

Relative Kinetic Stability Study of Hydronium, Zundel, and Eigen Cations through Quantum Mechanical Molecular Orbitals Approach

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Abstract – Despite the existence of Hydronium (H_3O^+), Zundel (H_5O_2^+), and Eigen (H_9O_4^+) states of proton as premier cationic species in several pH-related aqueous systems including electrochemical and biological fluid matrices, their critical roles in a wide range of industrial, chemical, and physical processes, and their typical thermodynamic and energetic instabilities, a comprehensive study focused on their relative kinetic stabilities through quantum mechanical molecular orbitals (QMO) approach is seldom reported. This insight is mainly aimed to compute their HOMO–LUMO interactions and band gaps (ΔE_{gap}) separately using hybrid density functional B3LYP method, and to determine most significant global quantum–chemical reactivity descriptors (QCDs) along with assessing the use of QCDs properties for predicting their relative chemical stabilities based on electronic localizations, electronic polarizabilities, and electrophilicities. The general results show that the H_9O_4^+ form relatively: (1) has the smallest HOMO–LUMO energy gap ($\Delta E = 9.75 \text{ eV}$), (2) has a maximum tendency for losing electrons ($IP = 9.46 \text{ eV}$) (less firmly-held electron cloud), (3) is the chemically softest ($\sigma = 0.21 \text{ eV}$) or reactive species having significant electronic polarizabilities, and (4) has the least degree of electron loving propensity (electrophilicity) ($\omega = 2.16 \text{ eV}$) than those for the H_5O_2^+ ($\Delta E = 11.31 \text{ eV}$, $IP = 16.28 \text{ eV}$, $\sigma = 0.18 \text{ eV}$, $\omega = 9.98 \text{ eV}$) and H_3O^+ ($\Delta E = 12.89 \text{ eV}$, $IP = 20.09 \text{ eV}$, $\sigma = 0.16 \text{ eV}$, $\omega = 14.44 \text{ eV}$) states. The originality of this study lies in elucidating relative kinetic stabilities of the three most stable hydrated states of the protons quantitatively through DFT based QMO approach.

Keywords – Hydrated protons, Kinetic stability, Frontier molecular orbitals, and Quantum chemical descriptors.

I. INTRODUCTION

According to molecular dynamics simulation and experimental insights of ionic hydration, different kinds of dissolved positive or negative ions have more or less tightly bound H_2O molecules through their mutual attractive forces. However, interactions between the dissolved H^+ ions and the immediate H_2O molecules are so strong that writing “ $\text{H}^+(\text{aq.})$ ” hardly does it justice [1], [2], [3]. This is due to the extraordinarily high charge density of the bare H^+ ion that can be concealed within the lone pair of oxygen atom of H_2O

resulting a formation of coordinate bond with latter, creating a Hydronium ion H_3O^+ . The activity of the bare H^+ ion in aqueous solution is not limited up to this but affects hydrogen-bonding network of at least one hundred surrounding H_2O molecules by sharing one to three H atoms of H_3O^+ for hydrogen bond (hereafter, H-bond) as observed through infrared spectroscopy technique [4]. The most noteworthy point is that the strength of these donated H-bonds are reported twice as strong as those present in between H_2O molecules of the bulk water, indicating that

other stable hydrated states of the proton such as Zundel (H_5O_2^+) and Eigen (H_9O_4^+) do exist in the aqueous type solutions [5], [6]. A very interesting and captivating experimental and theoretical fact on the conjugation process of H_3O^+ , H_5O_2^+ , and H_9O_4^+ ions is their involvement in proton transportation through vehicular and/or Grotthuss mechanisms which in turn are responsible for: (a) an extraordinarily high electrical conductivity of the acidic aqueous solutions, (b) enhancing ionic conductivity and ionization plus dissolution processes of strong and weak electrolytes, and (c) easing proton hopping dynamics in several types of proton exchange semipermeable membranes while incorporating into the membrane electrode assembly, in all the pH-related chemical, biological, industrial, environmental, and catalytic aqueous systems, and in fuel cells, redox flow battery technologies, electrolyzers etc. [7], [8], [9], [10]. Despite such wide abundancies of these three most stable forms of the hydrated protons in several aqueous type solutions and medicinal, biological fluid matrices, and their incredible significance in enhancing ionic and proton conductivity, the detailed studies concentrated on investigating their frontier molecular orbitals (hereafter, MOs) interactions plus global quantum-chemical reactivity descriptors are very limited. And, this type of investigation is indeed very indispensable not only for modeling the proton hydration phenomena in the aqueous type media but also for understanding their relative reaction kinetics (chemical reactivity and stability) quantitatively.

As stated earlier by the Nobel Laurette K. Fukui in his historic Journal article [11], the electrons most-probably reside in the MOs among which the electronic distribution occurring in the highest energy MO always plays vital role in determining chemical reactivity or stability. This is why, the chemists always show their keen interests to those MOs that are most spatially delocalized at the frontier (outer edges) part of the molecules: HOMO (low energy, high electron occupancy) and LUMO (high energy, zero occupancy). Again, the frontier molecular orbital theory says that the HOMO and LUMO orbitals and their interactions

incorporating energy gap (ΔE_{gap}) exists in between them play significant roles while predicting chemical stability of any molecular/ ionic specimens. As a rule, "smaller the HOMO–LUMO energy gap, more is the chemical reactivity of the molecules/ions" *i.e.*, such type of molecules/ions show strong ability to donate an electron or an electron pair in the chemical reactions most frequently from the HOMO to the LUMO, stressing further that a proper estimation of the ΔE_{gap} (band gap) for the concerned molecular/ionic specimen could be a key to unlock the most important physical meanings of some predominant global quantum-chemical reactivity indicators such as: (1) Ionization potential (IP), (2) Electron affinity (EA), (3) Electronegativity (χ), (4) Chemical hardness (η), (5) Chemical softness (σ), (6) Electronic chemical potentials (μ), and (7) Electrophilicity index (ω) [12], [13]. In theoretical/computational chemistry, the MOs approach of quantum mechanics is very often used to compute HOMO, LUMO, and their respective eigenvalues for the molecular/ionic specimens on the basis of which numeral indices for each of these reactivity-indicators can be determined mathematically through which the relative kinetic stabilities of the molecular/ionic specimens can be quantitatively elucidated quantum mechanically.

