A new isochemical model of the water molecule

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Abstract

Despite outstanding advances throughout this century, we still lack final knowledge on the structure of the water molecule because of a number of insufficiencies in available models identified in the text. In a preceding paper we submitted a covering of quantum chemistry called hadronic chemistry in its isochemical branch, and introduce a new model of the hydrogen molecule characterized by a bond at short distances of the two valence electrons into a singlet quasi-particle state called isoelectronium. In this paper we introduce, apparently for the first time, the isochemical model of the water molecule which is characterized by two isoelectronia, one per each H–O dimer and show that the model: (1) introduces a new strong force responsible for the molecular bond; (2) explains the reason why the water molecule has only two hydrogen atoms; (3) provides an accurate representation of the binding energy from the first axiomatic principles without ad hoc modifications; (4) permits a correct representation of electric and magnetic moments; and (5) reduces by at least a factor of 1000 computer usages for calculations due to a much faster convergent series. Experimental verifications, applications and novel predictions of the model are studied in subsequent papers. © 1999 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Water is an extremely important compound on Planet Earth in a biological as well as geophysical sense. For this reason, it has been subjected to comprehensive studies conducted since the beginning of quantitative science with outstanding results (see, e.g., Refs. [1,4,14,38,17,21]).

Despite that, a number of fundamental issues on the structure of the water molecule remain still open at the time of writing. Among them we note: the inability to explain why the hydrogen and water molecules only have two H-atoms (because the admitted forces, such as the exchange and van der Waals forces, are of nuclear type thus, being conceived and applicable for an arbitrary number of constituents); the binding energy still misses 1 to 2% under the strict implementation of the quantum axioms; accurate representations are based on structural changes of the Coulomb law, such as via Gaussian screenings whose axiomatic implications require a specific study; larger percentages are missing in the representation of electric and magnetic moments (which sometimes even have the wrong sign); calculations continue to require large computer times because of poorly convergent series; we still miss an explanation of the electron 'correlation energy'; and other still open basic issues.

When passing from the structure of one water molecule to more general profiles, the number of open basic issues increases. For instance, it is generally admitted that quantum chemistry has been unable to provide a systematic theory of the liquid state in general, let alone that of the water in particular.

Also, chemical reactions in general are irreversible,

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while the axiomatic structure of quantum chemistry is strictly reversible because the theory is strictly Hamiltonian and all known potential forces are reversible. This results in a seemingly irreconcilable incompatibility of the very axiomatic structure of quantum chemistry with chemical reactions in general, and those involving water in particular. In fact, there is no known rigorous way in which the reversible axiomatic structure of quantum chemistry can be turned into the irreversible form needed to represent irreversible events of the chemical reality.

When passing to water as a constituent of biological entities, the limitations of quantum chemistry reach their climax. In fact, biological structures such as a cell are not only irreversible (because they grow, age and die), but have such a complex structure to require multi-valued theories (also known in mathematics as hyperstructures). The expectation that quantum chemistry, with its reversible and single-valued structure, can effectively represent biological structures and their evolution is beyond the boundaries of science.

In view of the above limitations, in the preceding paper Ref. [2,24–29] we have constructed a covering of quantum mechanics under the name of hadronic mechanics. In essence, the two mechanics coincide everywhere, except the region inside a sphere of radius of the order of 1 fm ($= 10^{-13}$ cm) called hadronic horizon in which the broad theory holds. Hadronic mechanics then results to be a form of 'completion' of quantum mechanics much along the lines of the historical Einstein–Podolsky–Rosen argument, although achieved via the addition of contact, nonHamiltonian, nonlinear, nonlocal and nonpotential forces due to deep overlapping of the wavepackets of particles.

On more technical grounds, hadronic mechanics is based on new mathematics, called iso- geno- and hyper-mathematics for the characterization of generalized reversible, irreversible and multivalued systems, respectively.

On pragmatic grounds, hadronic mechanics can be easily constructed via a step-by-step transform $UU^\dagger$ of all aspects of quantum mechanics which is equal to the unit (unitary) everywhere, except inside the hadronic horizon (where it is nonunitary). NonHamiltonian effects due to deep wave overlappings can therefore, be easily added to a conventional model (when appropriate) via nonunitary transforms of the latter.

Following the construction of hadronic mechanics, the authors have constructed a corresponding covering of quantum chemistry under the name of hadronic chemistry [3,30], which also comprises three different branches, isochemistry for the representation of reversible yet generalized structures; genochemistry for the representation of irreversible structures; and hyperchemistry for the representation of irreversible multivalued structures.

Isochemistry was then applied for the construction of a new model of the hydrogen molecule and proved that it does resolve at least some of the insufficiencies of quantum chemistry, such as an explanation that the molecule has only two H-atoms; a representation of the binding energy exact to the seventh digit; computer calculations which converge at least 1000 times faster than those of quantum chemistry and other advances.

In this paper we shall study the isochemical branch of hadronic chemistry; we shall submit, apparently for the first time, the isochemical model of the water molecule; and we shall show that it does indeed permit the resolution of at least some of the insufficiencies indicated above.

A technical understanding of this paper, requires at least some knowledge of Refs. [2,24–29,3,30] whose review is omitted here for brevity.

2. Exactly solvable isochemical model of the water molecule with stable isoelectronium

In the preceding paper Ref. [3] we have introduced the main hypothesis of the isochemical molecular model according to which two electrons from two different atoms bond themselves into a singlet quasistable and quasiparticle state called isoelectronium which describes an oo-shaped orbit around the nuclei, as it is the case for planets in certain binary starts.

