COMPARISON OF METHODS FOR SOLVING THE VIBRATIONAL SCHRÖDINGER EQUATION IN THE COURSE OF SEQUENTIAL MONTE-CARLO-QUANTUM MECHANICAL TREATMENT OF HYDROXIDE ION HYDRATION

Jasmina Petreska, Ljupčo Pejov*

Institute of Chemistry, Faculty of Natural Sciences and Methematics, Ss. Cyril and Methodius University, Arhimedova 5, P.O. Box 162, 1000 Skopje, Republic of Macedonia
ljupcop@iunona.pmf.ukim.edu.mk

Three numerical methods were applied to compute the anharmonic O–H stretching vibrational frequencies of the free and aqueous hydroxide ion on the basis of one-dimensional vibrational potential energies computed at various levels of theory: i) simple Hamiltonian matrix diagonalization technique, based on representation of the vibrational potential in Simons-Parr-Finlan (SPF) coordinates, ii) Numerov algorithm and iii) Fourier grid Hamiltonian method (FGH).

Considering the Numerov algorithm as a reference method, the diagonalization technique performs remarkably well in a very wide range of frequencies and frequency shifts (up to 300 cm^{-1}). FGH method, on the other hand, though showing a very good performance as well, exhibits more significant (and non-uniform) discrepancies with the Numerov algorithm, even for rather modest frequency shifts.

Key words: hydroxide ion; ionic water solutions; solvation; hydrogen bonds; intermolecular interactions; anharmonic O–H vibrational frequency shifts; Monte-Carlo simulation; Fourier grid; Hamiltonian method; Numerov algorithm; diagonalization of Hamiltonian matrix

СПОРЕДБА НА НЕКОЛКУ МЕТОДИ ЗА РЕШАВАЊЕ НА ВИБРАЦИОНАТА ШРЕДИНГЕРОВА РАВЕНКА ПРИ СЕКВЕНЦИЈАЛЕН МОНТЕ КАРЛО-КВАНТНОМЕХАНИЧКИ ТРЕТМАН НА ХИДРАТАЦИЈАТА НА ХИДРОКСИДНИОТ ЈОН

За пресметување на анхармониските вибрациони фреквенции на валентниот ОН мод за слободен хидроксиден јон, како и за хидроксиден јон којшто се наоѓа во воден раствор, беа применети три нумерички методи кои се базираат на пресметување на еднодимензионална вибрациона потенцијална енергија при различни нивоа на теорија: 1) едноставна техника со дијагонализација на Хамилтоновата матрица, во која вибрациониот потенцијал е претставен во координати на Simons-Parr-Finlan (SPF), 2) алгоритам на Нумеров и 3) Fourier grid Hamiltonian метод (FGH).

Во споредба со алгоритамот на Нумеров, кој се користи како референтен метод, техниката која вклучува дијагонализација е особено добра во многу широко подрачје на фреквенции, како и поместувања на фреквенциите во однос на вредноста на парна фаза (до 300 cm^{-1}). Од друга страна, иако методата FGH покажува добри перформанси, сепак кај него постојат позначајни (и нерамномерни) недоследности во споредба со алгоритмот на Нумеров дури и за прилично мали поместувања на фреквенциите во однос на вредноста за парна фаза.

Клучни зборови: хидроксиден јон; јонски водни раствори; поместување на фреквенцијата; Монте Карло симулација; Fourier grid Hamiltonian метод; алгоритам на Нумеров; дијагонализација на Хамилтонова матрица.

1. INTRODUCTION

Intramolecular vibrational frequencies are a rather significant indicator of the type and strength of noncovalent intermolecular interactions when isolated molecular species are embedded in condensed phases or are brought into contact with other molecular species with which they interact. From the experimental side, conclusions concerning the type of non-covalent bond are often derived on the basis of spectroscopically determined frequency shifts. As the commercial and easy-to-use quantum chemical modeling codes become widespread, often such experimental studies are accompanied by quantum chemical computations of the "predicted" vibrational frequency shifts which are in turn compared to the experimental spectroscopic ones. However, with certain notable exceptions which will be discussed further in this paper, the available computer codes usually give the harmonic vibrational frequencies, which are almost routinely computed by diagonalization of the mass-weighted Hessian matrices. The "frequency shifts" are, therefore, in most cases calculated within the harmonic approximation. As discussed in our previous manuscripts [1–3 and references therein], very often it comes out that the "predicted (harmonic) frequency shifts" are in fortuitous agreement with the experimental data, though such results have often been used to "confirm" the experimental evidence for various aspects of the intermolecular interactions. The most straightforward remedy to the situation would be to compute the more realistic anharmonic frequencies and frequency shifts. Anharmonic contributions to the overall observed vibrational frequency shifts may be as high as 30 – 40 % [1–4]. To account for the anharmonicity effects (and other systematic deficiencies of computational methods), various variants of the scaled quantum mechanical force fields methods have been developed in the literature [5–9]. This approach is, however, based on system-specific "magic" scaling factors, which are by any means artificial. In the last years, also the vibrational self-consistent field methodology (VSCF) has become widely