A quite established mathematical formulation (Eqs. (1–3, 6)) for the hard and soft acids and bases (HSAB principle) with HOMO–LUMO interactions and energy gap ($\Delta E_{gap} = E_{LUMO} - E_{HOMO}$) gives us an exceptional explanation for estimating molecular/ionic reactivity or stability kinetically via the quantitative aspects of aforementioned global quantum-chemical reactivity parameters. Mathematically, one of such parameters η is directly related to second order derivative of total energy E (computationally derived) of a chemical/ionic system with respect to changes in the number of electrons (N) *i.e.* $\eta \propto \frac{\partial^2 E}{\partial N^2}$, which further has mathematical connections with other reactivity descriptors through the following formulations (Eqs. (4, 5, 7)) [14], [15], [16], [17];

$$IP = -E_{HOMO} \quad (1)$$

$$EA = -E_{LUMO} \quad (2)$$

$$\chi = \frac{(IP+EA)}{2} \quad (3)$$

$$\eta = \frac{(-E_{HOMO} + E_{LUMO})}{2} = \frac{\text{Band gap } (\Delta E_{gap})}{2} \quad (4)$$

$$\sigma = \frac{1}{\eta} \quad (5)$$

$$\mu = -\frac{(IP + EA)}{2} = -\chi \quad (6)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (7)$$

Being a density functional theory (hereafter, DFT) spatially dependent electron density based quantum mechanical model, its extraordinary ability to implement complicated type quantum mechanical mathematical procedures in the limited computational resources [18], [19], its remarkable skills for exploring ground state electronic structures of the multi-electron molecular/ionic systems, and computing HOMO, LUMO and their eigenvalues [19], [20], [21], [22], [23], [24], [25], [26] as well as its applicability for assessing the characteristic features of the global quantum-chemical reactivity descriptors theoretically [27], [28], [29] are awesome. In this study, the DFT model is applied to the three most stable forms of the hydrated protons: H_3O^+ , H_5O_2^+ , and H_9O_4^+ , and H_2O molecule separately, and computed their respective HOMO-LUMO orbitals interactions and energy gaps (ΔE_{gap}) quantum mechanically on the basis of which the global quantum-chemical reactivity descriptors IP , EA , η , σ , μ , ω , and χ for these chemical specimens are determined with the main objective of exploring their relative chemical reactivities or kinetic stabilities quantitatively. The H_2O molecule is taken here as a reference molecule due to its close association with these hydrated protons in the aqueous type systems. The structure of this paper is organized as follows: the computational details are outlined in section 2, the results and discussions are presented in section 3, and the conclusions are summarized in section 4.

II. COMPUTATIONAL DETAILS

Prior to determine the numeral values of the global quantum-chemical reactivity parameters for each hydrated proton: H_3O^+ , H_5O_2^+ , and H_9O_4^+ , and H_2O molecule, the most stable electronic structures of them were computed theoretically by using computationally designed molecular models as their trial structures. They were carefully built in *GaussView*: the Gaussian graphical interface [30], and the respective Cartesian coordinates of the atoms were extracted for geometry optimization. The concerned *Gaussian* keywords and methodologies were selected as instructed in *Gaussian 09* manual [31]. The hybrid functional based DFT method known as B3LYP was employed with the basis set of this type: 6-31G (d, p) i.e., the methodology applied was DFT: B3LYP/6-31G (d, p). The better and more reliable computational results were assured by using a greater basis set of the type 6-31G (d, p), where "6-31G" is the standard, split-valence double-zeta basis set: the functions that were used in *Gaussian* script computationally while describing the core and valence orbitals of the atoms; and the functions in parentheses " (d, p) " are polarization functions on heavy atoms and hydrogen that was used to properly describe

chemical bonds. Again, to direct *Gaussian* for running desirable computations, the ionic charge and spin multiplicity were specified as two integers in the format of (charge, spin multiplicity). Here, all the three hydrated protons are cationic with similar positive charge units, i.e., H_3O^+ , H_5O_2^+ , and H_9O_4^+ have charge units of +1 each, and that for the H_2O molecule is 0. Thus, the set of integers used in the *Gaussian* input file to describe former cationic forms and the latter neutral form were (1, 2), and (0, 1) respectively. Moreover, while solving the electronic Schrodinger equation iteratively, the self-consistent field (hereafter, SCF) with both default SCF procedure (SCF=Tight) and Berny algorithm for geometry optimizations to a local minimum were selected in *Gaussian 09* [31], [32]. Since the current interest of this author is to study relative kinetic stabilities of the three most stable hydrated protons: H_3O^+ , H_5O_2^+ , and H_9O_4^+ quantum mechanically (H_2O molecule is taken here as a reference), only the concerned global quantum-chemical reactivity descriptors (ionization potential (IP), electron affinity (EA), chemical hardness (η), chemical softness (σ), electronic chemical potentials (μ), electrophilicity index (ω), and electronegativity (χ)) were determined on the basis of DFT derived HOMO-LUMO energy gaps (ΔE_{gap}). For this, the *Gaussian* output files for each of them (such as *.log*, and *.fchk*) containing three dimensionally displayed chemical data were read by using GaussView, and extracted MOs, and HOMO-LUMO surface plots, molecular electronic configurations, and the concerned eigenvalues along with visualizing DFT derived ground state electronic structure in the 3D space. While determining the values of these global quantum-chemical reactivity descriptors quantitatively, the series of the mathematical equations formulated in Eqs. (1–7) in introduction section were used.

III. RESULTS AND DISCUSSIONS

3.1 HOMO-LUMO analysis and Energy gaps (ΔE_{gap}) for H_2O molecule and hydrated protons: H_3O^+ , H_5O_2^+ , and H_9O_4^+

As explained in introduction section, the HOMO-LUMO interactions and their energy gap are very significant quantum mechanical descriptors that can be directly used for deriving the values of wide-range global chemical reactivity parameters. The DFT derived surface plots of the HOMO and LUMO for an H_2O molecule and the hydrated protons H_3O^+ , H_5O_2^+ , and H_9O_4^+ are shown in Figure 1 to Figure 4 respectively, where HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), and the HOMO-LUMO energy gaps (ΔE_1 , ΔE_2 , ΔE_3 , and ΔE_4) are depicted in both *Hartree (a.u.)* and electron volt (eV) units. As can be seen in Figure 1, the HOMO surface

for the H_2O molecule is found to be distributed mainly over the central oxygen atom (highly localized on the oxygen atom) while the LUMO surface shows a significant probability electron density in the immediacy of the oxygen atom as well as two lobes protruding from the molecule in the proton directions. While referring it to molecular orbital diagram of the H_2O molecule available in any chemistry text books, the HOMO is the highest occupied, non-bonding, orthogonal around the O atom (no Sp^3 hybridization characteristics), and an O-localized $1b_1$ molecular orbital which mainly contributes to the "lone pair" effects, and the LUMO is the lowest unoccupied, and approximately spherical (contributed by $1s$ and $2s$ orbitals of the O atom) $2a_1$ molecular orbital. The variation of the electrons occupancy in these frontier molecular orbitals verifies the experimentally observed optical excitation phenomenon of an electron from the HOMO to the LUMO. Nevertheless, due to the presence of the hole on the top of the O atom appeared at the LUMO surface (Figure 1(a)), an attractive force is originated that makes the electrons to be remained close to the molecular center. Moreover, the DFT derived HOMO–LUMO energy gap $\Delta E1 = 9.7237 \text{ eV}$ for the H_2O molecule (depicted in Figure 1) not only approximates its band gap exists in between valence band and conductance band but also estimates its lowest energy transition frequency in UV visible spectroscopy.

