

## Letter

# Vibrational and correlation effects on properties of water

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**Abstract.** Large basis set, ab initio potential energy and property surfaces of water have been used with quantum Monte Carlo vibrational analysis in the evaluation of the molecule's rotational constants, zero-point energy, and dipole moment. While there are clearly differences in vibrational state parameters due to including correlation effects, the vibrational averaging effect on rotational constants is very nearly additive with the correlation effect. This has implications for evaluation and estimation of properties of molecules in specific vibrational states.

**Key words:** Water – Vibration – Rotational constants – Potential surface – Property surfaces

## 1 Introduction

Calculation of properties of molecules can be carried to various levels of sophistication. One might start by finding properties at the equilibrium structure using a small-to-moderate size basis and self-consistent field (SCF) wavefunctions in an ab initio calculation. From there, basis set saturation can be approached in any number of steps and electron correlation effects can be incorporated until reaching the highest level determination for a given structure. Of course, the directly measured properties of molecules reflect vibrational motion and therefore differ from the properties associated with an equilibrium structure. In this report, we consider one specific test system with very extensive vibrational analysis and find that certain effects of vibration tend to be additive, or mostly independent, of the effects of electron correlation. This offers guidance for property determination in the absence of a complete correlated potential energy surface.

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## 2 Computational approach

The basis set for the ab initio calculations on water consisted of the uncontracted primitives of an aug-cc-pVTZ set [1] plus a set of diffuse p functions on the hydrogens (exponent = 0.0268) and a set of diffuse d functions on the oxygen (exponent = 0.071) for a total of 119 basis functions. Electron correlation was included at the coupled cluster (CC) level through single and double substitutions (CCSD) with an approximation or near cancellation of certain small matrix elements, which we have designated ACCDS [2] and which Jankowski and Paldus designated ACP-D45 [3]. There have been formal and applied examinations of this approximation [4, 5], and in our experience it has proved quite faithful to CCSD [4]. A semiregular grid of 126 potential energy surface points [6] was generated at this level and at the SCF level. The grid covers O–H bond length variations of 0.2 Å from the equilibrium and H–O–H bond angle variations of 20°. Dipole and quadrupole moment surfaces at both levels were obtained by expectation evaluation of the moment components. Dipole and quadrupole polarizability surfaces [6] were obtained analytically at the SCF level using the derivative Hartree–Fock method [7].

The grid-point energies were least-squares fitted to a set of functions of the form  $r^k s^l t^m$ , where  $r$  and  $s$  are the two O–H distances and  $t$  is the H–H distance. We used  $t$  in place of the H–O–H angle  $\theta$  for convenience in the numerous evaluations of the potential carried out in the vibrational analysis; however, we note that the functions in the least-squares fit included all those and more necessary to make up or represent  $\cos^2 \theta$ ,  $t^{-1} \cos \theta$ ,  $t^{-2} \cos \theta$ , and  $t^{-1} \cos^2 \theta$ . For all terms except a constant term and those corresponding to  $\cos^2 \theta$ ,  $k$ ,  $l$ , and  $m$  were selected so that  $k + l + m < 0$ , thereby insuring that the contribution of the terms goes to the proper asymptotic limit, zero, at infinite separation. This was considered useful so that vibrational excursions in the dynamics simulation would be sampling a surface that has a valid long-range form, as opposed to an expansion with  $k + l + m > 0$  that becomes infinite at long range. We found this form of the potential workable in

the sense that with 30 unique terms (30 fitting parameters) the root-mean-square (rms) deviation of the fit from the 126 ab initio energies was only about  $1 \text{ cm}^{-1}$  ( $0.000006 \text{ a.u.}$ ) while the range of ab initio energies spanned more than  $0.1 \text{ a.u.}$  A complete specification of the SCF and correlated surface fits is given in Table 1.

Equilibrium structures were located for both surfaces by two techniques which yielded structures that were identical to better than  $0.0001 \text{ \AA}$ . The first technique was searching the functional fits of the surfaces to locate the points at which the first derivatives of the energy with respect to displacement in  $r$ ,  $s$ , and  $t$  were zero, to within a small tolerance. The second technique was simply identifying the minimum energy structure out of the many structures sampled in the vibrational analysis. At the correlated level used, our equilibrium structure, given in Table 2, agrees very well with those obtained by the very high level calculations previously done on water and those obtained experimentally (e.g., see Ref. [8]).