The main characteristics of the isoelectronium in the first nonrelativistic approximation were calculated and resulted in being: charge −2e, spin 0, magnetic dipole moment 0, mass 1.022 MeV and radius

$$r_c = b^{-1} \approx (\hbar^2/mV)^{1/2} = (\hbar/m\omega_0)^{1/2}$$

$$= 6.8432329 \times 10^{-11} \text{ cm} = 0.015424288 \text{ bohrs}$$

$$= 0.006843 \text{ Å}. \tag{1}$$

In the above nonrelativistic approximation, the mean life resulted in being infinite (full stability, see Ref. [3], Section 5 in general and Eq. (5.11) in particular), with the understanding that relativistic corrections are expected to render it finite (partial stability). All conventional forces of current use in chemistry (the exchange, van der Waals and other forces) then hold between the isoelectronium and the remaining electrons.

The model was applied to the isochemical model of the hydrogen molecule and implied: (1) the introduction of a new bonding force given by the Hulten force besides those in current use, which is so strong to overcome the repulsive Coulomb force (see Ref. [3], Section 5 in general and Eq. (5.6) in particular), thus being capable of representing the strong molecular
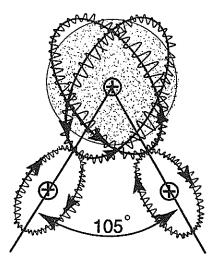
Fig. 1. A schematic view of the proposed isochemical model of the water molecule which is depicted in terms of orbits of the valence electrons (rather than in terms of density distributions) when at absolute zero degrees temperature and in the absence of rotations, vibrations, translations and other motions. The fundamental assumption is that the two valence electrons, one per each pair of atoms, correlate themselves into a bonded singlet state at a short distance we have called isoelectronium, which is assumed to be stable. In this case the only orbit yielding a stable water molecule is that in which the isoelectronium describes an oo-shaped orbit around the respective two nuclei of the H- and O-atoms. The isoelectronium is then responsible for the attractive force between the two atoms. The binding energy is instead characterized by the oo-shaped orbit of the isoelectronium around the two nuclei, conceptually represented in this figure via a standing wave for a particle of spin 0 and charge −2e. In this way the water molecule result in being characterized by two isoelectronia, one per each dimer H–O. The water molecule is then reducible to two intersecting H–O dimers with a common O-atom. Note that, already in the absence of molecular motions, the orbits of the two isoelectronia are perpendicular to the H–O–H plane, thus confirming a characteristic of the water molecule indicated in Ref.[1]. Needless to say, when rotations are added, they imply the rotation of the orbits of the isoelectronia around their individual symmetry axis, resulting in two spherical distributions of the electrons, thus recovering conventional spherical charge distributions. Conventional exchange, van der Waals and other forces then imply the reconstruction of the conventional charge distributions [1]. The model then permits a representation of: (1) the strong value of the molecular bond; (2) the reason why the H_2O) molecule has only two hydrogen atoms; (3) the exact representation of the binding energy, electric and magnetic moments; and other advances studied in the text. The model of the H–O dimer studied in the text is then extendable to other H-based dimers, such as H–C.

bonds as occurring in reality; (2) the immediate explanation of the reason why the molecule has only two hydrogen atoms, evidently because, once the two elec-

trons of the H_2 molecule are bonded into the isoelectronium, there is no possibility of bonding a third one; (3) a representation of the binding energy of the hydrogen molecule accurate to the seventh digit; (4) a decrease of computer usage for calculation at least 1000 fold; and (5) other advances studied in subsequent papers, such as the impossibility for the molecule to acquire a net magnetic polarity because the two o-branches of the isoelectronium orbit imply opposite rotational motion, with consequently opposite magnetic polarities in agreement with reality.

In this paper we introduce, apparently for the first time, the isochemical model of the water molecule $H_2O = H–O–H$ considered at °C and in the absence of any rotational, oscillation or other motion. The main hypothesis is that each electron from the two H-atoms couples in singlet with one 2p electron from the O-atom, resulting in two isoelectronia, one per each H–O dimer as in Fig. 1.

According to this model, the bonding force between the two H- and O-atoms is given by the Hulten force between the two valence electrons in the isoelectronia, plus contributions from the conventional exchange, van der Waals and other forces. The binding energy is instead characterized by the two oo-shaped orbits of the isoelectronia around the H–O–H nuclei.

Again, in the first nonrelativistic approximation we shall assume in this section (see next section for a different assumption) that the two isoelectronia of the water molecule are permanently stable and have charges −2e, spin 0, magnetic dipole moment 0, and the same radius as that in the H_2 molecule, Eq. (1). On the contrary, the radii of the two oo-branches of the H–O dimers are expected to be different between themselves, as well as different than the corresponding value in the H_2 molecule.

In this section we shall introduce, apparently for the first time, a hadronic/isoschroedinger equation for the water molecule which is evidently approximate, yet exactly solvable. We shall then show that the model is extendable to all other dimers comprising one hydrogen atom, such as H–C.

For this purpose, we approximate the H–O–H molecule as being composed of two intersecting identical dimers H–O with evidently only one oxygen atom. This requires a first correction due to the lack of independence of said dimers reviewed in Section 3. Moreover, in each H–O dimer we shall assume that the oxygen appears to the isoelectronium as having only one net positive charge +e located in the nucleus. This evidently requires a second correction which essentially represents the screening of the various electrons of the oxygen. Additional corrections are also in order along conventional lines [1].