Similarly, the HOMO and LUMO orbitals and their atom centered localizations for the H_3O^+ ion are shown in Figure 2, where the HOMO surface is found to be highly localized on the oxygen atom as in the case of H_2O molecule, and the LUMO surface shows a higher probability electron density in the immediate surrounding of the oxygen atom as well as three lobes protruding from the H_3O^+ ion in the proton directions. Alike this, the electron density localizations in the remaining two stable hydrated cations H_5O_2^+ and H_9O_4^+ are clarified by the distribution of their HOMO and LUMO orbital surfaces (Figure 3 and Figure 4). Just like in H_3O^+ , the HOMO surface of each H_5O_2^+ and H_9O_4^+ ion is observed to be two–O and four–O centered while their LUMO surfaces exhibit significant probability electron density in the proximity of their two–O and four–O atoms as well as protrusions that come out from the respective molecule in the directions of five–H and nine–H atoms. Since the HOMO for each of these three hydrated protons is the highest occupied, non-bonding, orthogonal around the O atom, and an O-localized molecular orbital, and the LUMO is the lowest unoccupied, and approximately flattened, distorted linear and

flat, and triangular planar O– and H– centered molecular orbital respectively, the concerned atomic sites of these ions may participate most actively in several types of energy transfer events. Apart from this, a variation of the electrons occupancy in their frontier molecular orbitals speculates the easy occurrence of optical excitation phenomenon of the electron from the concerned HOMO to LUMO. Again, as in the H_2O molecule, presence of the holes on the top of each O atom of H_3O^+ , H_5O_2^+ and H_9O_4^+ ions appeared at their respective LUMO surfaces imply that the electrons do remain close to the molecular centers due to the force of attractions originated from these holes. Furthermore, the DFT derived HOMO–LUMO energy gaps $\Delta E2 = 12.8917 \text{ eV}$, $\Delta E3 = 11.3104 \text{ eV}$, and $\Delta E4 = 9.7521 \text{ eV}$ for the H_3O^+ , H_5O_2^+ and H_9O_4^+ ions (depicted in Figure 2, Figure 3, and Figure 4) respectively not only imprecise their band gap exists in between valence band and conductance band but also figure out their lowest energy transition frequency in UV visible spectroscopy.

Here, the band gap for the H_9O_4^+ hydrated state ($\Delta E4 = 9.7521 \text{ eV}$ as equal as band gap for the H_2O molecule: $\Delta E1 = 9.7237 \text{ eV}$) is observed to be lower than that for the H_5O_2^+ ($\Delta E3 = 11.3104 \text{ eV}$) which is further lower than that for the H_3O^+ ($\Delta E2 = 12.8917 \text{ eV}$), the unpaired electron present in the HOMO of the first ion must undergo fastest transition to the LUMO (as faster as in H_2O) than in other hydrated protons after absorbing specific light ray photons. Accordingly, such optical electronic transition phenomenon while occurring in the H_5O_2^+ hydrated state would be faster than in the H_3O^+ but slower than in the H_9O_4^+ ion. Similarly, the relatively smaller band gap $\Delta E4$ of the H_9O_4^+ hydrated state further infers that this cation is more reactive but less stable kinetically than the H_5O_2^+ , and H_3O^+ ions *i.e.*, the electrons/charges of the former ion can migrate from the HOMO to the LUMO more faster than in the latter two ions which eventually enhances the energy transfer events or initiates the ionic type chemical reactions (HOMO electrons are very often considered as the most reactive). The same conceptual analysis can be applied to the H_5O_2^+ ion, and confirmed its less (more) kinetic stability than the H_3O^+ (H_9O_4^+) ion. The detailed analysis on their kinetic stabilities or chemical reactivities can only be performed after computing the mathematical indices of their global quantum–chemical reactivity descriptors quantitatively. The same is presented more clearly and concisely in the following subsections.