The dipole moment information from the ab initio calculations was used for a computational test of averaging effects. The magnitude of the dipole moment vector was computed from the components at each of 60 of the surface points, and the set of magnitudes was fitted to a sum of 24 selected functions of the form  $r^k s^l t^m$  where  $-3 \leq k + l + m \leq 1$ . The rms deviation of this fit was  $0.000016 \text{ a.u.}$

Ground vibrational state simulations were performed by the diffusion quantum Monte Carlo (DQMC) [11] method. DQMC exploits an equivalence of the differ-

ential equation for diffusion and the time-dependent differential Schrödinger equation on replacing the time variable,  $t$ , in the Schrödinger equation by an imaginary time variable,  $t = it$ . MC techniques that would yield a numerical solution of the diffusion equation are instead used to simulate the solution of the modified Schrödinger equation via pseudo particles, or psips [11], that propagate in randomized, discrete steps in imaginary time. After many time steps, the distribution of psips reflects the ground state because of the exponential decay in imaginary time of higher-energy states that may have been mixed initially. An exact solution of the Schrödinger equation corresponds to the DQMC limiting case of an infinite number of pseudo particles, the length of the  $t$  time steps approaching zero, and the number of time steps approaching infinity. The selected time step was short,  $0.002 \text{ a.u. (time)}$  [ $1.0 \text{ a.u. (time)}$  or  $1.0 h/(2\pi E_h) = 2.41888 \times 10^{-17} \text{ s}$ ], and in each calculation, 150,000 time steps were carried out. A sizable number of psips, 8000, was used. This diffusion simulation yields weights for each psip that reflect but are not strictly the same as the quantum probability densities [12] at the corresponding positions of the psips. A true probability density may be obtained by descendant weighting, or weighting each psip at time  $t_0$  by the number (weights) of its descendants in further propagation [13, 14], and from this properties may be evaluated as expectation values.

Obtaining rotational constants via descendant weighting called for the construction and diagonalization of the inertia tensor at each point sampled by the psips in the simulations. The eigenvalues from the diagonalization had to be sorted into  $I_A$ ,  $I_B$  and  $I_C$ , and this was done by an axis-following scheme. At the first ( $t = 0.0$ ) structure in each psip's propagation, the sorting of the principal moments of inertia was conventional, by size ( $I_A < I_B < I_C$ ). On the subsequent propagation step, these axes were followed in the sense that the new principal axes were associated with the old ones on the basis of the dot products of their unit vectors. That is, the new axis closest in direction to the last A-axis became the A-axis, and so on. The axis-following was continued step-to-step. If the sorting were done simply by size, a few very wide amplitude excursions may suddenly interchange axis identities, and the resulting difference between the biggest and smallest on-average rotational constants may be artificially larger. The value of  $\langle A + B + C \rangle$  is necessarily invariant to the choice of sorting.

A correctable difficulty with the inverse power fit of the potential is that it is not suited for very close-in regions where a sum of attractive and repulsive inverse power terms can yield a sharply changing, unphysical potential. We confirmed that our functional fit was adequate to insure that this behavior was in regions where the true potential should be high enough to preclude essentially all sampling by the psips. To correct the difficulty, cut-offs in  $r$ ,  $s$ , and  $t$  were set ( $0.7 \text{ \AA}$  for  $r$  and  $s$  and  $0.9 \text{ \AA}$  for  $t$ ), and then the potential for structures with values less than these cut-offs was fixed (i.e., set high) to exclude sampling of the close-in regions. A series of DQMC calculations was used to determine and check the cut-offs by showing

**Table 1.** Potential energy surface fits

Functions: exponents of $r$ , $s$ , and $t$						Coefficients (a.u.)	
$k$	$l$	$m$	$k$	$l$	$m$	Correlated	SCF
0	0	0				-75.2816601	-74.6275842
-1	1	-1	1	-1	-1	-1.081495	-1.014935
-1	-1	1				-0.658619	-1.187522
-1	1	-2	1	-1	-2	2.300160	1.925646
-1	-1	0				-4.142417	-0.164961
-2	2	-1	2	-2	-1	-0.0679589	-0.0522307
-2	0	1	0	-2	1	0.330938	0.522477
-2	-2	3				-0.0113755	-0.0064732
-2	2	0	2	-2	0	0.0408697	0.0396197
-2	0	2	0	-2	2	-0.0931694	-0.115063
-2	-2	4				0.0316749	0.0333057
-1	0	-1	0	-1	-1	-1.031447	-7.032351
-1	0	-2	0	-1	-2	-9.171014	13.598985
-2	0	-1	0	-2	-1	3.199477	2.666237
-1	-1	-1				15.634561	4.679763
-2	0	-2	0	-2	-2	-12.729256	-14.762174
-1	-1	-2				-12.497603	-3.115927
-1	0	-3	0	-1	-3	15.133950	-13.480418
-3	0	-1	0	-3	-1	3.619934	6.367660
-2	0	-3	0	-2	-3	7.773552	19.021008
-3	0	-2	0	-3	-2	-2.410703	-7.232063
-6	0	0	0	-6	0	3.040318	1.037828
-8	0	0	0	-8	0	-5.691878	-2.400912
-10	0	0	0	-10	0	3.301273	1.433596
0	0	-8				-154.770246	16.191474
0	0	-10				534.938783	-58.497364
0	0	-12				-629.936963	57.564453