A study of these corrections has indicated that they can all be represented via one single Gaussian screen-

ing of the Coulomb law of the type

$$\frac{+e}{r} \rightarrow \frac{+e(1 \pm e^{-\alpha r^2})}{r},$$ (2)

where β is a positive parameter to be determined from experimental data, the sign $-$ applies for the screened O-nucleus as seen from an electron (because of the repulsion caused by the electron clouds of the oxygen), while the sign $+$ applies for the screen O-nucleus as seen from the H-nucleus (because of the attraction this time caused by said electron clouds).

The resulting model is structurally equivalent to the isochemical model of the hydrogen molecule of Ref. [3], except for the modifications indicated about, and can be outlined as follows.

By denoting with the sub-indices 1 and a the hydrogen, 2 and b the oxygen, prior to the indicated screening and in the absence of all hadronic effects, the conventional Schroedinger equation of the H–O dimer with the oxygen assumed to have only one elementary charge $+e$ in the nucleus is given by

$$\left(\frac{1}{2\mu_1}p_1 p_1 + \frac{1}{2\mu_2}p_2 p_2 - \frac{e^2}{r_{1a}} - \frac{e^2}{r_{2a}} - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2b}} + \frac{e^2}{R} \right.$$
$$\left. + \frac{e^2}{r_{12}} \right) | \psi \rangle = E | \psi \rangle.$$ (3)

As it was the case for the H_2-molecule, our task is that of subjecting the above model to a transform which is nonunitary only at the short mutual distances $r_c = b^{-1} = r_{12}$ of the two valence electrons (here assumed to be inside the hadronic horizon), and becomes unitary at bigger distances $\hat{I}_r \leq 10^{-13}$ cm $\neq I$, $\hat{I}_r \gg 10^{-13}$ cm $= I$. This guarantees that our isochemical model coincides with the conventional model everywhere except for small contributions at small distances.

We assume that the state and related Hilbert space of systems (3) can be factorized in the familiar form (in which each term is duly symmetrized or antisymmetrized)

$$| \psi \rangle = | \psi_{12} \rangle \times | \psi_{1a} \rangle \times | \psi_{1b} \rangle + | \psi_{2a} \rangle + | \psi_{2b} \rangle \times | \psi_R \rangle,$$

$$\mathscr{H}_{\text{Tot}} = \mathscr{H}_{12} \times \mathscr{H}_{1a} \times \mathscr{H}_{1b} \times \mathscr{H}_{2a} \times \mathscr{H}_{2b} \times \mathscr{H}_R.$$ (4)

The nonunitary transform we are looking for shall act only on the r_{12} variable characterizing the isoelectronium, while leaving all other variables unchanged. The simplest possible solution is given by

$$U(r_{12})U^{\dagger}(r_{12}) = \hat{I} = e^{[\psi(r_{12})/\hat{\psi}(r_{12})] \int dr_{12} \hat{\psi}^{\dagger}(r_{12})_{1\downarrow} \times \hat{\psi}(r_{12})_{2\uparrow}},$$ (5)

where the ψ's represent conventional wavefunction and the $\hat{\psi}$'s represent isowavefunctions.

We now construct the isochemical model by transforming short-range terms (isochemistry) and adding untransformed long-range ones (chemistry), thus resulting in the radial equation

$$\left(-\frac{\hbar^2}{2\mu_1}\nabla_1^2 - \frac{\hbar^2}{2\mu_2}\nabla_2^2 + \frac{e^2}{r_{12}}\hat{T} - \frac{e^2}{r_{1a}} - \frac{e^2}{r_{2a}} - \frac{e^2}{r_{1b}} \right.$$
$$\left. - \frac{e^2}{r_{2b}} + \frac{e^2}{R} \right) | \hat{\psi} \rangle = E | \hat{\psi} \rangle.$$ (6)

By using the derivation of Ref. [3] and by recalling that the Hulten potential behaves at small distances like the Coulomb one, Eq. (6) becomes

$$\left(-\frac{\hbar^2}{2\mu_1}\nabla_1^2 - \frac{\hbar^2}{2\mu_2}\nabla_2^2 - V\frac{e^{-r_{12}b}}{1 - e^{-r_{12}b}} - \frac{e^2}{r_{1a}} - \frac{e^2}{r_{2a}} \right.$$
$$\left. - \frac{e^2}{r_{1b}} - \frac{e^2}{r_{2b}} + \frac{e^2}{R} \right) | \hat{\psi} \rangle = E | \hat{\psi} \rangle.$$ (7)

The above model can be subjected to an important simplification. In fact, in the first approximation herein considered, the H–O dimer (7) can be reduced to a restricted three body problem similar to that possible for the conventional H_2^+ ion [1], but not for the conventional H_2 molecule, according to the equation

$$\left(-\frac{\hbar^2}{2\mu_1}\nabla_1^2 - \frac{\hbar^2}{2\mu_2}\nabla_2^2 - V\frac{e^{-r_{12}b}}{1 - e^{-r_{12}b}} - \frac{2e^2}{r_a} - \frac{2e^2}{r_b} \right.$$
$$\left. + \frac{e^2}{R} \right) | \hat{\psi} \rangle = E | \hat{\psi} \rangle.$$ (8)

The indicated corrections due to the screening of the various electrons in the oxygen and other corrections are needed in the 'sensing' of the O-nucleus by the isoelectronium as well as by the H-nucleus, yielding in this way our final model

$$\left(-\frac{\hbar^2}{2\mu_1}\nabla_1^2 - \frac{\hbar^2}{2\mu_2}\nabla_2^2 - V\frac{e^{-r_{12}b}}{1 - e^{-r_{12}b}} - \frac{2e^2}{r_a} \right.$$
$$\left. - \frac{2e^2(1 - e^{-\alpha r_b})}{r_b} + \frac{e^2(1 + e^{-\alpha R})}{R} \right) | \hat{\psi} \rangle = E | \hat{\psi} \rangle$$ (9)

where α is a positive parameter and E is half of the binding energy of the water molecule.