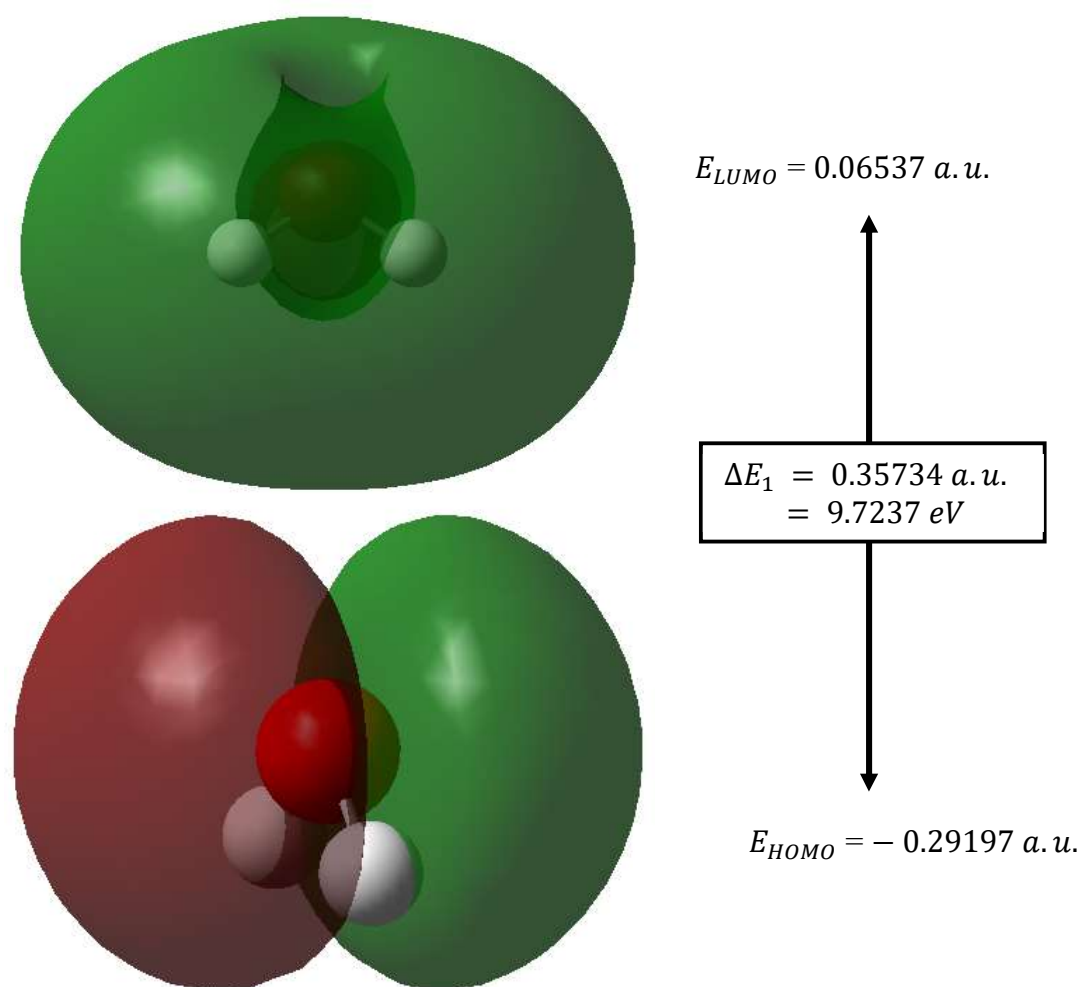


Figure 1. DFT computed surface plots of HOMO and LUMO depicting HOMO–LUMO energy gap ΔE_1 for H_2O molecule.

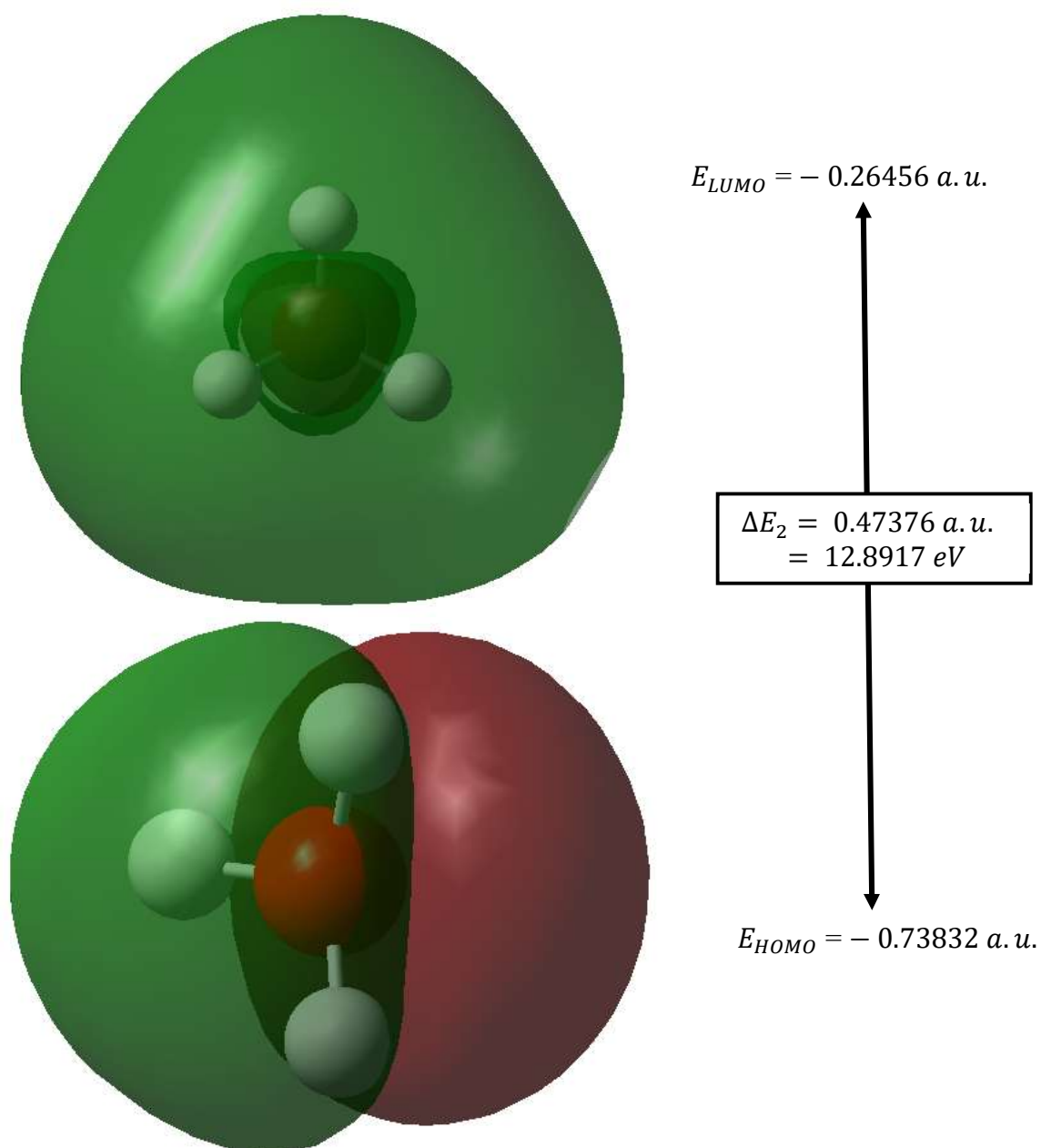


Figure 2. DFT computed surface plots of HOMO and LUMO depicting HOMO–LUMO energy gap ΔE_2 for H_3O^+ ion.

