to reproduce the experimental data.

Why EH fails can be inferred from the simple H–H subsystem discussed earlier. It can be shown, by solving (1.14) in the general case, that the bonding state lowers the initial $h_{11} = h_{22} = -13.6$ eV energy by $-h_{11}(1 - K_{WH})s_{12}/(1 + s_{12})$ and the