available and implemented in computed codes [10, 11]. The second-order perturbative approach has also been efficiently automated by Barone for building the anharmonic force constants and evaluation of vibrorotational parameters and implemented in the Gaussian series of codes [12]. An efficient local mode approximation-based method for calculation of Near Infra-red (NIR) and NIR-VCD spectra up to the second X-H stretching overtone region has recently been proposed by Abbate *et al.* [13, 14]. All of these methodologies are, however, computationally demanding. In the case when one is interested in a localized mode for which the coupling with other intra- and intermolecular motions may be regarded as negligible, the following approach can be adopted. A cut through the complete vibrational potential energy surface (PES) is computed moving in an appropriate way only the atoms that are relevant to the mode in question. In such way, the one-dimensional (1D) vibrational potential is obtained, which may be further used to solve the vibrational Schrödinger equation. Solving the vibrational Schrödinger equation for an arbitrary anharmonic potential is, however, not a unique procedure. Numerous algorithms have been proposed to accomplish this task. In our previous studies [1–3 and references therein], we have used a simple diagonalization procedure based on the representation of the 1D vibrational potential in the Simons-Parr-Finlan type coordinates [15], and found out that it performs remarkably well for a variety of purposes. In the present case, we want to test the performances of this simple approach and of another simple method for solving the vibrational Schrödinger equation, the Fourier grid Hamiltonian approach [16, 17]. The benchmark with respect to which we test the two methodologies is the standard Numerov algorithm, as implemented in the LEVEL 8.0 code [18]. We apply this testing procedure to the problem of computation of the anharmonic O–H stretching vibrational frequencies for a free hydroxide anion and of the aqueous OH⁻ ion, by a sequential Monte-Carlo-quantum mechanical procedure which we have recently implemented [19].

2. COMPUTATIONAL DETAILS

2. 1. *General computational methodology aspects*

To generate the structure of liquid (OH⁻(aq)), first a series of Monte-Carlo (MC) simulations were carried out. All MC simulations were performed in the *NPT* ensemble, implementing the Metropolis sampling algorithm, at $T = 298$ K, $P = 1$ atm. We first carried out a MC simulation of one hydroxide anion plus 83 water molecules placed in a cubic box with side length of 13.35 Å, imposing periodic boundary conditions. These simulation conditions correspond to the experimental data in Ref. [20] referring to the highest dilution under which the hydroxide ion O–H stretching band could still be clearly resolved or at least distinguishable with the applied numerical techniques. However, this system is relatively small from the viewpoint of long-range corrections (LRC) to the interaction energy, which were calculated for interacting atomic pairs between which the distance is larger than the cutoff radius defined as half of the unit cell length. The Lennard-Jones contribution to the interaction energy beyond this distance was estimated assuming uniform density distribution in the liquid (*i.e.* $g(r) \approx 1$), while the electrostatic contribution was estimated by the reaction field method involving the dipolar interactions. We have therefore proceeded with a series of MC simulations using larger unit cells (e.g. 2, 3, 4 and 5 OH⁻ ions with 162, 243, 324 and 405 water molecules, and also in a separate series of simulations we have added 1, 2, 3, 4 and 5 Na⁺ counterions in the corresponding simulation boxes). Details about these additional simulations are given in our previous paper devoted to the subject [19]. In the present study, we focus our attention on the performances of methods used to solve the vibrational Schrödinger equation and we therefore limit our discussion to the simplest periodic system that we have considered (1 hydroxide ion plus 83 water molecules). In all MC simulations carried out in the present study, intermolecular interactions were described by a sum of Lennard-Jones 12–6 site-site interaction energies plus Coulomb terms:

$$U_{ab} = \sum_{i}^{a} \sum_{j}^{b} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j e^2}{4\pi\varepsilon_0 r_{ij}} \quad (1)$$

where i and j are sites in interacting molecular systems a and b, r_{ij} is the interatomic distance between sites i and j, while e is the elementary charge. The following combination rules were used to generate two-site Lennard-Jones parameters ε_{ij} and σ_{ij} from the single-site ones:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (2)$$

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j} \quad (3)$$

For water, we have used the SPC model potential parameters [21], while the charge distribution in the case of hydroxide anion was described implementing a somewhat modified charged-ring (CR) description, proposed in Ref. [22]. More technical details about the actual implementiation of the CR description of charge distribution in the hydroxide ion can be found in our previous paper [19]. The parameters which were used in all MC simulations are summarized in Table 1.