**Table 2.** Results of calculations

	SCF	ACCDS
Equilibrium:		
$R_{\text{OH-eq}}$ (Å)	0.9408	0.9566 <sup>a</sup>
$R_{\text{HH-eq}}$ (Å)	1.5060	1.5136
$q_{\text{eq}}$ (deg)	106.32	104.58 <sup>a</sup>
$m_{\text{eq}}$ (D)	1.8394 <sup>b</sup>	1.8746
$A_{\text{eq}}$ (GHz)	887.3	824.4
$B_{\text{eq}}$ (GHz)	442.2	437.7
$C_{\text{eq}}$ (GHz)	295.1	285.9
Ground vibrational state:		
$\langle A \rangle$ (GHz)	947.4	870.6 <sup>c</sup>
$\langle B \rangle$ (GHz)	425.2	420.7 <sup>c</sup>
$\langle C \rangle$ (GHz)	284.1	274.9 <sup>c</sup>
$\langle m \rangle$ (D)	1.8435	1.8871
$\langle A \rangle - A_{\text{eq}}$ (GHz)	60.1	46.2
$\langle B \rangle - B_{\text{eq}}$ (GHz)	-17.0	-17.0
$\langle C \rangle - C_{\text{eq}}$ (GHz)	-11.0	-11.0
Zero-point energy (cm <sup>-1</sup> )	4969.3	4710.1

<sup>a</sup> Equilibrium structural values determined from a 1987 CCSDT-1 calculation [9] are 0.9591 Å and 104.45°. Values from an earlier CI-SDQ calculation [10] are 0.9573 Å and 104.58°. Equilibrium values based on experimental data [9] are 0.9581 Å and 104.48°

<sup>b</sup> The SCF dipole is that obtained from the ACCDS calculation at the SCF equilibrium geometry

<sup>c</sup> Experimental rotational constants collected by Herzberg [15] are  $A = 27.877$ ,  $B = 14.512$ , and  $C = 9.258$  cm<sup>-1</sup>, which in MHz are 835.73, 435.06, and 278.36, respectively

that small changes in the cut-offs had no effect on calculated values; that is, they were acting in regions where the wavefunction would otherwise be negligible.

### 3 Results and discussion

The equilibrium and vibrational ground-state values calculated for water with the SCF and correlated potential surfaces are given in Table 2. The zero-point energy with the ACCDS surface is 4710 cm<sup>-1</sup>, which is somewhat greater than an experimentally derived value of 4634 cm<sup>-1</sup> [8]. The rotational constants (Table 2) agree well with spectroscopic values [15]. Using  $\langle A + B + C \rangle$  for comparison because it is invariant to sorting, the calculation overshoots the spectroscopic value by 1.1%. As a calculational experiment to assess contributions to the error, a DQMC evaluation was performed wherein the potential function was altered in a slight way. The coefficients of attractive terms that depended only on  $r$  or only on  $s$  and repulsive terms that depended only on  $t$  (i.e., no mixed terms) were diminished by 1%, whereas the coefficients of pure  $r$  and pure  $s$  repulsive terms and pure  $t$  attractive terms were increased by 1%. With that small change in the surface,  $\langle A + B + C \rangle$  was found to be in error by -0.6%; with this small parameter change, the experimental value has been bracketed. For the constant with the greatest difference,  $\langle A \rangle$ , the error is reduced from 4.2% to 1.6%. We therefore judge the ACCDS potential surface to have very small lingering errors, and generally to be of high quality for the regions of the surface sampled by ground-state vibrational excursions.

There is a 5.2% diminishment in the zero-point energy from using the correlated surface versus the SCF surface. Were this obtained with a harmonic picture, it would correspond to a 10.2% diminishment in the sizes of the force constant, a reduction typical for correlation effects (i.e., equivalent to scaling the SCF force constants by 90%). The correlated surface is softer, as is well understood, but the coupling of this difference in the surface to the average vibrational excursion is demonstrated to be small by our calculations. This is shown by the mostly equal SCF and correlated vibrational contributions to the  $A$ ,  $B$  and  $C$  rotational constants (Table 2). Consistent with the view [16, 17] that electron correlation tends to be more significant in its effect on harmonic force constants than on anharmonic constants, the results indicate that net vibrational averaging effects of like molecules could be obtained to fairly good accuracy using an SCF surface for the dynamical contribution.

