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Ab initio SCF and CI studies on the ground state of the water molecule. II. Potential energy and property surfaces

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Self-consistent field and configuration interaction calculations for the energy and one-electron properties of the ground state of the water molecule were carried out with a $(5s4p2d/3s1p)$ 39-function STO basis set. The CI treatment included all single and double excitation configurations (SD) relative to the SCF configuration, and a simple formula due to Davidson was used to estimate the energy contribution of quadruple excitations and thus produce a set of corrected (SDQ) energies. The calculations were carried out for 36 molecular geometries (22 symmetric and 14 asymmetric) in the neighborhood of the equilibrium geometry. Least-squares analysis was used to determine theoretical equilibrium geometries and to derive quartic and cubic expansions for the energy and one-electron properties in terms of internal displacement coordinates. Considerable improvement was found in the SD and particularly in the SDQ results relative to SCF, with the SDQ equilibrium geometry being in excellent agreement with experiment and the harmonic force constants also showing much better agreement than other *ab initio* results. Results for higher-order force constants are difficult to assess because of the large uncertainties in both theoretical and experimental results. The dipole moment function obtained in these calculations should be quite useful in the assessment and analysis of infrared intensity data and isotope effects.

I. INTRODUCTION

This paper is the second in a series concerned with the use of self-consistent field (SCF) and configuration interaction (CI) calculations for describing and analyzing the electronic and vibrational structure of the water molecule in its ground electronic state. Paper I of this series[1] presented a comparison of several contracted Gaussian-type (CGTO) and Slater-type (STO) basis sets in terms of computed SCF and CI energies and one-electron properties of the molecule at one geometry very near the experimental equilibrium geometry. The best results were obtained with a basis set of 39 Slater-type orbitals, which gave an SCF energy within 0.003 hartree of the estimated Hartree–Fock limit and a CI energy which accounts for 75% of the estimated correlation energy. This basis set (denoted 39-STO) has been used in the present study to calculate potential energy and property surfaces for the ground state in the neighborhood of the equilibrium geometry at both the SCF and CI levels. Quartic and cubic polynomials in terms of displacement coordinates, derived by least-squares fitting to computed property values, have been used to represent the results.

A forthcoming paper will present vibrational analyses of the SCF and CI potential energy and property surfaces based on a perturbation theory formalism that includes the effect of anharmonicity.[2-4]

II. CALCULATIONS

Electronic wavefunctions and properties were calculated at 36 points on the potential surface. Of these, 35 points were generated by the formulas

$$\begin{aligned} R_1 &= R_0 + k\delta R, \\ R_2 &= R_0 + l\delta R, \\ \theta &= \theta_0 + m\delta\theta, \end{aligned} \tag{1}$$

where R_1 and R_2 are the two OH bond lengths, θ is the bond angle, $R_0 = 1.811096$ bohr (0.958390 Å), $\theta_0 = 104.44992°$, $\delta R = 0.03$ bohr (0.015875 Å), $\delta\theta = 3°$, and $k, l, m = 0, \pm 1, \pm 2$. The central point $(k = l = m = 0)$ is the geometry used in Paper I and by several other authors, while the step sizes δR and $\delta\theta$ are the same as those used in earlier studies of the H_2O potential surface,[2,3] and correspond to one third to one quarter of the root-mean-square zero-point vibrational amplitudes of the molecule.[5] Of the possible combinations of k, l, m in the indicated range $(-2 \leq k, l, m \leq 2)$, only the 21 symmetric geometries $(k = l)$ for which $|k| + |m| \leq 3$ and the 14 asymmetric points for which either $-1 \leq k, l, m \leq 1$ or $m = 0$ and $|k + l| \leq 2$ were used. (Because of symmetry it was sufficient to consider only those points for which $|k| \geq |l|$.) The 36th point was the interpolated minimum obtained from a quartic polynomial least-squares fit to the CI energies of the first 35 points. (No calculations were carried out at the interpolated minimum of the SCF potential surface.) The geometries and computed energies for all 36 points are given in Table I.