Under the latter approximation, the model permits, for the first time to our knowledge, the achievement of an exact solution for the structure of the water molecule which however, exists only for the case of the fully stable isoelectronium. In fact, for the unstable

isoelectronium the model becomes a four-body structure which, as such, admits no exact solution.

Besides being exactly solvable, model (9) exhibits a new explicitly attractive force among the neutral atoms of the H–O dimer which is absent in conventional quantum chemistry; the equation also explains the reasons why the water molecule admits only two H-atoms; as we shall see in the remaining sections, the model also permits the exact representation of the binding energy, electric and magnetic moments; the model also yields much faster convergence of a series with much reduced computer times, and resolves other insufficiencies of conventional models.

Finally, the model is evidently extendable with simple adjustment to an exact solution of other dimers involving the hydrogen, such as H–C. In addition, it permits the identification of electric and magnetic polarizations which are not predictable with quantum chemistry.

3. Gaussian approximation of the isochemical model of the water molecule with unstable isoelectronium

The solution of the exactly solvable Eq. (9) will be studied elsewhere. In this section we shall study a Gaussian approximation of the isochemical model of the water molecule in which the Hulten potential is essentially approximated to a certain Gaussian form.

It should be indicated from the outset that such an approximation implies an evident weakening of the Hulten attraction among the two isoelectrons of the isoelectronium which, in turn, implies the instability of the isoelectronium itself, thus reaching a model which is somewhat intermediate between the full isochemical model and the conventional quantum mechanical model of the water.

Despite this approximate character, the results of this section are significant because they show the capability by isochemistry to achieve an essentially exact representation of the binding energy, electric and magnetic moments and other characteristics of the water molecule.

But any potential can be exactly reproduced by a sufficient number of Gaussians, including the Hulten potential. Therefore, the exact representations of this section reached for only one Gaussian can be evidently expected to persist for the full isochemical model.

Finally, Gaussian and other screenings of the conventional Coulomb law are now known to be outside the equivalence class of quantum chemistry because they require a nonunitary transform [3]. The Gaussian approximation of this section is, therefore, fully within the basic, nonunitary, axiomatic structure of hadronic chemistry, while similar screenings have questionable axiomatic foundations when believed to be part of quantum chemistry.

The results of this second study can be outlined as follows. Since HOOH will be slightly more 'allowed' under collisions of HO^- with neutral H_2O and the internal repulsion within the anion could favor the release of $(2e)^{-2}$ to form OH^+. Collisions of OH^+ with OH^- will then further enhance the concentration of HOOH and transport of $(-2e)$ will contribute to the current.

The question here is whether under extreme cases of forced conduction a singlet-pair of electrons (isoelectronium, can be 'triggered' (in the nomenclature of Santilli [6] and Animalu and Santilli [31]) within a water molecule to form and release a $-2e$ charged isoelectronium particle which will provide an additional conduction mechanism analogous to Cooper-pairs of electrons in superconducting solids. Since the energy depth of the V_0 parameter in the isoelectronium Hulten potential of the original 1978 derivation by Santilli [6] and Animalu and Santilli [31] is not known, nor how closely the Gaussian representation fits the Hulten form, we can only match the radius of the two potentials and calculate the energy differences caused by the 'sticky-electrons' model in which a transient form of isoelectronium can occur (the Gaussian potential may well not be deep enough to ensure a permanent bound state for isoelectronium).

The 'sticky-electron' model is a parametric model which includes the magnetic dipole attraction between singlet-paired electrons as well as the nonlocal merging of the wave-packets of each electron at short distance. The radius of the Gaussian screening is then determined empirically by fitting the calculated energy as nearly as possible to the most accurate energy values available. As used here it should be emphasized that the off-axis positions of the Gaussian-lobe basis sets [7,8,32–36,9,43,37] ensure that angular correlation is included as well as radial dependence and can include the magnetic dipole attraction of opposite electron spins as well as merger of wavepackets. One radial screening parameter used with off-axis basis sets parametrically covers all forms of short range attraction which may include angular dependence. Thus, the present model can give us an approximate energy difference required to release an electron-pair from OH^-.

$$OH^- \rightarrow OH^+ - 2e. \tag{10}$$

It will be seen below that the energy difference between OH^- and OH^+ as calculated, allowing a transient form of isoelectronium, is well within the voltages accessible using capacitive discharge through water. Such a mechanism which would allow $(-2e)$ particles to flow through water would not be superconductivity

since the freely moving molecules and ions are not constrained to lattice positions as in solids so that resistive I^2R heating will still occur. This is mainly due to the fact that conduction in liquids occurs by mobility of both anions and cations along with size differences, polarizability differences and special mechanisms such as the hydrogen-bonding 'domino' effect for H^+ transport. In solid-state conduction only the electrons move (ignoring in-place phonon oscillations because the atoms do not travel from one electrode to the other; the apparent motion of positively charged 'holes' is also due to the motion of electrons while the atoms merely oscillate about the mean lattice positions), but in solutions there is two-way traffic with positive and negative ions traveling in the opposite directions and with differing velocities; this will certainly lead to resistive heating even up to the vaporization of the water as well as a high probability of ion collisions. It should be noted that in recent work Zhitenev et al. [10] have measured migration of paired-electrons to quantum dot wells in Gaas and Boyd and Yee [11] have observed 'bipolaron' electron pairs in alkali halide lattice vacancies. Calculations leading to unexpected bipolarons in crystal lattice vacancies have also been observed by using the method of Fois et al. [12]. These findings in solids lend support to the concept of an electron pair as an individual particle, called isoelectronium here.

