

# Towards quantitative diatomics-in-molecules model for the water molecule

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## Abstract

The diatomics-in-molecules (DIM) model is developed for the water molecule which allows us to extend the set of molecular parameters quantitatively predicted with the help of this theory. It is shown that not only mixing of the neutral and ionic states when constructing the polyatomic basis functions as prescribed by the previous works is necessary for an accurate description of the ground state potential energy surface, but certain corrections due to a multicenter charge distribution in the polyatomic molecule are required. The results of new ab initio calculations for the potential curves of the ion-pair states of OH are employed. Finally, the energies of H<sub>2</sub>O are obtained from the 9 × 9 DIM Hamiltonian matrix what makes feasible further applications of this surface in molecular dynamics simulations of water containing intermolecular complexes. The molecular constants predicted by DIM including harmonic frequencies are perfectly consistent with the reference data. The H<sub>2</sub>O potential energy surface of spectroscopic accuracy created by Partridge and Schwenke have been used for the point-by-point comparison of DIM and ab initio results showing the efficiency of the present model. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

This study is part of the project devoted to the development of reliable but simple interaction potentials for use in molecular dynamics simulations of the properties of molecular aggregates. Among various approaches currently applied in this field we distinguish the diatomics-in-molecules (DIM) method. Recent successful results obtained with this strategy for such delicate properties as structures and vibrational spectra of Ar<sub>n</sub>HF [1], Ar<sub>n</sub>(HF)<sub>2</sub> [2,3], RgHal<sub>2</sub> [4,5], (HF)<sub>2</sub> [6] species have prompted us to turn to the grounds of the DIM theory. Ever since its introduction in 1963 by Ellison [7], the DIM technique has been employed for constructions of potential energy surfaces (PES) of molecular systems for

use in chemical reaction dynamics as well as molecular structure areas (e.g. Refs. [8–13]). Recently, the DIM-based schemes have been successfully tested in modelling intermolecular interactions [1–6,14–23].

The structure of the single water molecule was the very first application of the DIM method [7]. The predicted equilibrium geometry parameters, namely, the O–H distances  $R_e$  and the valence angle  $\alpha_e$ , as well as the atomization energy  $E_{at}$  in the ground electronic state looked fairly promising and stimulated further developments of the theory [8,9]. In mid-1980s Kuntz and co-authors in a series of papers presented a detailed picture of potential surfaces of H<sub>2</sub>O in the ground and excited electronic states relevant to the oxygen–hydrogen reactions [24–27]. The DIM model has been optimized [25] in the sense

that some diatomic fragment parameters have been adjusted in order to achieve the best agreement with the available experimental data.

In this work we concentrate our attention not on the global representation of ground and excited state potentials of  $\text{H}_2\text{O}$  but rather on the accurate molecular constants defined by the shape of the ground state PES not far from the global minimum, namely:  $R_e$ ,  $\alpha_e$ ,  $E_{\text{at}}$ , the energy  $E_s$  and O–H distances  $R_s$  of the saddle point at the linear  $D_{\infty\text{h}}$  geometry, which have been considered in previous DIM calculations, and the force constants. The latter properties are of a special interest here. We did not find in literature successful attempts to compute fairly accurate vibrational frequencies of polyatomic molecules with the help of the DIM theory. Keeping in mind the main directions of our studies with the DIM potential surfaces mentioned above, namely, modelling properties of molecular aggregates, the interest in calculating the vibrational frequencies comes to the surface. In this work, the calculations of harmonic frequencies with the DIM potentials have been carried out with the molecular dynamics techniques by computing the power spectra as the Fourier transforms of velocity–velocity autocorrelation functions.

The recent high level ab initio calculations carried out by Partridge and Schwenke [28] for the ground state PES of  $\text{H}_2\text{O}$  with a spectroscopic accuracy provide a unique opportunity to perform the point-by-point comparison of the sections of PES predicted by ab initio and DIM and therefore to learn the origins of possible shortcomings of the latter model.