T a b l e 1

The atomic charges and Lennard-Jones parameters used in the Monte Carlo simulations

(See text for details)

Site	σ_{ii} / Å	ε_{ii} / (kcal mol⁻¹)	q / e
SPC model of water			
H_w	0.0000	0.0000	0.41000
O_w	3.1650	0.1550	-0.82000
Hydroxide ion modified CR model			
H_{ion}	0.0000	0.0000	0.07420
O_{ion}	3.5338	0.0242	0.00000
X_{ion}	0.0000	0.0000	-0.05371

All simulations consisted of thermalization phase of at least $2.52 \cdot 10^7$ MC steps, which was subsequently followed by averaging (simulation) phase of at least $1.26 \cdot 10^8$ MC steps. Series of configurations from the MC simulation runs

were sequentially used to calculate the "in-liquid" O–H stretching potential of the hydroxide ion by a quantum-mechanical (QM) approach. Due to the high statistical correlation between MC-generated configurations which are sufficiently close to each other, performing QM calculations on such configurations would be a waste of time, as they will not add any new statistically relevant contribution to the results. A much better approach, as explained in the works of Coutinho *et. al.* [23–26], would be to choose statistically uncorrelated configurations (*i.e.* configurations with low statistical correlation) and perform the QM computational part only on these configurations. The choice of statistically uncorrelated configurations is essentially based on time series analysis methods for Markovian random processes [27, 28] (such as the MC chain generated by the Metropolis sampling algorithm). The energy autocorrelation function has been used as an indicator for mutual statistical correlation between subsequent MC-generated configurations, defined with:

$$C(n) = \frac{\langle \delta E_i E_{i+n} \rangle}{\langle \delta E^2 \rangle} = \frac{\sum_i (E_i - \langle E \rangle)(E_{i+n} - \langle E \rangle)}{\sum_i (E_i - \langle E \rangle)^2} \quad (4)$$

Integrating the energy autocorrelation function (more precisely, the fit of this function by a sum of two exponentially-decaying functions) from 0 to infinity, we have computed the correlation time (correlation step):

$$\tau = \int_0^\infty C(n)\mathrm{d}n \quad (5)$$

The computed $C(n)$ from the MC simulation phase of OH⁻ ion and 83 water molecules, together with the two-term exponential decay function fit is presented in Figure 1. Subsequent integration gives a correlation step of 435. In this particular case, MC configurations mutually separated by 1305 steps ($3 \cdot \tau$) are correlated less than 10 %. For sequential QM calculations which were further carried out in the present study from this periodic box, we chose 100 uncorrelated configurations from the equilibrated MC runs, separated by as much as 15000 MC steps.
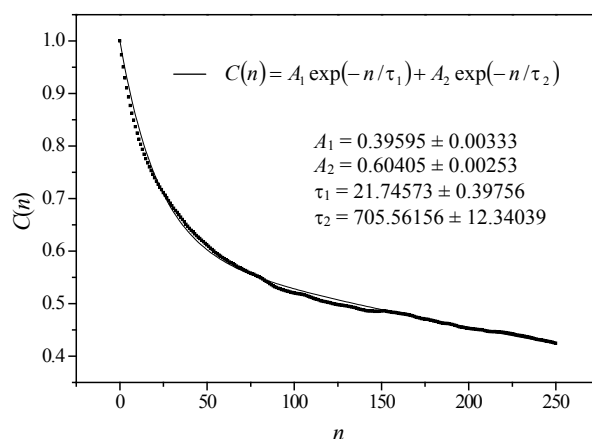

Fig. 1. Energy autocorrelation function computed from the MC simulation together with the fitting function

In that case, the mutual correlation between the configurations is negligible ($3.5 \cdot 10^{-8}$ %). The sequential QM calculations were carried out for 100 point-charge embedded supermolecular clusters containing the central OH⁻ ion and all of the water molecules residing in the first hydration shell, as determined from the analysis of the corresponding $O_{ion} \cdots O_{water}$ radial distribution function (Figure 2). Charge-embedding of the "QM" (*i.e.* full wavefunction) region of the liquid will be discussed below. For each of the considered OH⁻ ions, residing in different in-liquid environments (statistically uncorrelated, *i.e.* spanning appropriately the configurational space), a series of point-charge-embedded *supermolecular* cluster single-point energy calculations were carried out to obtain the one-dimensional (1D) *anharmonic* O–H stretching potential energy function.
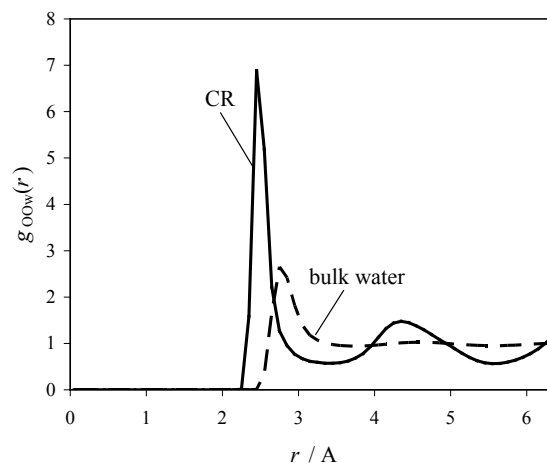

Fig. 2. O⋯O radial distribution function for the OH⁻(aq) base on the CR description of the charge distribution in the ion and of bulk water