The calculations given here do not prove the presence of isoelectronium particles in high current aqueous electrical conduction, they only indicate the energy threshold necessary to form $(-2e)$ within the conducting solution by double-ionization of OH^-. It is not easy to envision an experiment that would be able to analyze components of a given current due to a multiple ion species in terms of the amount of current due to $(-2e)$ particles and none is proposed here. However, there may be a chemical test for such a mechanism. Once OH^- is double-ionized to form OH^+, collisions with $(-2e)$ particles would regenerate OH^- ions just as collisions of H^+ with OH^- will reform H_2O and no new species will be evident. However, if OH^- collides with OH^+ a new chemical species (HO–OH) will be formed that may last long enough in the 'liquid plasma' to behave as a strong oxidizing agent. Thus, organic compounds with double bonds (alkenes) which have negligible conductance could be added to water undergoing a high current flow to cause hydroxylation of such compounds [13] (i.e., conversion of alkenes to epoxides which are then readily hydrolyzed in the presence of H^+ to diols). Enhanced concentrations of epoxides and diols would be indirect evidence of double ionization of OH^-.

$$OH^+ + OH^- \rightarrow HO\text{-}OH$$

$$CH_2{=}CHR + HO{-}OH \rightarrow \underset{\underset{O}{\diagdown \diagup}}{CH{=}CHR} + H_2O$$

$$\tag{11}$$

If isoelectronium can be detected indirectly by a chemical method this would in itself be an important inference on the existence of a two-electron, spin-paired particle. More important, 'isochemical reactions' could be driven by high conduction 'liquid plasma' environments where isoelectronium is at an enhanced concentration.

Another case of interest is that of aqueous 'mixtures' of insoluble organic compounds forming a separate 'oil layer' over water in an intense magnetic field of several Tesla. At normal thermal energy of room temperature kT (RT per mole) the main energy form would be a random Brownian motion. However, in the presence of a strong magnetic field HO^+ and HO^- would be constrained to favor circular motions in the magnetic field by the 'cyclotron effect', but there is no obvious source of HO^+. Since two ions of opposite sign charges would be favored to collide by both electrical attraction and by opposite path curvature in a magnetic field, there is an enhancement that when created as a normal result of the $(H^+, OH^-, H^-, H_2O_2, HO_2^-, H_2O)$ equilibrium system studied by Pourbaix [5], any natural concentration of HOOH would be augmented by collision of H^+ with HOO^-. In addition there is some slight change that H^+ would collide with OH^- with sufficient excess energy to produce OH^+ and H^-. Thus, the presence of an intense magnetic field

$$H^+ + HOO^- \rightarrow HOOH, \tag{12a}$$

$$H^+ + OH^- \rightarrow H^- + OH^+ \tag{12b}$$

$$OH^+ + OH^- \rightarrow HOOH \tag{12c}$$

would cause positive and negative ions to collide more easily while traveling in the opposite rotational arcs in such a way as to enhance the concentration of HOOH which could then epoxidate alkenes and upon hydrolysis would lead to diols. A direct measure of this effect would be to determine the enhanced solubility of alkenes in water. The alkenes are only slightly soluble in water ('oil and water do not mix') but alkenes converted to diols will have a measurably greater solubility in water due to the attached –OH groups. Again, if such enhanced solubility of alkenes in water can be caused by intense magnetic fields, this would be indir-

ect evidence of the existence of an electron-pair particle.

Note below in the description of the calculations that the key to this work is that it is easy to calculate the energy of OH⁻ when one subtracts a small amount from the two-electron repulsion terms in the usual HFR–SCF treatment due to the attraction of singlet-paired electrons at close range within 1.0 picometer. In the recent 'Handbook of Computational Quantum Chemistry' by Cook [14,38] (p. 438) it is noted that solutions to the HFR–SCF scheme may not always exist for anions! However, in the method used here convergence of the HFR–SCF process was normal for an SCF process, presumably because the so-called 'self-energy' error of the Hartree–Fock method [15] (each electron repels all electrons including itself) is largely cancelled by the new attractive terms used here. In effect this description of OH⁻ is possible because of the easy convergence of the 'correlated-SCF' process.

The model adopted here is to use the usual Hartree–Fock–Roothaan self-consistent-field equations [16] (which also has some formal flaws such as the self-interaction terms [15]) and question the form of the Coulomb interaction of the electrons. Note that reducing the values of the Coulomb integrals will lower the energy by reducing the electron–electron repulsion while reducing the exchange terms will raise the energy, but the (1/2) factor reduces the effect of the exchange terms. Thus, a reduction of the value of the integrals will lower the energy. Note that Goodgame and Goddard [15] have already recommended reducing the atomic self-energy by subtracting 1.39 eV from Hartree–Fock exchange integrals in the cases of Cr_2 and MO_2.

$$FC = ESC;$$

$$F_{i,j} = H_{i,j} + \Sigma\Sigma p_{k,l}[(i,j/k,l) \tag{13a}$$

$$- 1/2(i,k/j,l)], $$

$$(i,j/k,l) = \int\int \chi_i(1)\chi_j(1)/(1/r_{12})/\chi_k(2)\chi_l(2)d\tau_1\, d\tau_2, \tag{13b}$$

$$P_{i,j} = 2\Sigma_n cn,\, ic_{n,j} \tag{13c}$$

(sum n only over occupied orbitals).