The latest set of molecular constants of the water molecule predicted with the DIM theory has been reported by Kuntz et al. [25,27]. Depending on details of their adjustment of diatomic input information the quantities fall into the following ranges:  $\alpha_e = 96.5 \div 103.3^\circ$  (the accurate value is  $104.5^\circ$  [28,29]),  $R_e = 1.00 \div 1.01 \text{ \AA}$  (0.957 [29], 0.958 [28]),  $E_{\text{at}} = 9.32 \div 9.87 \text{ eV}$  (10.08 [29], 9.59 [9]), the energy of the saddle point  $D_{\infty\text{h}}$  with respect to that of the equilibrium configuration  $E_s = 2.61 \div 5.86 \text{ eV}$  (1.74 [29], 1.38 [28]). No attempts have been known for us to compute the vibrational frequencies for the water molecule with the DIM potential surfaces.

As stated above, since the very first applications the DIM models give reasonable estimates of selected molecular constants  $R_e$ ,  $\alpha_e$ ,  $E_{\text{at}}$  for the water

molecule. However, we point out that still there are noticeable discrepancies between the DIM and accurate quantities. In particular, we stress that the  $R_e$  values in all previous DIM treatments are systematically overestimated by  $0.04 \div 0.05 \text{ \AA}$ . In the present work we show how to improve these quantities as well as how to estimate reasonable force constants of  $\text{H}_2\text{O}$ .

We believe that recent successes of the DIM applications are to a large extent due to the inclusion into the DIM basis sets the functions arising not only from the neutral constituents but from the ion-pair states as well. These excited electronic states of the diatomic fragments play crucial role in accounting for many-body effects in interaction potentials [1,5,6,15–19,23]. Their importance in the DIM construct is recognized by many researchers; in particular, in the calculations of Kuntz et al. [24–27] the ion-pair states are taken into account resulting in a reasonable description of the water potential surfaces. However, the knowledge of ion-pair potential curves of diatomic fragments is not as good as that of the lowest energy potentials. These states usually are not probed by experiments and their ab initio calculations require considerable efforts. Such efforts have been undertaken recently by us for the OH species [30] which allow us to declare that the corresponding potential energy curves are presently known with better accuracy than before. Therefore testing these diatomic potentials in the benchmark DIM calculations of the water potential energy surface presents one more motivation of this work.

As in our previous studies [4–6] we establish the hierarchy of the DIM-based models and show efficiency of every step. On the low level is the DIM model with the contributions from the neutral atomic states only. Next is the neutral-ionic model, and on the top is the construct which takes into account the corrections to the neutral-ionic model of the previous step. Namely, we improve the main shortcoming of the diatomic fragment approach by taking into account the multicenter charge corrections which are dictated by quantum chemistry analysis of the diatomic fragments and of the entire polyatomic molecule. We show that at all these levels the ‘rough’ properties of DIM treatment (crude value of  $R_e$ ,  $\alpha_e$ ,  $E_{\text{at}}$ ) are nicely reproduced, but the more delicate properties (precise value of  $R_e$ ,  $E_s$  and vibrational

frequencies) can be accurately obtained at the highest level only. Direct comparison of the cuts of potential surface, DIM versus high level ab initio data [28], provides an additional support to these conclusions.

## 2. Quantum chemistry data

We shall compare our DIM results for the potential energy surface to the ab initio-based data by Partridge and Schwenke [28]. The points on their PES are reproduced by using the author's FORTRAN subprogram available from the FTP server.

This PES has been created with the modern correlation consistent polarized valence basis sets (up to 6Z) augmented with diffuse functions. The orbitals have been optimized with the complete active space self-consistent-field (CASSCF) approach and used in the multireference configuration interaction (MRCI) scheme. The computed points have been slightly empirically adjusted to improve the agreement between the computed and experimental lines for thousands transitions. We consider this surface as an excellent reference to test the DIM models.