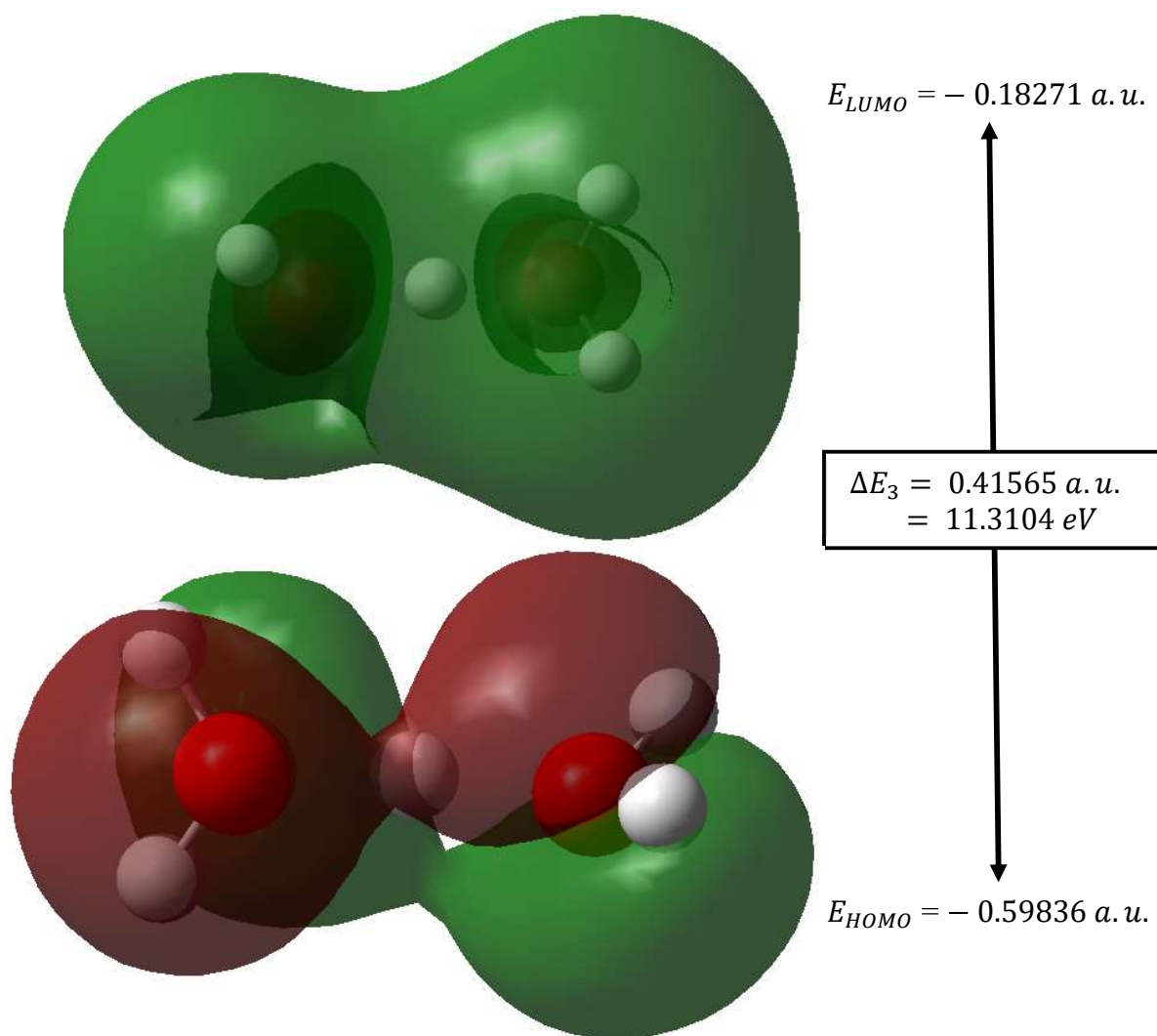


Figure 3. DFT computed surface plots of HOMO and LUMO depicting HOMO–LUMO energy gap ΔE_3 for H_3O_2^+ ion.

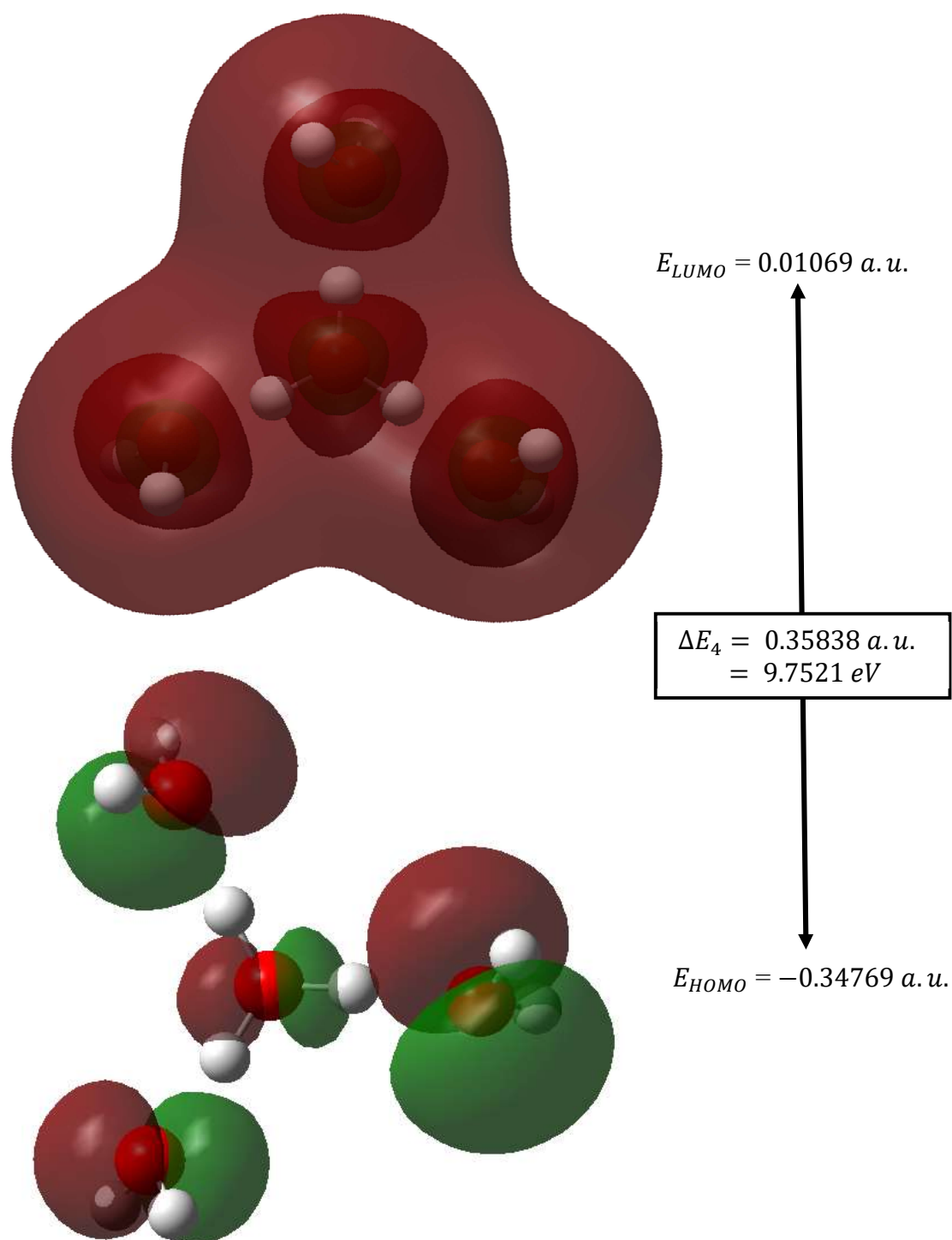


Figure 4. DFT computed surface plots of HOMO and LUMO depicting HOMO–LUMO energy gap ΔE_4 for H_9O_4^+ ion.