This series of calculations were carried out varying the O–H distance from 0.850 to 1.325 Å (in steps of 0.025 Å), moving simultaneously both the oxygen and hydrogen atom, while keeping the center of mass of the OH⁻ ion fixed (*i.e.* mimicking as closely as possible the actual OH stretching mode). The O–H stretching potential energy functions for the point-charge embedded supermolecular systems were computed at Hartree-Fock (HF), second-order Möller-Plesset perturbation theoretic (MP2) and Density Functional Theory (DFT) levels of theory for all selected 100 oscillators. The standard Pople-style 6-31++G(*d,p*) basis set was employed for the orbital expansion, solving the HF and the Kohn-Sham (KS) SCF equations iteratively. Within the DFT approach, the combination of Becke's three-parameter adiabatic connection exchange functional (B3, [29]) with the Lee-Yang-Parr correlation one (LYP, [30]) was used. The "fine" (75, 302) grid was used for numerical integration in all DFT calculations (75 radial and 302 angular integration points). MC simulations were performed with the DICE statistical mechanics Monte Carlo suite of codes [31]. All quantum-chemical calculations were performed with the Gaussian 03 series of codes [32]. To compute in a more rigorous way the in-liquid O–H stretching frequency of the OH⁻ ion, besides the short-range intermolecular interactions with the first hydration shell water molecules, it is necessary to account for the long-range (electrostatic) influence from the "bulk" water molecules in an appropriate manner. These molecules have not been explicitly included in the QM cluster, as noted before. To fulfill this aim, the QM clusters were immersed in a "bath" of point charges, which were placed at the positions of oxygen and hydrogen atoms of the bulk water molecules, as generated by the MC simulations. In order to test the convergence aspects, the bulk solvent water molecules contained within spheres of successively larger radii surrounding the central hydroxide ion were included as point-charges and the O–H stretching potential energy functions for several MC-generated configurations were computed until a sufficient convergence of the O–H stretching frequencies was achieved (up to 4–5 cm⁻¹). Such convergence was achieved for a sphere radius

value of 9 Å, which was subsequently used as a final cut-off value for truncation of the long-range electrostatic interactions of the central hydroxide ion with the bulk water molecules. In this way, about 80 bulk water molecules were included as "point-charge water molecules" in the quantum-mechanical energy calculations. The values of the point charges chosen to model the long-range electrostatic interactions were the actual SPC charges which were used in the MC simulations: –0.82 *e* for O and +0.41 *e* for H.

2.2. *Methods for solution of the vibrational Schrödinger equation*

2.2.1. *Diagonalization of the Hamiltonian matrix*

The energies computed by the HF, DFT and MP2 methods were least-squares fitted to a fifth-order polynomial in Δr_{OH} ($\Delta r = r - r_e$):

$$V = V_0 + k_2 \Delta r^2 + k_3 \Delta r^3 + k_4 \Delta r^4 + k_5 \Delta r^5 \quad (6)$$

The resulting potential energy functions were subsequently cut after fourth order and transformed into Simons-Parr-Finlan (SPF) type coordinates [15]:

$$\rho = 1 - r_{OH,e}/r_{OH} \quad (7)$$

(where $r_{OH,e}$ is the equilibrium, i.e. the lowest-energy, value). The one-dimensional vibrational Schrödinger equation was solved variationally. Usage of only 15 harmonic oscillator eigenfunctions as a basis was shown to lead to excellent convergence of the computed vibrational frequencies. Superiority of the SPF-type coordinates over the "ordinary" bond stretch ones when a variational solution of the vibrational Schrödinger equation is sought has been well established, as they allow for a faster convergence (with the number of basis functions used) and a greatly extended region of convergence. The fundamental anharmonic O–H stretching frequency (corresponding to the $|0\rangle \rightarrow |1\rangle$ transition) was computed from the energy difference between the ground ($|0\rangle$) and first excited ($|1\rangle$) vibrational states.

2.2.2. *Numerov method*

Numerov method, which is sometimes also called Cowell's method, is an implicit second-order method for approximate solution of second-order differential equations of the form:

$$y''(x) = f(x, y) \tag{8}$$

with initial conditions:

$$y(x_0) = y_0 ; y'(x_0) = y_0' \tag{9}$$

with the integrand $f(x,y)$ being independent on y'. It is based on summing the Taylor series approximations for $y(x + h)$ and $y(x − h)$, substituting $f(x,y)$ for $y''(x)$ and the expression:

$$\frac{[f(x+h, y(x+h)) - 2f(x, y) + f(x-h, y(x-h))]}{h^2} \tag{10}$$

for the second derivative with respect to *x*. The final result obtained after the described procedure is:

$$y(x+h) + y(x-h) = 2y(x) + h^2 f(x, y) +$$

$$+ \frac{h^2}{12} [f(x+h, y(x+h)) - 2f(x, y) +$$

$$+ f(x-h, y(x-h))] \tag{11}$$

If we adopt the following notation:

$$x_n = x_0 + nh \tag{12}$$

$$f_n = f(x_n, y_n) \tag{13}$$

and denoting as y_n the approximation to $y(x_n)$, the following recursive formula based on Numerov algorithm can be derived:

$$y_{n+1} = 2y_n - y_{n-1} + h^2 (f_n + (f_{n+1} - 2f_n + f_{n-1})/12) \tag{14}$$

To begin the recursion, however, two successive starting values of *y* are required, one of which is y_0 while the other one is approximated by a suitable method. In the present study, we have used the implementation of Numerov method in the LEVEL 8.0 code by Le Roy and coworkers [18].