It is worth expanding the knowledge of quantum chemistry data on  $\text{H}_2\text{O}$  by the analysis of the charge distribution which is helpful in understanding the structure of this molecule. It turns out to be important that the balance of charges on the oxygen and hydrogen centres in the water molecule differs from that in the diatomic fragment OH; moreover, the partial charges in  $\text{H}_2\text{O}$  strongly depend on the valence angle  $\alpha$ . We can see these trends from the calculations carried out with the basis set aug-cc-pDVZ following the Weinhold's scheme [31] of natural orbital population analysis. Fig. 1 demonstrates the behaviour of the charge on hydrogen centres in the water molecule on the valence angle showing a substantial increase of the polarization upon bending the molecule and approaching the linear saddle point configuration ( $\alpha = 180^\circ$ ). Comparison of the charges in  $\text{H}_2\text{O}$  and OH (the latter is also indicated in Fig. 1) has led us to the conclusion that an attempt to reproduce the properties of the three-atomic system  $\text{H}_2\text{O}$  (with larger charges) by combining within the DIM construct the contributions from the fragments OH (with considerably less

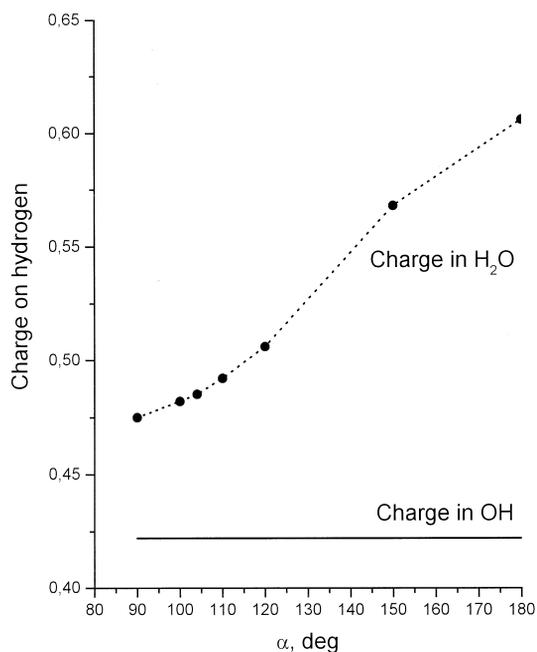


Fig. 1. Natural charges on the hydrogen centers in  $\text{H}_2\text{O}$  (depending on the valence angle) and OH( $X^2\Pi$ ) computed following Ref. [31] with the aug-cc-pDVZ bases.

charges) may lead to certain errors. In particular, it is clear that the shortening of the equilibrium O–H distances when passing from OH to  $\text{H}_2\text{O}$ , the effect that has been underestimated in all previous DIM calculations, is related to these changes in charge distributions. This consideration encountered us to introduce the so-called multicenter charge corrections described below.

The quantum chemistry data unambiguously show that the charge polarization is substantial in the water molecule. In the DIM language this means that the polyatomic basis sets should include ionic contributions, and therefore the use of ionic states is necessary for any reasonable DIM model. The list of ionic states needed in this case includes the ion-pair states which dissociate to  $\text{O}^- + \text{H}^+$  and the anionic states  $\text{OH}^-$ . Analysis of previous ab initio calculation results [32–34] shows that we face some ambiguities when attempting to use the literature data for the excited state potential curves of OH. Therefore we have recomputed the OH energies by using the following strategy (complete details are given in a separate publication [30]). Potential curves of the OH

fragment correlating to the dissociation limits  $O(^3P) + H(^2S)$ ,  $O(^1D) + H(^2S)$ ,  $O(^1S) + H(^2S)$ ,  $O^-(^2P) + H^+$ ,  $O^-(^2P) + H(^2S)$  have been computed at the CI/CASSCF level with the aug-cc-pVTZ basis sets. A balanced treatment of the excited state potentials is achieved by using the state-averaging MO optimization procedure. We emphasize that for the ion-pair states  $3^2\Pi$  and  $C^2\Sigma^+$  we have obtained the curves the shapes of which are different from known before and a new representation is suggested for the potential curve of the autoionizing  $^1\Pi(OH^-)$  state. The newly computed ab initio potential curves of OH and  $OH^-$  have been used in the present DIM calculations with an exception for the lowest energy  $X^2\Pi$  and  $A^2\Sigma$  states of OH for which more accurate ab initio points [35] reproducing the experimental RKR data within  $10\text{ cm}^{-1}$  are known.