3.2 Global quantum–chemical reactivity descriptors for H₂O molecule and hydrated protons: H₃O⁺, H₅O₂⁺, and H₉O₄⁺

3.2.1 Ionization Potential (IP), Electron Affinity (EA), and Electronegativity (χ)

Ionization potential (IP) of any molecular or ionic specimen is defined as the amount of energy required to remove most loosely bound electron out of the nuclear influence from an isolated molecular or ionic species in its ground electronic state [33], [34]. Being this an endothermic type energy given to discharge an electron, it can mostly measure the binding force of the electrons that are held by the positively charged nucleus. Sometime, the magnitude of the IP is used to determine the strength of the chemical bonds as well. Most importantly, its absolute value can be used as a quantum–chemical descriptor for studying kinetic stability of the molecular or ionic specimens. As a rule, those molecules or ions which have low IP values always have less–tightly held electrons and hence, behave as good reducing agents (high tendency for losing electrons or undergoing oxidation) having high reactivity, less stability and chemically inertness, and can generate their cationic forms very likely and vice versa. Contrastingly, an electron affinity (EA) of the molecules or ions means their likelihood of gaining an electron. It is an exothermic energy that measures the change in potential energy of the molecular or ionic specimens (amount of energy released) while adding an extra electron from outside to their isolated form in the ground electronic state [33], [35]. The absolute value of it is usually used to find out the electron donating/accepting properties of the molecular/ionic species while monitoring their concerned charge–transfer reactions: molecules/ions having more or less positive EA values tend to behave mostly as electron acceptor or donor species respectively. Similarly, the third parameter electronegativity (χ) measures an ability of the

bonded atoms or group of atoms in a molecule/ion or molecules/ions to attract shared electron pair towards themselves [33]. It is used to identify the polar region/s of the molecule: higher the electronegativity value, the more an atom or a substituent group attracts electrons towards itself creating the oppositely charged terminals. As a whole, all these three parameters are respectively related to the DFT derived energy for the HOMO and LUMO as formulated above in Eqs. (1–3). All the calculated values (*eV*) of them for the H₂O molecule, and hydrated protons H₃O⁺, H₅O₂⁺, and H₉O₄⁺ are presented in Table 1. The relatively lower IP value for the H₉O₄⁺ ion (*IP* = 9.4611 *eV*) than that for the H₅O₂⁺ (*IP* = 16.2822 *eV*) and H₃O⁺ (*IP* = 20.0907 *eV*) signifies that former ion loses electrons more easily (more likely to generate its cationic form as the electrons are less–firmly held and remain as a polarizable electron cloud) than the latter two ions, and so on whereas comparatively higher EA value for the H₃O⁺ ion (*EA* = 7.1990 *eV*) indicates that it can more readily accept an electron (relatively high intensity to accept electrons (electron acceptor)) than the H₅O₂⁺, and H₉O₄⁺ ions. Alternatively, the H₅O₂⁺, and H₉O₄⁺ ions have high propensity to give up their electrons due to the presence of weakly nucleus–pulled electrons cloud. Besides this, such theoretically predicted relatively high electron accepting tendency of the H₃O⁺ ion would be a strong supportive evidence for validating several experimentally and molecular dynamics simulations observed solvation structures in cold water system: a freezing point depression study determined [H₃O⁺(H₂O)₆] as a solvated cluster [36], and *ab initio* method molecular dynamics simulations showed [H₃O⁺(H₂O)₂₀] as an average sized hydrated cluster [37]. The detailed about the electronic polarizabilities and electronic firmness in these hydrated states can be predicted on the basis of the DFT derived numeral values for the chemical hardness (η) and softness (σ) as explained in the following subsection 3.2.2.

Table 1. DFT computed quantum chemical descriptors for H₂O and hydrated protons.

Parameters (eV)	Molecular/Ionic specimens			
	H ₂ O	H ₃ O ⁺	H ₅ O ₂ ⁺	H ₉ O ₄ ⁺
<i>E</i> _{HOMO}	−7.9449	−20.0907	−16.2822	−9.4611
<i>E</i> _{LUMO}	1.7788	−7.1990	−4.9718	0.29089
ΔE_{gap}	9.7237	12.8917	11.3104	9.7521
<i>IP</i>	7.9449	20.0907	16.2822	9.4611
<i>EA</i>	−1.7788	7.1990	4.9718	−0.2909
χ	3.083	13.645	10.627	4.585
η	4.862	6.446	5.655	4.876
σ	0.206	0.155	0.177	0.205
μ	−3.083	−13.645	−10.627	−4.585
ω	0.977	14.442	9.985	2.156

3.2.2 Chemical Hardness (η) and Softness (σ)

After the qualitative correlation concept between Lewis acids and Lewis bases was extended and generalized by R. G. Pearson in 1963 into Hard and Soft categories, several consequences were derived from their closely associated terminologies: "chemical hardness" and "chemical softness". This attempt of classification is more popularly known by Hard and Soft Acids and Bases (HSAB) principle. According to it, the term "hard" refers to those chemical species which have a high charge density and are not very polarizable, and participate in ionic bonding interactions whereas "soft" applies to those which are large and strongly polarizable [12], [13], [34]. Even though this principle was originally developed as a qualitative and intuitive concept, it has become a quantum chemistry/physics based fundamental theory nowadays that enables chemists/physicists to understand chemical stabilities or reactivities without any reference to large supercomputers and databases. This is because of its close connection to quantum mechanically derived quantitative observables especially DFT derived HOMO and LUMO energies (E_{HOMO} and E_{LUMO}), their orbital interactions, and energy gaps (ΔE_{gap}). As shown in Eqs. 4 and 5 in introduction section, these molecular orbitals based quantitative parameters have shown their direct relations to the corresponding electronic descriptors for "hard" and "soft": chemical hardness (η) and chemical softness (σ) [38]. Since the η is quantitatively expressed within the DFT computational scheme as a second order derivative of the total energy E of a chemical/ionic system with respect to changes in the number of electrons N , a mathematically derived expression for its accurate estimation (Eq. (4)) gives us a direct relation to the HOMO–LUMO interactions and their energy gap (ΔE_{gap}). Eventually, an inverse of the η gives us σ (Eq. (5)) that can quantitatively measure how intensely the atom or group of atoms acquire electrons. In a broader sense, the η and σ are the actual quantum mechanical parameters that can describe the chemical reactivities or kinetic stabilities of the molecular/ionic specimens quantitatively.