The rms amplitudes of vibration for the ground state of water are small [8], and given the moderate changes in the dipole moment that we find along its surface, vibrational averaging effects should be small. The averaging of the magnitude of the dipole moment yields small differences from equilibrium values (Table 2). At the ACCDS level of treatment, the vibrational averaging effects is 0.012 D. For comparison, the averaging effect using the SCF potential surface, but the same dipole surface, is 0.004 D. The corrections differ by a factor of 3, but of course, both are simply very small corrections. The correlation effect on the dipole moment at the ACCDS equilibrium structure is more sizable, a diminishment of 0.105 D. Experimental values for the dipole moment of water in its ground vibrational state are  $1.8546 \pm 0.0006$  D [18] and  $1.8546 \pm 0.0004$  D [19]. The latter of these studies indicates that vibrational averaging effects are very small, given that a dipole moment only 0.0001 D less was obtained for D<sub>2</sub>O [19]. The vibrational averaging of the dipole moment performed here does not strictly correspond to the measurement approach and thus can yield differences [20]; however, the small effect of isotopic substitution [19] is consistent with an equilibrium dipole moment value of H<sub>2</sub>O being only a few ten thousandths of a Debye less than 1.8546 D or within about 0.02 D of the ACCDS equilibrium value. The difference between the ACCDS dipole moment at the SCF equilibrium and at the ACCDS equilibrium (Table 2) is twice the size of this lingering error; more important is that it is much bigger than the effect of vibrational averaging.

The calculations we have carried out provide high-quality potential energy and property surfaces for water [6], the latter based on well-correlated ab initio results for the dipole and quadrupole moments. The nonapproximate analysis of the vibrational ground state afforded by QMC techniques provides a true assessment of the quality of the potential surface through the zero-point energy and rotational constants, and it shows a near additivity of correlation effects and vibrational averaging effects for the rotational constants. This is in line with the existing recognition of how electron correlation plays a role in the harmonic and anharmonic force constants of small molecules.

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## References

1. (a) Kendall RA, Dunning TH Jr, Harrison RJ (1992) *J Chem Phys* 96: 6796; (b) Woon DE, Dunning TH, Jr (1993) *J Chem Phys* 98: 1358
2. Chiles RA, Dykstra CE (1981) *Chem Phys Lett* 80: 69
3. Jankowski K, Paldus J (1980) *Int J Quantum Chem* 18: 1243
4. Dykstra CE, Liu S-Y, Daskalakis MF, Lucia JP, Takahashi M (1987) *Chem Phys Lett* 137: 266
5. Paldus J, Cizek J, Takahashi M (1984) *Phys Rev A* 30: 2193
6. The potential energy and property grid point values are available via anonymous ftp. The URL is [ftp://chem.iupui.edu/pub/dykstra/H<sub>2</sub>Osurface](ftp://chem.iupui.edu/pub/dykstra/H2Osurface)
7. Dykstra CE, Jasien PG (1984) *Chem Phys Lett* 109: 388
8. Ermler WC, Hsieh HC (1990) In: Dunning TH Jr (ed) *Advances in molecular electronic structure theory – vol 1*. JAI Press, Greenwich, Conn., pp 1–44
9. Bartlett RJ, Cole SJ, Purvis GD, Ermler WC, Hsieh HC, Shavitt I (1987) *J Chem Phys* 87: 6579
10. Rosenberg BJ, Ermler WC, Shavitt I (1976) *J Chem Phys* 65: 4072
11. Anderson JB (1975) *J Chem Phys* 63: 1499
12. Reynolds PJ (1990) *J Chem Phys* 92: 2118
13. Coker DF, Watts RO (1987) *J Phys Chem* 91: 2513
14. Kalos MH (1970) *Phys Rev A* 2: 250
15. Herzberg G (1966) *Molecular spectra and molecular structure III*. Van Nostrand Reinhold, New York
16. Pulay P, Meyer W, Boggs JE (1978) *J Chem Phys* 68: 5077
17. Pulay P, Lee J-G, Boggs JE (1983) *J Chem Phys* 79: 3382
18. Clough SA, Beers Y, Klein GP, Rothman LS (1973) *J Chem Phys* 59: 2254
19. Dyke TR, Muentner JS (1973) *J Chem Phys* 59: 3125
20. Hollenstein H, Marquardt RR, Quack M, Suhm MA (1994) *J Chem Phys* 101: 3588