### 3. Diatomics-in-molecules models

The DIM formalism is documented in many papers [9,10] and only brief introduction is given here for a particular application to  $H_2O$ . The three-atomic Hamiltonian operator is partitioned into diatomic and monoatomic parts as follows

$$H_{H_2O} = H_{OH^{(1)}} + H_{OH^{(2)}} + H_{H^{(1)H^{(2)}}} - H_O - H_{H^{(1)}} - H_{H^{(2)}}. \quad (1)$$

With the selected set of polyatomic basis functions (PBF) this Hamiltonian is converted into the matrix form, and the total Hamiltonian matrix whose eigenvalues give estimates of the polyatomic energies is

composed of the diatomic and monoatomic matrices as prescribed by Eq. (1). The fragment matrices are constructed on the base of monoatomic  $V_a$  and diatomic  $V_{ab}$  energies which are supposed to be known from independent sources. In Table 1 the set of PBFs used in our DIM models is shown together with the needed states of each diatomic fragment. For every diatomic constituent, the initial basis set should be transformed in such a manner that the specific electronic states with respect to the spatial and spin quantum numbers should be recognized. To accomplish this goal, the conventional rotation  $R_a^{ab}$  and spin transformation  $T_{ab}$  matrices applied to the original basis set should be constructed [9] and the practical formula for the  $H_{ab}$  diatomic matrix looks as follows

$$H_{ab} = (R_b^{ab})^+ \cdot (R_a^{ab})^+ \cdot T_{ab}^+ \cdot B_{ab}^{-1} \cdot V_{ab} \cdot B_{ab} \cdot T_{ab} \cdot R_a^{ab} \cdot R_b^{ab}. \quad (2)$$

Here, the so-called mixing-state matrix  $B_{ab}$  is responsible for coupling the diatomic energies with the same spin and spatial symmetries, in this case, the states of OH  $A^2\Sigma^+$ ,  $B^2\Sigma^+$  and  $C^2\Sigma^+$  in one block, and  $X^2\Pi$ ,  $2^2\Pi$  and  $3^2\Pi$  in another block are mixed. The orthogonal matrices  $B_{ab}$  may be parametrized as the matrices of spatial rotations with the parameters (mixing parameters) taken partly from quantum chemistry calculations of diatomic fragments OH and partly by adjusting some sections of the  $H_2O$  potential surface. The mixing parameters are not strictly defined within the DIM theory itself. Therefore for each DIM model described below we

Table 1

The polyatomic basis functions (PBF) and diatomic fragments states required for the DIM models of  $H_2O$

	$V_O$	$V_{H^{(1)}}$	$V_{H^{(2)}}$	$V_{OH^{(1)}}$	$V_{OH^{(2)}}$	$V_{H^{(1)H^{(2)}}}$
1	$^1S(O)$	$^2S(H)$	$^2S(H)$	$B^2\Sigma^+(OH)$	$B^2\Sigma^+(OH)$	$^1\Sigma_g^+(H_2)$
2	$^1D_{ZZ}(O)$	$^2S(H)$	$^2S(H)$	$A^2\Sigma^+(OH)$	$A^2\Sigma^+(OH)$	$^1\Sigma_g^+(H_2)$
3	$^1D_{XX-YY}(O)$	$^2S(H)$	$^2S(H)$	$2^2\Pi(OH)$	$2^2\Pi(OH)$	$^1\Sigma_g^+(H_2)$
4	$^1D_{XX-YY}(O)$	$^2S(H)$	$^2S(H)$	$^2\Delta(OH)$	$^2\Delta(OH)$	$^1\Sigma_g^+(H_2)$
5	$^3P_Y(O)$	$^2S(H)$	$^2S(H)$	$X^2\Pi(OH)$	$X^2\Pi(OH)$	$^3\Sigma_g^+(H_2)$
6	$^2P_X(O^-)$	$^2S(H)$	$H^+$	$^1\Pi(OH^-)$	$3^2\Pi(O^-H^+)$	$2\Sigma_{g,u}^+(H_2^+)$
7	$^2P_Z(O^-)$	$^2S(H)$	$H^+$	$X^2\Sigma^+(OH^-)$	$C^2\Sigma^+(O^-H^+)$	$2\Sigma_{g,u}^+(H_2^+)$
8	$^2P_X(O^-)$	$H^+$	$^2S(H)$	$3^2\Pi(O^-H^+)$	$^1\Pi(OH^-)$	$2\Sigma_{g,u}^+(H_2^+)$
9	$^2P_Z(O^-)$	$H^+$	$^2S(H)$	$C^2\Sigma^+(O^-H^+)$	$X^1\Sigma^+(OH^-)$	$2\Sigma_{g,u}^+(H_2^+)$