2.2.3. *Fourier grid Hamiltonian method*

The Fourier grid Hamiltonian method [16, 17] is a discrete variable representation-based technique (DVR), in which the continuous range of coordinate values φ is represented by a grid of discrete values φ_i. We used a uniform discrete grid of φ values:

$$\varphi_i = i\Delta\varphi \tag{15}$$

where $\Delta\varphi$ is the uniform spacing between the grid points. The state function $|\psi\rangle$ is represented as a vector on a discretized grid of points in either coordinate space or momentum space. The two alternative representations are:

$$|\psi\rangle = \psi^\varphi = \sum_i |\varphi_i\rangle \cdot \Delta\varphi \cdot \psi(\varphi_i) = \sum_i |\varphi_i\rangle \cdot \Delta\varphi \cdot \psi_i^\varphi \tag{16}$$

and

$$|\psi\rangle = \psi^k = \sum_i |k_i\rangle \cdot \Delta k \cdot \psi(k_i) = \sum_i |k_i\rangle \cdot \Delta k \cdot \psi_i^k \tag{17}$$

where $|\varphi_i\rangle$ are basis functions. The reciprocal grid size in momentum space is given by:

$$\Delta k = \frac{2\pi}{N\Delta\varphi} \tag{18}$$

where $N\Delta\varphi$ is the total length of the coordinate space covered by the grid. If we denote the (unitary) matrix which performs a fast Fourier transformation (FFT) between the two representations by *F*, we obtain:

$$\psi^k = F\psi^\varphi \tag{19}$$

Since the kinetic energy operator is diagonal in momentum representation, while the potential energy operator is diagonal in coordinate representation, we used the FFT approach to solve the stationary Schrödinger equation for the intramolecular torsional motion by the FGH method as developed by Marston *et al.* [16, 17]. Defining a column vector ϕ_n of the form:

$$\phi_n = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \\ 0 \end{bmatrix} - n \text{ - th row} \qquad (20)$$

we may write the *n*-th column of the Hamiltonian matrix implementing a forward and reverse FFT in the following way [40]:

$$H_{in} = \left[\left(F^{-1}TF + V\right)\phi_n\right]_i \qquad (21)$$

The FGH calculations were carried out by the FGH1 code [17].

3. RESULTS AND DISCUSSION

In the present study we are primarily interested in the O–H frequency shifts upon solvation of the hydroxide anion. Since all X-H vibrations are known to be large-amplitude motions, and therefore, inherently considerably anharmonic, to compute the corresponding frequencies with a sufficient accuracy it is necessary to go beyond the widely used harmonic approximation in quantum chemistry. Harmonic vibrational frequencies are easily and straightforwardly obtained by the available quantum chemistry codes by diagonalization of the Hessian matrices, a procedure which has become almost a routine, it has been shown in the literature that theoretically calculated *harmonic* X-H vibrational frequency shifts may in some cases even be in fortuitous excellent agreement with the experimental data, due to cancellation of errors [1–4]. As mentioned before, anharmonic contributions to the overall observed vibrational frequency shifts, on the other hand, may be as high as 30 – 40 %. In cases in which the coupling of the X-H motion with the other inter- and intramolecular motions is expected to be small, a simple and convenient approach is to solve the one-dimensional Schrödinger equation using a computationally feasible approach. However, there are numerous algorithms for solution of the radial Schrödinger equation, and it is of certain interest to compare their performances in the sense of both computational feasibility and mutual quantitative agreement. As described before, to obtain the 1D vibrational potential energy function ($V = f(r_{OH})$) for an OH oscillator in a particular aqueous environment, a series of 20 pointwise HF, DFT or MP2 energy calculations were performed for each O–H oscillator, varying the O–H distances from 0.850 to 1.325 Å with a step of 0.025 Å. The nuclear displacements corresponding to the O–H stretching vibration were generated keeping the center-of-mass of the vibrating hydroxide ion fixed. The first of the described algorithms for solution of the vibrational Schrödinger equation allows rather quick computation of vibrational energy levels (and their differences, corresponding to the anharmonic vibrational frequencies). It is based on efficient sampling of the 1D vibrational potential, subsequent transformation to the SPF coordinates, and usage of only a small number of the harmonic oscillator basis functions for the diagonalization. In our previous work, this algorithm has been efficiently used for various purposes [1–3 and references therein]. However, this algorithm has not been used so widely in the literature, and thus when one wants to perform numerous computations of the vibrational energy levels (as e.g. in the present case for 100 OH oscillators) it would be highly desirable to compare its performances with those of another algorithms. The Numerov algorithm, described in the previous section, has been implemented in the publicly available LEVEL [18] code written by Le Roy and collaborators. This code has been widely used for solution of the radial Schrödinger equation [33, 34 and references therein]. The Fourier grid Hamiltonian method [16, 17], on the other hand, has been claimed to be the simplest method for solution of both time–independent and time-dependent Schrödinger equation. It has become more and more popular in recent years. Therefore, it is of certain importance to test and compare its performances.