As a rule, smaller the HOMO–LUMO energy gap ΔE_{gap} , smaller (larger) will be the numeral value for the η (σ), which means more easily the HOMO electron shifts to LUMO (more reactive the molecular specimens are). Alternatively, those molecular/ionic specimens which possess larger (smaller) ΔE_{gap} are said to have high degree of hardness (softness), and hence becomes less reactive or hard specimens (more reactive or soft). For the H_2O molecule, and hydrated protons: H_3O^+ , $H_5O_2^+$, and $H_9O_4^+$, the

calculated values for the η , and σ are listed in Table 1. Even though all these molecular/ionic specimens are closely associated to each other in the aqueous type solutions, their degree of relative chemical hardness and softness can be different to each other. As can be seen in Table 1, the $H_9O_4^+$ ion has a slightly lower (higher) value of the $\eta = 4.876 \text{ eV}$ ($\sigma = 0.205 \text{ eV}$) than that for the $H_5O_2^+$: $\eta = 5.655 \text{ eV}$ ($\sigma = 0.177 \text{ eV}$), and H_3O^+ : $\eta = 6.446 \text{ eV}$ ($\sigma = 0.155 \text{ eV}$) ions, implying that the $H_9O_4^+$ state has the least degree of chemical hardness (or the chemically softest species) and hence, relatively the most reactive (or less stable) hydrated species of the proton kinetically having more significant electronic polarizable characters than in other two states. Since the η , and σ values for the $H_9O_4^+$ ion ($\eta = 4.876 \text{ eV}$; $\sigma = 0.205 \text{ eV}$) are quite close to that for the H_2O molecule ($\eta = 4.862 \text{ eV}$; $\sigma = 0.206 \text{ eV}$), they must have almost similar or quite comparable kinetic stabilities. On the same basis, the second most reactive and relatively harder hydrated proton is predicted as $H_5O_2^+$ followed by the least reactive and relatively the hardest hydrated proton H_3O^+ . In terms of electronic polarizability, the relatively hardest and the least reactive hydrated proton H_3O^+ must have restricted electronic polarizations due to the presence of firmly-held electron cloud than in the $H_5O_2^+$, and $H_9O_4^+$ ions which must have respectively more easily and the most easily polarizable electron clouds, further making them to be characterized as a relatively softer and the softest hydrated proton respectively. Such a weak inbound electronic cloud or firmness, and the most electronic polarizability characteristics of the $H_9O_4^+$ hydrated state makes itself to loose electron comparatively most easily, *i.e.*, it should have the lowest value of IP as listed in Table 1 (the concerned consequences are already explained in subsection 3.2.1). Energetically, this state of the proton (eigen: $H_9O_4^+$) is known for its relatively highest stability, the zundel state $H_5O_2^+$ is for its second highest stability, and the hydronium ion H_3O^+ is for its least stability, and the same is their order of thermodynamic stabilities ($H_9O_4^+ > H_5O_2^+ > H_3O^+$) as well [6], but the tendencies of their HOMO electrons to initiate the particular charge transfer events or chemical reactions (HOMO to LUMO transition event) are predicted as just opposite in order ($H_9O_4^+ < H_5O_2^+ < H_3O^+$) because the HOMO electrons are considered as the most reactive electrons, and their prompt transition to the LUMO (due to less HOMO–LUMO energy gap) determines the kinetic stabilities of the ionic/molecular specimens quantum mechanically as clarified earlier in section 3.1.

3.2.3 Electronic chemical potential (μ) and Electrophilicity index (ω)

The electronic chemical potential (μ) of density functional theory measures the escaping tendency of an electronic cloud of the molecular or ionic specimens. It is a constant for the ground state of an atom, molecule, or ion throughout all space. Quantum mechanically, it is one of the most important descriptors that scales electrons fleeing propensity from one molecular/ionic specimen to another during their mutual chemical combinations in the ground electronic state conditions [27]. This is a type of physical phenomenon that always occurs on the basis of electronegativity equalization principle: whenever two molecules/ions, A and B with $\mu_A > \mu_B$ approach each other for a polar type chemical reaction, the electron cloud from the molecule/ion 'A' fluxes towards the molecule/ion 'B', and achieves the equilibrated electronic chemical potential μ_{AB} in the interacting chemical system. In other words, the molecules/ions having higher (lower) μ values always behave as electron-donors or nucleophiles (electron-acceptors or electrophiles), and a difference in the chemical potentials $\Delta\mu$ of the two participating molecules/ions in such polar chemical reaction measures the degree of global electron density transfer (GEDT) [28]. Mathematically, μ is a negative of the electronegativity (χ) of Pauling and Mulliken as formulated in Eq. (6) [27], [28]. Therefore, the chemical potential concept is same as the electronegativity concept. As a rule, more negative the μ value is, more difficult is to lose an electron (instead, more easy is to gain) or more tightly the electrons are held in the molecular/ionic specimens. Similarly, another quite significant quantum-chemical reactivity descriptor "Electrophilicity index (ω)" is defined as a measure of energy lowering consociated with a maximum amount of electron flow between donor and acceptor species as proposed by Parr *et al.* [39]. It estimates the electrophilic characters of the molecular or ionic specimens. In other words, it measures an extra electron density accepting tendency of the electron-loving chemical species (electrophiles) quantitatively. This is why, it is considered as the most significant parameter in electrophile-nucleophile chemistry while identifying the electrophilicity of the majority of the organic reactions [40]. Mathematically, it is directly proportional to the square of chemical potential (μ^2), and inversely proportional to the chemical hardness (η) as shown in the equation formulated in Eq. (7) [37], [41], [42]. As a whole, those chemical compounds which have higher values of μ^2 , but lower values of η would ultimately have higher values of ω , and hence, must behave as the most effective electrophiles. The calculated values of them for the