optimized the mixing parameters, first of all attempting to reproduce the reference values of the HOH valence angle and the energies  $E_{\text{at}}$  and  $E_s$ .

For the DIM applications we need fragment energies  $V_{\text{ab}}$  for the OH, OH<sup>-</sup>, H<sub>2</sub>, H<sub>2</sub><sup>+</sup> diatomic molecules. The treatment of OH and OH<sup>-</sup> in this work is clarified in Section 1. The potential curves of H<sub>2</sub> and H<sub>2</sub><sup>+</sup> have been taken from precise quantum mechanics calculations [36,37]. Proper symmetrization of the original basis functions has been performed in order to distinguish correct contributions from the g–u states of the homonuclear fragments H<sub>2</sub> and H<sub>2</sub><sup>+</sup> following Refs. [6,17].

We have tested several DIM-based models to create the PES for H<sub>2</sub>O. One can see from Table 1 that the lowest eigenvalue of the DIM H<sub>2</sub>O matrix correlates with the matrix elements referring to the combination of the atomic ground states <sup>3</sup>P(O) × <sup>2</sup>S(H) × <sup>2</sup>S(H). If we ignore all other contributions, then the DIM construct would reduce to the simplest expression corresponding to the primitive pair-wise potential scheme:

$$V_{\text{H}_2\text{O}} = V_{\text{OH}^{(1)}}(^2\Pi) + V_{\text{OH}^{(2)}}(^2\Pi) + V_{\text{H}^{(1)}\text{H}^{(2)}}(^3\Sigma_u^+). \quad (3)$$

It is easy to see that such an approach would give the linear equilibrium geometry of the  $D_{\infty h}$  symmetry instead of the true  $C_{2v}$  bent structure and this model is not considered here.

The blocks of the Hamiltonian matrices of the size  $5 \times 5$  occur if the excited singlet state of oxygen species (<sup>1</sup>D, <sup>1</sup>S) are added to the ground state constituent <sup>3</sup>P. We shall refer to this approach as a neutral model or Scheme (a). We show below that the results of this neutral model predict more or less reasonable molecular constants for the water molecule, however, still far from the desired accurate values. The receipt for improving the situation is basically known: ionic states should be added to the basis set as it is prescribed by rows 6–9 in Table 1. We shall address this model as a neutral-ionic model or Scheme (b). As we shall see below, this improvement is a necessary but not sufficient step.

A detailed analysis shows that it is impossible to achieve the slight decrease of the equilibrium  $R_{\text{OH}}$  distances when passing from OH (0.97 Å) to H<sub>2</sub>O (0.96 Å) by using these ((a) and (b)) DIM models.

On the opposite, the equilibrium O–H distances increase (up to 1.00 ÷ 1.01 Å) in these DIM schemes. We believe that attempts to compute the correct curvatures of the PES, namely the force constants of H<sub>2</sub>O, are useless if the correct geometry trends are not precisely reproduced by a DIM model. It is clear that there are no chances to reduce  $R_{\text{OH}}$  at the expense of mixtures of the ground and excited electronic states of OH including the ion-pair states as well since all the excited bound states have their minima greater than that of X <sup>2</sup>Π.