In Table 2, the anharmonic frequencies corresponding to the fundamental $|0\rangle \rightarrow |1\rangle$ vibrational transition for the free OH$^-$ ion computed on the basis of the same 1D vibrational potential (computed as described before) are

given, together with the experimental gas-phase data [35]. In Tables 3 and 4 the average frequencies and frequency shifts computed at the three different theoretical levels with three different algorithms are compared to the experimental values [20]. Experimental data have been obtained by Raman spectroscopy, so the average frequency shifts are directly comparable to the experiment (*i.e.* no additional scaling due to the IR intensity distribution is required). Since the Numerov algorithm seems to be the most widely used general-purpose approach to solution of the vibrational Schrödinger equation, we regard it in this context as a sort of benchmark towards which the performances of other methods will be compared. Therefore, in Figures 3 and 4 we have plotted the anharmonic frequency shifts of the aqueous hydroxide ion with respect to the gas-phase value computed by diagonalization

and FGH approach *vs.* the shifts obtained by the LEVEL code. The straight lines in Figures 3 and 4 correspond to $y = x$ lines. As can be seen from Figures 3 and 4, the diagonalization method in SPF-type coordinates works remarkably well for frequency shifts up to about 300 cm⁻¹. The only remarkable discrepancy between this method and the Numerov algorithm appears for a very large upshift of about 600 cm⁻¹, *i.e.* in the case of a very steep O–H stretching potential. For most of the cases relevant to the present study, however, the performance of this relatively simple and efficient method is therefore excellent. Though the general performance of the FGH method may be also characterized as quite good, as can be seen most illustratively from Figure 4, the disagreement between this and the Numerov approach is more nonuniform and discrepancies are seen for even moderate frequency shifts.

T a b l e 2

Calculated anharmonic frequencies for the isolated hydroxide ion with the three different algorithms for solution of the vibrational Schrödinger equation at the three different levels of theory (see text for details). Experimental fundamental frequency is listed as well

$OH^-(g)$	HF	B3LYP	MP2	Exp. [a]
		v / cm⁻¹		
Diagonalization	3868	3552	3652	
Numerov	3913	3566	3667	3556
FGH	4112	3702	3792	

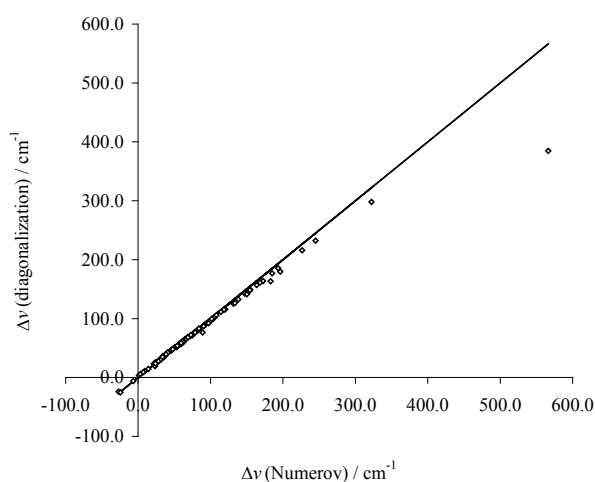[a] The gas-phase value is taken from Ref. [35].

Fig. 3. A plot of the anharmonic frequency shifts computed by the diagonalization technique vs. the corresponding values computed by Numerov algorithm
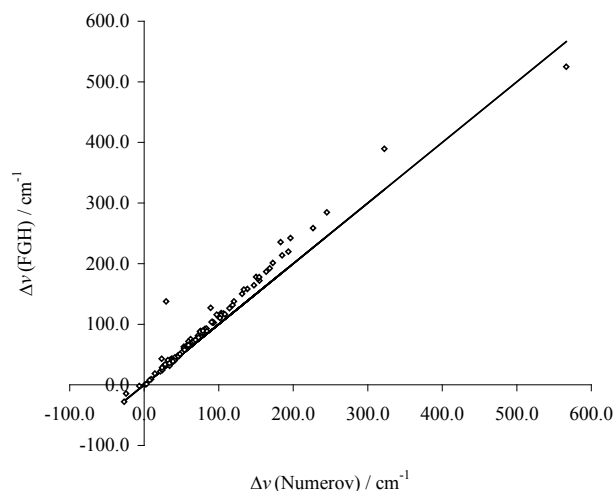

Fig. 4. A plot of the anharmonic frequency shifts computed by the FGH technique vs. the corresponding values computed by Numerov algorithm

Considering the overall performances of the theoretical levels implemented (which were discussed in details in our previous publications), as can be seen from Table 4, the computed average MP2 frequency shifts in the present study were in excellent agreement with the shift computed from the experimental data which have been obtained by Raman spectroscopy.

Table 5 summarized the standard deviations computed for the frequency distributions using the three methodologies at three levels of theory. It can be seen that the diagonalization technique leads to the narrowest frequency distribution, while the spread in the frequency values is largest when the FGH method is used. On the other hand, comparison between theoretical methods, leads to a conclusion that the spread of the frequency distributions increases in the order B3LYP < MP2 < HF. The relation of these parameters to the experimentally measurable half-widths of the Raman spectral bands is discussed elsewhere [19].