The 1995 paper on Cooper pairs by Animalu and Santilli [31] invokes the nonlocal hadronic attractive force evident in the π^0-meson as applied to a pair of singlet-paired electrons which form a boson quasi-particle. However, the 'collapsed' positronium rapidly decays since the particle–antiparticle annihilation takes

place in less than a picosecond. In the electron–electron case it is believed that there may be a stable quasi-particle. After using a nonlocal isotopic nonlinear transformation, the hadronic attraction was transformed back to real-space and modeled with a Hulten potential. In this work considerable effort was made to evaluate the matrix elements for the Hulten potential without success. Examination of the original 1978 paper on positronium collapse by Santilli [6] and Animalu and Santilli [31] revealed that the Hulten potential is not necessarily a unique representation of the hadronic force; at least a linear combination of similar potentials could be used to represent the Hulten if the matrix element of such other potentials could be evaluated. The depth of the screened Gaussian approximation is determined here by requiring that the width at half height of the Gaussian is equal to the 'b' value of the Hulten 'horizon', the radius at which the Coulomb repulsion is zero. Thus, the screened-Gaussian potential probably has a depth which is too shallow, although the V_0 depth parameter for the Hulten potential is not known at present.

This work assumes that until the matrix elements of a two-electron interaction for singlet-pairs can be found for the Hulten potential, a Gaussian-screened-Coulomb potential can be used to describe the real-space form of the hadronic attraction and a parameter fitted to experimental energies the screening exponent probably includes other effects such as the magnetic dipole interaction of two electrons with opposite spin-magnetic-moments. This form has the important property that it can be merged with the general case of the four-center Coulomb or exchange integral derived by Shavitt [17] using the famous Gaussian transform technique.

The Gaussian transform two-electron integral, for four Gaussian spheres has been used in a number of Gaussian-lobe basis SCF programs written by Mosier and Shillady [18], Shillady and Baldwin [39], Shillady and Talley [19], Shillady and Richardson [40] and others. It is important to note that the formula is completely general in orientation of four Gaussian sphere lobe-orbitals as well as the distance between two electrons. As modified for description of correlation of two electrons, such a general formula can describe angular correlation as well as distance interaction. Thus, matrix elements of a screened-Coulomb interaction were subtracted from the usual $(1/r)$ Coulomb repulsion to model the real-space form of the hadronic attraction of two electrons. This work added the Gaussian screening as $\exp(-\alpha r^2)/r$ so that the special properties of Gaussians could be used, especially the properties that the product of two Gaussians form another Gaussian (times a rec-entering factor) and that polar coordinates readily separate into factorable x, y and z components. The goal is to evaluate the two-

Table 1
Isoelectronium results for selected molecules[a]

	OH$^+$	OH$^-$	H$_2$O	HF
SCF-energy (DH)	−74.860377	−75.396624	−76.058000	−100.060379
Hartree–Fock[c]				−100.07185[c]
Iso-energy[b]	−75.056678	−75.554299	−76.388340	−100.448029
Horizon RC (A)	0.00038	0.00038	0.00038	0.00030
QMC energy[c,d]			−76.430020[d]	−100.44296[c]
Exact non-rel.				−100.4595[c]
Iso-dipole (D)	5.552581	8.638473	1.847437	1.8413778
Exp. dipole			1.84 [2]	1.82

[a] Notes: (HD$^+$) Dunning–Huzinaga (10 S/6P), [6,2,1,1,1/4,1,1] + H2S1 + H2P1 + 3D1.
[b] Iso-energy calibrated to give maximum correlation for HF.
[c] Hartree–Fock and QMC energies from Luchow and Anderson [22].
[d] QMC energies from Hammond et al. [21].

electron four-center matrix elements of the Gaussian-screened-Coulomb potential shown below.

$$Y(r) = (1 - 2 \ \exp[-(\alpha r^2)]/r. \tag{14}$$

Amazingly, the Gaussian-transform variable 's' can be simply shifted by the 'α' value of the screened-Gaussian exponent and carried through the original derivation until the last step when integration over 's' is required. Alpha is usually a very high number, this work used 0.13441885×10^7. At this point the usual Coulombic interaction resorts to a well-known auxiliary function F_0 which has been studied by Mosier and Shillady [18], Shillady and Baldwin [40] and others. Since both $s^{1/2}$ and $(s+\alpha)^{1/2}$ occur in the denominator of the screened-Coulomb form, two poles occur in the integral. A change of variable absorbs the pole due to $(s+a)^{-1/2}$ and shifts the other pole due to $(s)^{-1/2}$ to the lower limit of the integral. A smooth spike is evident at the lower limit of the numerical integration using a 70 point Simpson's rule integration (two ranges are used with 20 points more closely spaced near the pole and 50 points for the remaining range).