This observation led us to the idea to introduce a correction which takes into account the differences in the charge distributions of H<sub>2</sub>O compared to OH. Fig. 1 clearly shows that the charges on the atoms in H<sub>2</sub>O are considerably larger than those in OH. Therefore the contraction of the OH bond when forming H<sub>2</sub>O from OH fragments should be related to an increase of the partial charges. In the DIM formalism this effect may be taken into account two-fold. First, the double charged O<sup>2-</sup> species may be included into the basis set (as it has been considered in the works of Kuntz et al. [24–27]) or secondly, this charge modification can be introduced directly into the DIM matrix elements. We choose the second option and add to the DIM energy the multicenter charge correction term which is responsible for an extra charges on atoms in the H<sub>2</sub>O molecule compared to the OH fragments

$$\Delta V = -\frac{\delta_{\text{O}} \cdot \delta_{\text{H}^{(1)}}}{r_{\text{OH}^{(1)}}} - \frac{\delta_{\text{O}} \cdot \delta_{\text{H}^{(2)}}}{r_{\text{OH}^{(2)}}} + \frac{\delta_{\text{H}^{(1)}} \cdot \delta_{\text{H}^{(2)}}}{r_{\text{H}^{(1)}\text{H}^{(2)}}} \quad (4)$$

$$(\delta_{\text{O}} = \delta_{\text{H}^{(1)}} + \delta_{\text{H}^{(2)}}).$$

The model thus obtained is considered here as the highest rank one (Scheme (c)).

#### 4. Results and discussions

The lowest level DIM approach of this work (Scheme (a)) corresponds to the neutral model according to which the first five functions of Table 1 constitute the basis set. In this case the mixing occurs between the A<sup>2</sup>Σ<sup>+</sup> and B<sup>2</sup>Σ<sup>+</sup> states of OH (the mixing parameter of the 2 × 2 block of the matrix  $B_{\text{OH}}$  is  $\beta_{\Sigma}^{(a)}(\text{AB})$ ), and the X <sup>2</sup>Π and 2 <sup>2</sup>Π

states of OH (the mixing parameter is  $\beta_{\Pi(X2)}^{(a)}$ ). These mixing parameters are adjusted in such a manner that the precise value of the valence angle  $\alpha_e$  is reproduced, the second condition is to approach the atomization energy  $E_{at}$  and the energy  $E_s$  at the linear saddle point H–O–H as close as possible to the reference data. The final values of mixing parameters are as follows:  $\beta_{\Sigma(AB)}^{(a)} \approx 0$ ,  $\beta_{\Pi(X2)}^{(a)} = 23^\circ$ .

The results of this approximation are shown in Table 2. As stated above, the equilibrium value of O–H distances (0.99 Å) is by 0.3 Å greater than expected (0.96 Å [28,29]) what is, however, typical for all previous DIM treatments. The O–H distances of the saddle point  $R_s$  are also greater than the reference data [28]. The diagonal force constants  $\partial^2 E / \partial R^2$  and  $\partial^2 E / \partial \alpha^2$  computed at the equilibrium point are considerably different from the accurate values [28], what is reflected by the DIM (Scheme (a)) harmonic frequencies (3501, 1544 and 3605  $\text{cm}^{-1}$ ) with the deviations from the accurate data by  $-331$ ,  $-105$  and  $-338 \text{ cm}^{-1}$  respectively.

The next step in our approach is to include the ionic states and to add next four functions of Table 1 to the basis set (Scheme (b)). In this case the structure of the mixing-state matrices  $B_{OH}$  is more complicated since more diatomic states of the OH fragment are coupled. We have parametrized the corresponding blocks of these matrices referred to the  $^2\Sigma^+$  (A, B and C) and  $^2\Pi$  (X, 2 and 3) states by products of  $2 \times 2$  planar rotational submatrices with the mixing parameters adjusted by the same principles as for the Scheme (a):  $\beta_{\Sigma(AB)}^{(b)} \approx 0$ ,  $\beta_{\Sigma(AC)}^{(b)} = 76^\circ$

and  $\beta_{\Sigma(BC)}^{(b)} \approx 37^\circ$ ,  $\beta_{\Pi(X2)}^{(b)} = 23^\circ$ ,  $\beta_{\Pi(X3)}^{(b)} = 19^\circ$  and  $\beta_{\Pi(23)}^{(b)} = 25^\circ$ . It should be noted that these values are fairly close to the mixing parameters shown in Figs. 2 and 3 of Ref. [27] although in the latter case they have been derived quite differently.