T a b l e 3

Calculated average anharmonic frequencies (in cm^{-1}) for the 100 OH$^-$ (aq) oscillators with the three different algorithms, at three levels of theory, together with the experimentally determined frequency of the Raman band

OH$^-$(aq)	HF	B3LYP	MP2	Exp. [a]
		$<v>$ / cm^{-1}		
Diagonalization	4063	3682	3731	
Numerov	4130	3701	3749	3633
FGH	4386	3846	3886	

T a b l e 4

Calculated average anharmonic frequency shifts (in cm^{-1}) with respect to the isolated ion for the 100 OH$^-$ (aq) oscillators with the three different algorithms, at three levels of theory, together with the experimental data (see text for details)

OH$^-$(aq)	HF	B3LYP	MP2	Exp. [a]
		$<\Delta v>$ / cm^{-1}		
Diagonalization	195.0	129.4	78.5	
Numerov	217.8	135.0	82.7	77
FGH	273.3	144.0	94.2	

[a] The experimental data were taken from Ref. [20].

T a b l e 5

Calculated standard deviations of the frequency distributions (in cm^{-1}) for the 100 OH$^-$ (aq) oscillators with the three different algorithms, at three levels of theory

OH$^-$(aq)	HF	B3LYP	MP2
		σ / cm^{-1}	
Diagonalization	66	47	63
Numerov	85	51	77
FGH	110	59	82

[a] The experimental data were taken from Ref. [20].

4. CONCLUSIONS

For a series of 100 in-liquid OH oscillators in the case of aqueous hydroxide ion, which have been obtained from a Monte Carlo simulation, using the charge-embedded finite-cluster approach, we have computed the anharmonic O–H stretching frequencies and the corresponding frequency shifts using three methods for solution of the vibrational Schrödinger equation: i) method of diagonalization of the Hamiltonian matrix in SPF-type coordinates, ii) Numerov method, iii) Fourier grid Hamiltonian method. These calculations were carried out on the basis of one-dimensional OH stretching vibrational potentials computed at three levels of theory: B3LYP, HF and MP2/6-31++G(d,p). In the case of most oscillators, for frequency shifts up to about 300 cm^{-1}, the simple diagonalization technique performs remarkably well, the computed shifts with this method being in excellent agreement with those obtained with the Numerov algorithm. Though being somewhat simpler, the Fourier grid Hamiltonian approach gives frequency shifts which are in larger discrepancy with those computed by Numerov algorithm, even for moderate frequency shifts. The discrepan cies in the last case are also significantly nonuniform.

REFERENCES

[1]   V. Kocevski, Lj. Pejov, On the assessment of some new meta-hybrid and generalized gradient approximation functionals for calculations of anharmonic vibrational frequency shifts in hydrogen-bonded dimers. *J. Phys. Chem. A*, **114**, 4354–4363 (2010).

[2]   Lj. Pejov, K. Hermansson, On the nature of blue-shifting hydrogen bonds: *ab initio* and density functional studies of several fluoroform complexes. *J. Chem. Phys.*, **119**, 313–324 (2003).

[3]   Lj. Pejov, A gradient-corrected density functional and MP2 study of phenol-ammonia and phenol-ammonia(+) hydrogen bonded complexes. *Chem. Phys.*, **285**, 177–193 (2002).

[4]   B. Silvi, R. Wieczorek, Z. Latajka, M. E. Alikhani, A. Dkhissi, Y. Bouteiller, Critical analysis of the calculated frequency shifts of hydrogen-bonded complexes, *J. Chem. Phys.*, **111**, 6671–6678 (1999).

[5]   C. E. Blom, C. Altona, Application of self-consistent-field ab-initio calculations to organic-molecules. 2. Scale factor method for calculation of vibrational frequencies from ab-initio force constants - ethane, propane and cyclopropane, *Mol. Phys.*, **31**, 1377–1391 (1976).

[6]   P. Pulay, G. Fogarasi, G. Pongor, J. E. Boggs, A. Vargha, Combination of theoretical ab initio and experimental information to obtain reliable harmonic force-constants - scaled quantum-mechanical (SQM) force-fields for glyoxal, acrolein, butadiene, formaldehyde, and ethylene, *J. Am. Chem. Soc.*, **105**, 7037–7047 (1983).

[7]   G. Fogarasi, Recent developments in the method of SQM force fields with application to 1-methyladenine, *Spectrochim. Acta A*, **53**, 1211–1224 (1997).

[8]   G. Szasz, A. Kovacs, Investigation of the density-functional theory-derived scaled quantum mechanical method for cage-like systems: the vibrational analysis of adamantine, *Mol. Phys.*, **96**, 161–167 (1996).

[9]   A. Kovacs, V. Izvekov, G. Keresztury, G. Pongor, Vibrational analysis of 2-nitrophenol. A joint FT-IR, FT-Raman and scaled quantum mechanical study, *Chem. Phys.*, **238**, 231–243 (1998).

[10] R. B. Gerber, J. O. Jung, in *Computational Molecular Spectroscopy*, P. Jensen, P. R. Bunker (eds.), Wiley and Sons: Chichester, 2000.