This work was carried out using 64 bit double precision arithmetic which provides 14 significant figures. A simple offset (δ) of 1.0×10^{-15} has provided useful results with this simple offset to avoid numerical overflow. While this pole is formally a problem in needing a continuous function to integrate, numerical integration seems to handle this well out to 14 significant figures; particularly since the routines used for the Coulombic integrals are known to be accurate only to 12 significant figures. The area under the pole-spike is estimated as a narrow triangle upon a rectangle 1.0×10^{-15} wide with the height of the triangle set at 3.43207×10^8 times the height of the point set 1.0×10^{-15} into the range of integration (the first Simpson point). The present code for this screened-

Coulomb integral is presently slower than the corresponding $F_0 e$ [17] function used for the Coulombic integrals due to the 70 point Simpson integration, but the integrand is nearly flat after the spike at $s = 0.0$ so that the portion of the integrand can be evaluated more rapidly with fewer points. For the results presented here, the simple offset of the lower limit by 1.0×10^{-15} is adequate for this report. Further details on the auxiliary integral can be found in a previous paper on the H$_2$ molecule [20,41,42]. Work in progress indicates it may be possible to express the new auxiliary integral to an analytical expression involving the Erf(x) function, but until further checks are completed this work used the Simpson integration. Note the integral is a result of a simplification of a 12-fold integration over the volume elements of two electrons and has been reduced to a one-dimensional integration multiplied by appropriate factors.

4. Results

The geometry given for H$_2$O by Dunning [20,41,42] was used to carry out the usual HFR–SCF calculation after an additional 3 d orbital mimic [19,40] was optimized for the O-atom and (2 S,2p) orbitals were added for the H-atoms. The exponent for the O3 d orbitals was optimized to three significant figures and the (O3 d,H2 s,H2p) exponents were (2.498, 0.500, 1.000). These polarization orbitals were added to the Dunning–Huzinaga (10s6p) [20,41,42] basis with the H1 s orbitals scales to 1.2 which produced a lower energy than that of a 6-31G** basis using the GAMESS program. The bond length of OH$^+$ was optimized using GAMESS at the 6-31G** basis level and fund to be 1.0062 Å. The same bond length was used for OH$^-$ since the anion calculation using the

usual HFR–SCF process was not feasible and in any case the bond length is only slightly longer than that in water. The horizon cutoff value of 0.00038 Å optimized for H_2O was also used for OH^+ and OH^-. The spike in the numerical integral routine was optimized by fitting the r_c cutoff value so as to obtain as near as possible the non-relativistic energy of the HF molecule as determined from quantum Monte Carlo calculations [21]. The dipole moments for the ions are not very useful since ion dipoles are origin dependent, but they were calculated using the center-of-mass as the origin.

As we see in Table 1, the difference in energy between OH^- and OH^+ is 0.497621 hartrees (13.54 electron volts) according to the correlated-SCF calculations. It is clear from the standard SCF energy value for H_2O that this basis is very good, but not quite at the Hartree–Fock limit of energy. In addition, the fitting of the numerical integration spike so as to nearly reproduce the total energy of HF is not exact. These two artifacts introduce an energy uncertainty of about 0.0115 hartrees, but this is less uncertain than that of the quantum Monte Carlo energy of Luchow and Anderson [22]. Note that the iso-dipoles for H_2O and HF are very close to the experimental values which indicate that the calculated wavefunctions are of high quality as well as the energy values.

Since the ionization energy of a neutral H-atom is 13.60 eV and the energy difference of 13.54 eV would convert OH^- to OH^+, a threshold of about 13.7 eV should maintain H^+ in a solution as well as transfer ($-2e$) through an aqueous solution to or from the OH^-/OH^+ system. These calculations indicate that there may be an enhancement of current flow above a potential above 13.7 V across an aqueous cell and that the enhanced concentration of HOOH may be measurable above a potential of 13.7 V. It is worth repeating that this estimate is possible largely due to the easy convergence of the correlated-SCF process for a negative ion species; a process which is formally not defined under the usual Hartree–Fock–Roothaan process [14,38] and most quantum chemists are familiar with the difficulty in treating negative ions using the standard Hartree–Fock–Roothaan method.

Admitting that the correlated-SCF equations are a parametrized approximation of the Santilli derivation of the Hulten potential [6,31] for a bound electron-pair, the method has the advantage of easy incorporation into an existing Hartree–Fock–Roothaan Gaussian basis program merely by subtracting a small 'correlation integral' from the usual two-electron integrals. With some thought one should realize that fitting the single parameter (Gaussian screening exponent, α) to experimental energies and/or quantum Monte Carlo results will incorporate another attraction in the form of a magnetic dipole interaction between the spin moment of paired electrons. Including the magnetic

dipole interaction and substituting a Gaussian form for the Hulten exponential potential leaves only a simulation of the bound electron-pair 'isoelectronium' predicted by Santilli. Thus, these results are for a model in which the usual HFT–SCF method is corrected for at least two attractive interactions of electrons causing them to approach each other as if they were 'sticky'; hence the term 'sticky-electron-pair model'.

5. Conclusions

In the preceding paper [3,30] of this series we have presented a covering of quantum chemistry under the name of hadronic chemistry and applied the new discipline to the construction of a new model of molecular structures based on the bonding of a pair of valence electrons from different atoms into a singlet quasi-particle state called isoelectronium. In the preceding paper [3] we then applied the model to the structure of the hydrogen molecule by achieving results such as: a representation of the binding energy and other features of the hydrogen molecule accurate to the seventh digit; an explanation of the reason why the hydrogen molecule has only two hydrogen atoms; a reduction of computer usage at least 1000-fold; and other advances.