We see (Table 2) that no considerable improvement is achieved for all the quantities of our interest (beyond the geometry and energy at the saddle point  $E_s$ ). The computed harmonic frequencies (3502, 1565 and 3589  $\text{cm}^{-1}$ ) are practically the same as at level (a).

Finally, the correction due to the multicenter charge distribution described by Eq. (4) has been added to the lowest eigenvalue of the  $9 \times 9$  Hamiltonian matrix of the Scheme (b). The excess charges of Eq. (4) are defined through the single parameter, the partial charge on the hydrogen center  $\delta_H$  ( $\delta_O = \delta_{H(1)} + \delta_{H(2)}$ ), for which the following parametrization is suggested (we have considered the shapes of this function resembling the form of the quantum chemistry charge dependence on the valence angle shown in Fig. 1)  $\delta_H = 0.762 \cdot e^{-1.87 \cdot R_{OH}^2} \cdot R_{OH}^2 \cdot (0.97 - 0.13 \cdot \cos \alpha)$  with the coefficients selected by comparing the cuts of the DIM potential energy surface along the  $R_{OH}$  ( $R_{OH} = R_{OH(1)} = R_{OH(2)}$ ) at  $\alpha_{HOH} = 104.4^\circ$  with the ab initio data of Partridge and Schwenke [28]. The mixing parameters have been adjusted by the same principles as described above but minor changes in their optimal values compared to the Scheme (b) have been found:  $\beta_{\Sigma(AB)}^{(b)} = -14^\circ$ ,  $\beta_{\Sigma(AC)}^{(b)} = 76^\circ$  and  $\beta_{\Sigma(BC)}^{(b)} = 51^\circ$ ;  $\beta_{\Pi(X2)}^{(b)} = 21^\circ$ ,  $\beta_{\Pi(X3)}^{(b)} = 17^\circ$  and  $\beta_{\Pi(23)}^{(b)} = 22^\circ$ .

Table 2  
Molecular constants of  $\text{H}_2\text{O}$  computed at different levels

		DIM			ab initio[28]	Previous DIM [24–27]
		Scheme (a)	Scheme (b)	Scheme (c)		
$E_{at}$	(eV)	9.16	8.91	9.58	–	9.32 ÷ 9.87
$R_e$	(Å)	0.986	0.988	0.959	0.959	1.00 ÷ 1.01
$\alpha_e$	(°)	104.4	104.4	104.4	104.4	96.5 ÷ 103.3
$E_s$	(eV)	3.75	1.63	1.37	1.38	2.61 ÷ 5.86
$R_s$	(Å)	1.02	1.003	0.959	0.933	1.005 ÷ 1.101
$\partial^2 E / \partial R^2$	(mdin/A)	7.123	7.056	8.54	8.442	–
$\partial^2 E / \partial \alpha^2$	(mdin/A)	0.670	0.686	0.750	0.707	–
$\omega_1$	( $\text{cm}^{-1}$ )	3501	3502	3847	3834	–
$\omega_2$	( $\text{cm}^{-1}$ )	1544	1565	1657	1650	–
$\omega_3$	( $\text{cm}^{-1}$ )	3605	3589	3910	3945	–