[11] G. M. Chaban, J. O. Jung, R. B. Gerber, Ab initio calculation of anharmonic vibrational states of polyatomic systems: Electronic structure combined with vibrational self-consistent field, *J. Chem. Phys.*, **111**, 1823–1829 (1999).

[12] V. Barone, Anharmonic vibrational properties by a fully automated second-order perturbative approach, *J. Chem. Phys.*, **122**, 14108 (2005).

[13] F. Gangemi, R. Gangemi, G. Longhi, S. Abbate, Calculations of overtone NIR and NIR-VCD spectra in the local mode approximation: camphor and camphorquinone, *Vib. Spectrosc.*, **50**, 257–267 (2009).

[14] F. Gangemi, R. Gangemi, G. Longhi, S. Abbate, Experimental and ab initio calculated VCD spectra of the first OH-stretching overtone of (1*R*)-(-) and (1*S*)-(+)-*endo*-borneol, *Phys. Chem. Chem. Phys.*, **11**, 2683–2689 (2009).

[15] G. Simons, R. G. Parr, J. M. Finlan, New alternative to dunham potential for diatomic-molecules, *J. Chem. Phys.*, **59**, 3229–3234 (1973).

[16] C. C. Marston, G. G. Balint-Kurti, The Fourier grid Hamiltonian method for bound state eigenvalues and eigenfunctions, *J. Chem. Phys.*, **91**, 3571–3576 (1989).

[17] R. D. Johnson, FGHD1 – program for one-dimensional solution of the Schrödinger equation, Version 1.01.

[18] R. J. Le Roy, LEVEL 8.0: A Computer Program for Solving the Radial Schröodinger Equation for Bound and Quasibound Levels, University of Waterloo Chemical Physics Research Report CP-663 (2007); see http://leroy.uwaterloo.ca/programs/.

[19] J. Petreska, Lj. Pejov, K. Coutinho, K. Hermansson, submitted for publication.

[20] T. Corridoni, A. Sodo, F. Bruni, M. A. Ricci, M. Nardone, Probing water dynamics with OH⁻, *Chem. Phys.*, **336**, 183–187 (2007).

[21] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, J. Hermans, Intermolecular Forces, edited by B. Pullmam (Reidel, Dordrecht, 1981), p.331.

[22] I. S. Ufimtsev, A. G. Kalinichev, T. J. Martinez, and R. James Kirkpatrick, Chem. Phys. Lett. **442**, 128 (2007).

[23] K. Coutinho, M. J. de Oliveira, S. Canuto, Sampling configurations in Monte Carlo simulations for quantum mechanical studies of solvent effects, *Int. J. Quantum Chem.*, **66**, 249–253 (1998).

[24] K. Coutinho, S. Canuto, Solvent effects in emission spectroscopy: A Monte Carlo quantum mechanics study of the n <-pi(*) shift of formaldehyde in water, *J. Chem. Phys.*, **113**, 9132–9139 (2000).

[25] S. Canuto, K. Coutinho, Solvent effects from a sequential Monte Carlo-Quantum mechanical approach, *Adv. Quantum Chem.*, **28**, 89–105 (1997).

[26] K. Coutinho, S. Canuto, M. C. Zerner, A Monte Carlo-quantum mechanics study of the solvatochromic shifts of the lowest transition of benzene, *J. Chem. Phys.*, **112**, 9874–9880 (2000).

[27] C. Chatfield, *The Analysis of Time Series*. An Introduction, Chapman and Hall, London (1984).

[28] R. Krätschmer, K. Binder, D.Stauffer, Linear and nonlinear relaxation and cluster dynamics near critical points, *J. Stat. Phys.* **15**, 267–297 (1976).

[29] A. D. Becke, Density-functional thermochemistry. 3. The role of exact exchange, *J. Chem. Phys.*, **98**, 5648–5652 (1993).

[30] C. Lee, W. Yang, R. G. Parr, Development of the colle-salvetti correlation-energy formula into a functional of the electron-density, *Phys. Rev. B*, **37**, 785–789 (1988).

[31] K. Coutinho, S. Canuto, DICE: *A Monte Carlo program for molecular liquid simulation*, University of São Paulo, Brazil, 1997.

[32] M. J. Frisch et al, Gaussian 03, Revision C.02, Gaussian, Inc. Wallingford CT, 2004.

[33] A. Shayesteh, R. D. E. Henderson, R. J. Le Roy, P. F. Bernath, Ground state potential energy curve and dissociation energy of MgH, *J. Phys. Chem. A*, **111**, 12495–12505 (2007).

[34] H. Li, R. J. Le Roy, Spectroscopic properties of MgH_2, MgD_2, and MgHD calculated from a new ab initio potential energy surface, *J. Phys. Chem. A*, **111**, 6248–6255 (2007).

[35] J. C. Owrutsky, N. H. Rosenbaum, L. M. Tack, R. J. Saykally, The vibration-rotation spectrum of the hydroxide anion (OH⁻), *J. Chem. Phys.*, **83**, 5338–5339 (1985).