In this paper we have applied the isochemical model of molecular bonds to the water and other molecules with similar results. In fact, the isochemical model of the water and other molecules presented in this paper is supported by the following conceptual, theoretical and experimental evidence:

1. It introduces a new strong binding force (which is absent in current models) capable to explain the strength and stability of the molecules.
2. It explains the reason why the water molecule has only two hydrogen atoms.
3. It permits a representation of the binding energy of the water and other molecules which is accurate to several digits.
4. It represents electric and dipole moments and other features of the water and other molecules also accurate to several digits.
5. It permits a reduction of computer usages in calculations at least 1000-fold; as well as permitting other achievements similar to those obtained for the hydrogen molecule.

Moreover, as it happened for the hydrogen molecule [3,30], the value of the radius of the isoelectronium computed via dynamical equations in Section 3 has been fully confirmed by independent calculations for the water and other molecules conducted via the Gaussian-lobe basis set.

The emission of electron pairs in superconductivity

has been emphasized in the preceding papers. We indicate here preliminary yet direct experimental verifications of the isochemical model of molecular bonds offered by the ongoing experiments on photoproduction of the valence electrons in helium indicating that electrons are emitted in pairs [23]. The systematic repetition of these experiments specifically for water is recommended here. The statistical percentages of electron pairs over the total number of emitted electrons would then establish whether the isoelectronium is fully or only partially stable.

We should also recall that Shillady's computer program of isochemistry, called SASLOBE, has been shown in this paper to be capable of producing an essentially exact representation of experimental data on the water and other molecules 1000 times faster than conventional programs.

We should finally note that the representation of the binding energy, electric and magnetic moments and other characteristics of the water and other molecules exact to several digits confirms a main result of the preceding paper [3,30], namely, the identification of experimental evidence on the insufficiency of quantum mechanics and the validity of the covering hadronic mechanics for the representation of nonlinear, nonlocal and nonpotential–nonunitary effects due to deep overlappings of the 'extended wavepackets' of electrons with a 'point-like charge structure'.

These results evidently provide sufficient credibility to warrant systematic theoretical and experimental studies on the new isochemical model of water and other molecules.

In closing, we would like to indicate, for future study, that the new isochemical model of the water molecule implies new predictions of theoretical and industrial significance. In particular, in a future paper we plan to present theoretical and experimental evidence on an apparent enhancement of the energy content of hydrogen when subjected to certain magnetic and other polarizations.

As additional possibilities we note that, in this work the correlated-SCF method is used to easily obtain an energy for the OH^- anion in water, while the OH^+ ion is easily treated in either the standard or modified method. The difference in energy between the eight-electron OH^+ system and the 10-electron OH^- system is found to be 13.54 eV. This represents the energy needed to remove $(-2e)$ from OH^-. This indicates there may be a threshold for current flow in terms of $(-2e)$ as a quasi-particle in aqueous media at 13.6 eV. This voltage will also maintain H^+ in a solution to some extent. Organic alkenes in a solution should undergo epoxidation followed by solvolysis to diols under the conditions of abundant $(-2e)$.

Another interesting result is that the natural trace amounts of HOOH in water may be increased in water

by merely placing the sample in an intense magnetic field. Positive and negative ions will traverse short arc segment paths driven by simple thermal Brownian motion in a way which will lead to an increase in collisions of oppositely charged ions. In particular, OH^- and OH^+ may undergo collisions more frequently leading to an increase in HOOH.

This additional HOOH should then be available to react with alkenes to form epoxides which will then hydrolyze in water to form diols. Such diols would be much more soluble in water than the original alkenes. This leads to the important possibility that merely exposing water-insoluble alkenes to water in a magnetic field will lead to a chemical reaction of the alkenes to form modified compounds which are more soluble in water. In other words, organic oils containing some double bonds may be made somewhat more soluble in water just by mechanical emulsification of the oils in water in an environment of a high magnetic field.

Thus, mixtures of oils and water could be mechanically agitated in a magnetic field of several Tesla to produce new oils which are chemically similar to the original oils (assuming a large organic structure) but more soluble in water after exposure to the magnetic field. There are numerous important applications of such a process to 'make oils water soluble'.

The industrial applications of the above novel predictions are under development at various corporations and they will be treated in detail in future papers.

References

[1] Eisenberg D, Kauzmann W. In: The Structure and Properties of Water. New York: Oxford University Press, 1969. p. 226.

[2] Santilli RM. In: Elements of Hadronic Mechanics, 2nd ed, vol. I and II. Kiev: Ukraine Academy of Sciences, 1995.

[3] Santilli RM, Shillady DD. Isochemical model of the hydrogen molecule. Int J Hydrogen Energy 1998; (in press).

[4] Barrow GM. Physical Chemistry, 6th ed. New York: McGraw-Hill, 1996 (Chap. 8).

[5] Pourbaix M. In: Atlas of Electrochemical Equilibria in Aqueous Solutions. Houston, TX: National Assoc Corrosion Engr, 1974. p. 99.

[6] Santilli RM. Hadronic J 1978;1:574.

[7] Boys SF. Proc Roy Soc (London), A 1950;200:542.

[8] Whitten JL. J Chem Phys 1963;39:349.

[9] LeRouzo H, Silvi B. Int J Quantum Chem 1978;13:297.

[10] Zhitenev NB, Ashoori RC, Pfeiffer L, West KW. Phys Rev Letters 1997;79:2308.

[11] Boyd RJ, Yee MC. J Chem Phys 1982;77:3578.

[12] Fois ES, Selloni A, Parinello M, Car R. J Phys Chem 1988;92:3268.