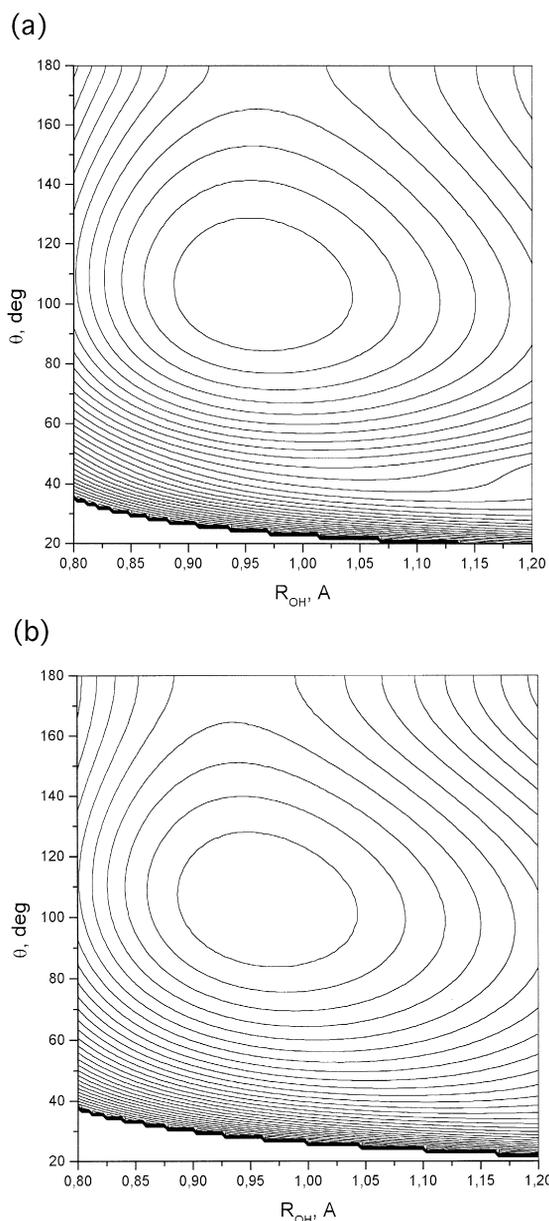


Fig. 2. Contour plots for potential energy surfaces of symmetric  $\text{H}_2\text{O}$ : (a) DIM results; (b) ab initio calculations of Partridge and Schwenke [28]. The contour values are at increments of  $2500 \text{ cm}^{-1}$ .

As one can see from Table 2, the latter correction results in a dramatic improvement of the molecular constants of the water molecule as predicted by the DIM theory. All the quantities of Scheme (c) are in

much better agreement with the reference values than those of other DIM approaches. The set of DIM (Scheme (c)) computed frequencies, namely,  $3847$ ,  $1657$  and  $3910 \text{ cm}^{-1}$ , is characterized by the deviations from the precise values by  $+13$ ,  $+7$  and  $-35 \text{ cm}^{-1}$ , respectively, which are not as small as we would wish, but which are considerably better (the errors are an order less compared to Schemes (a) and (b)) than those predicted without the charge correction procedure (4).

The panels of Fig. 2a,b show the direct comparison of the DIM (model (c)) potential surface with the reference Partridge–Schwenke ab initio results. It is obvious that our highest rank DIM-based model gives a very good representation of the desired potential. Various one-dimensional cuts through the surface show the same coincidence of the DIM and ab initio results.

## 5. Conclusions

The starting point of this study is the belief that the DIM theory can be used on competitive grounds for creation of reliable and cheap potential energy surfaces not only for simple molecules like water, but for intermolecular complexes what makes this method very attractive for molecular dynamics simulations of properties of molecular ensembles. However, it is hard to expect its successful applications if such important dynamical quantities as vibrational frequencies cannot be accurately reproduced. In this respect the findings of this work seem fairly promising. We show how the DIM-based model can be accomplished for one of the well characterized molecular systems, namely  $\text{H}_2\text{O}$ , allowing the correct description of the harmonic frequencies. Point-by-point comparison the DIM and accurate ab initio results for important sections of the DIM potential surface promises that the anharmonic vibrations will be nicely reproduced as well. We are planning to verify this issue in future.

Returning to the grounds of the DIM theory, it is important to confirm the findings of previous researches in this field that the proper treatment of mixing of the neutral and ion-pair states is necessary for a correct description of the polyatomic ground state correlating to the neutral dissociation limits. A

good knowledge of the potential curves for the highly excited ion-pair diatomic states is required for the DIM scheme. These potential curves can be accurately calculated with the modern tools of quantum chemistry.

On the top of the hierarchy of the DIM-based models described here we consider the so-called multicenter charge correction which provides a final polish of the shape of the potential surface and allows one to improve finally the equilibrium geometry parameters of the molecule and to predict correctly such delicate characteristics as curvatures at the minimum energy point. All these improvements can be viewed as the steps towards a quantitatively consistent DIM scheme.

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