H₂O molecule and three most stable hydrated protons H₃O⁺, H₅O₂⁺, and H₉O₄⁺ are listed in Table 1. The extremely higher values of μ^2 , and ω but relatively comparable value of η for the H₃O⁺ ion ($\mu_1^2 = 186.186 \text{ eV}$, $\omega = 14.442 \text{ eV}$, $\eta = 6.446 \text{ eV}$) than that for the H₅O₂⁺ ($\mu_2^2 = 112.933 \text{ eV}$, $\omega = 9.985 \text{ eV}$, $\eta = 5.655 \text{ eV}$) and H₉O₄⁺ ($\mu_3^2 = 21.022 \text{ eV}$, $\omega = 2.156 \text{ eV}$, $\eta = 4.876 \text{ eV}$) ions indicates that the first ion has a high degree of electrophilicity or strong electrophilic character (difficult (easy) to lose (gain) electron, and presence of firmly-held electron cloud) than the latter two ions, and accordingly, the last ion has the least degree of electron loving propensity due to its polarizable and less firmly-held electron cloud as explained in subsection 3.2.2. However, this type of the electrophilic characteristics shown by all the three hydrated states of the protons are predicted as far better than that shown by the H₂O molecule ($\mu_0^2 = 9.505 \text{ eV}$, $\omega = 0.977 \text{ eV}$, $\eta = 4.862 \text{ eV}$), but it is an obvious conclusion because H₂O molecule is a neutral species having a central 'O' atom bearing two lone pair electrons that makes it to behave as a weak nucleophile or Lewis base (not as an electrophile). The $\Delta\mu$ value for the H₅O₂⁺ and H₃O⁺ ($\Delta\mu = \mu_2 - \mu_1$) ionic pair is calculated as 3.018 eV , for the H₉O₄⁺ and H₃O⁺ ($\Delta\mu = \mu_3 - \mu_1$) is calculated as 9.06 eV , and for the H₉O₄⁺ and H₅O₂⁺ ($\Delta\mu = \mu_3 - \mu_2$) is calculated as 6.042 eV , indicating that the degree of GEDT between these ionic pairs is significantly high. It eventually ascertains here that the electron density flux may transfer faster from H₉O₄⁺ to H₃O⁺ than from H₉O₄⁺ to H₅O₂⁺, and the slowest is from H₅O₂⁺ to H₃O⁺, further guarantying quantitatively a presence of more polarizable electronic cloud in the H₉O₄⁺ state and so on. Therefore, it can be said here unanimously that there is a high chance of occurring substantial electron/charge transfer (*i.e.*, delocalization of the electron density) among these ionic pairs [43] even though sufficient experimental and molecular dynamics simulation results are not available to validate such theoretically predicted fact.

IV. CONCLUSION

Due to the predominant availability and crucial roles of the three most stable hydrated protons: Hydronium H₃O⁺, Zundel H₅O₂⁺, and Eigen H₉O₄⁺ in various pH-related catalytic, environmental, industrial, biological, and medicinal aqueous fluid matrices, and in wide range of electrochemical technologies such as lead acid battery, redox flow battery, and fuel cell where acidic aqueous electrolytes are used to enhance proton conductivity, understanding their relative kinetic stabilities in such aqueous type media quantitatively is indeed indispensable. This theoretical insight computed

their HOMO–LUMO energies separately through hybrid DFT based quantum mechanical molecular orbitals approach, and estimated their most closely associated global quantum–chemical reactivity descriptors (QCDs): HOMO–LUMO energy gaps (ΔE_{gap}), ionization potential (IP), electron affinity (EA), chemical hardness (η), chemical softness (σ), electronic chemical potential (μ), electrophilicity index (ω), and electronegativity (χ) as precisely as possible on the basis of which the relative chemical stabilities of these three hydrated states of the protons were revealed. The main QCDs properties assessed here were ΔE_{gap} , electronic localizations, electronic polarizabilities, electrophilicities, and degree of global electron density transfer (GEDT).

At first, the DFT computed surface plots for frontier molecular orbitals of all these three states were thoroughly analyzed, and observed that HOMO is the highest occupied, non-bonding, orthogonal around the O atom, and an O-localized molecular orbital whereas LUMO is the lowest unoccupied, and approximately flattened (H_3O^+), distorted linear and flat ($H_5O_2^+$), and triangular planar ($H_9O_4^+$) O- & H- centered molecular orbital. And then, the DFT based QCDs were interpreted quantitatively on the basis of which the Eigen state of the proton $H_9O_4^+$ is predicted as kinetically the most unstable cationic form. More specifically, this hydrated state relatively: (1) has the smallest HOMO–LUMO energy gap ($\Delta E = 9.75 \text{ eV}$) inferring least kinetic stability, (2) has a maximum tendency for losing electrons ($IP = 9.46 \text{ eV}$) implying the presence of less firmly-held electron cloud, (3) is the chemically softest ($\sigma = 0.21 \text{ eV}$) or reactive species having significant electronic polarizabilities, and (4) has the least degree of electron loving propensity (electrophilicity) ($\omega = 2.16 \text{ eV}$) but high degree of GEDT than those for the Zundel $H_5O_2^+$ ($\Delta E = 11.31 \text{ eV}$, $IP = 16.28 \text{ eV}$, $\sigma = 0.18 \text{ eV}$, $\omega = 9.98 \text{ eV}$) and Hydronium H_3O^+ ($\Delta E = 12.89 \text{ eV}$, $IP = 20.09 \text{ eV}$, $\sigma = 0.16 \text{ eV}$, $\omega = 14.44 \text{ eV}$) forms. It is believed here that this contribution has illuminated mathematical indices of the most significant chemical–reactivity descriptors for the foremost hydrated states of the protons which in turn are highly useful for predicting their kinetic stabilities quantitatively.

Even though all these theoretically derived HOMO and LUMO interactions and their band gaps (ΔE_{gap}), and the mathematical values of the global quantum–chemical reactivity parameters for the H_3O^+ , $H_5O_2^+$ and $H_9O_4^+$ hydrated states, and H_2O molecule would be as reliable as those obtained from high-level computational methods, this research work was mainly limited to computationally cheap

yet decent hybrid density functional B3LYP with 6–31G (d, p) basis set due to the shortage of enough computational resources. One may use more advanced theoretical models with systematically convergent basis sets for explicitly correlated wave functions [44] to strengthen the results reported here.

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