The calculations carried out at each of the 36 points used the 39-STO $(5s4p2d/3s1p)$ basis set,[1,6] and included SCF and CI wavefunctions, energies, and one-electron operator expectation values, as described for point 1 in Paper I. The CI calculations (designated by the symbol SD in the following) included all single and double excitations relative to the SCF configuration, using the canonical SCF occupied and virtual orbitals at each point. This involved 4120 configuration functions (CF's) for the symmetric (C_{2v}) geometries and

TABLE I. Potential energy surface of the water molecule from SCF and CI calculations, using a 39-STO ($5s4p2d/3s1p$) basis set.[a]

Point	Geometry[b]			Energy,[c] $-(E+76)$		
No.	k	l	m	SCF	SD[d]	SDQ[e]
1	0	0	0	0.06422577	0.33980247	0.3547926
2	0	0	1	0.06414298	0.33961279	0.3545784
3	0	0	−1	0.06381601	0.33952631	0.3545451
4	1	1	0	0.06256213	0.33899141	0.3542622
5	−1	−1	0	0.06489634	0.33963488	0.3543528
6	1	1	1	0.06239286	0.33870841	0.3539520
7	1	1	−1	0.06224509	0.33881457	0.3541158
8	−1	−1	1	0.06490378	0.33954215	0.3542371
9	−1	−1	−1	0.06439010	0.33925574	0.3540002
10	0	0	2	0.06359281	0.33898092	0.3539254
11	0	0	−2	0.06289035	0.33876205	0.3538139
12	2	2	0	0.06000885	0.33730488	0.3528640
13	−2	−2	0	0.06445973	0.33837471	0.3528284
14	1	0	0	0.06339247	0.33939464	0.3545249
15	−1	0	0	0.06455959	0.33971641	0.3545702
16	1	−1	0	0.06372334	0.33930400	0.3542976
17	1	−1	1	0.06363925	0.33911313	0.3540816
18	1	−1	−1	0.06331505	0.33902921	0.3540515
19	2	0	0	0.06211138	0.33854437	0.3538181
20	−2	0	0	0.06433688	0.33907962	0.3538004
21	2	−1	0	0.06243928	0.33844911	0.3535857
22	−2	1	0	0.06349768	0.33866267	0.3535228
23	2	−2	0	0.06221064	0.33780319	0.3528060
24	1	1	2	0.06176162	0.33798841	0.3532094
25	−1	−1	2	0.06443821	0.33900174	0.3536777
26	1	1	−2	0.06141913	0.33815623	0.3534925
27	−1	−1	−2	0.06336092	0.33838182	0.3531571
28	2	2	1	0.05975677	0.33693209	0.3524623
29	2	2	−1	0.05978076	0.33722366	0.3528158
30	−2	−2	1	0.06456100	0.33838238	0.3528151
31	−2	−2	−1	0.06385328	0.33788902	0.3523672
32	1	0	1	0.06326568	0.33915757	0.3542620
33	1	0	−1	0.06302990	0.33916892	0.3543287
34	−1	0	1	0.06452113	0.33957447	0.3544045
35	−1	0	−1	0.06410243	0.33938957	0.3542713
36	SD minimum[f]			0.06460895	0.33986661	0.3547548

[a] For basis set specification, see Footnote 6.

[b] The geometry is specified by $R_1=1.811096+0.03k$ bohr, $R_2=1.811096\pm 0.03l$ bohr, $\theta=104.44992+3m$ deg. See Eq. (1).

[c] In hartrees.

[d] CI with all single and double excitations.

[e] SD pluse estimate of quadruple excitations contribution, Eq. (2).

[f] $R_1=R_2=1.800398$ bohr, $\theta=104.93015°$.

7996 functions for the asymmetric (C_s) points. The basis set integrals (including property integrals), the SCF wavefunctions, and the transformations from basis set integrals to molecular orbital integrals were obtained by means of the POLYCAL programs,[7] while the CI calculations were carried out with programs developed at Battelle Memorial Institute and The Ohio State University, as described in Paper I. The SCF coefficients and CI density matrices obtained for all points are available in a technical report.[8]

Since the energy differences between neighboring points were generally of the order of several hundred microhartrees, and since the coefficients in a quartic polynomial fit to the surface depend on fourth differences, it was important to assure high precision, of the order of 1 μhartree or better, in the individual energies. This was accomplished by tightening the accuracy tolerances in the basis set integral calculations (to better than 0.1 μhartree) and in the convergence of the SCF and CI wavefunction calculations. The fact that the computed potential surfaces were smooth and substantially free from random errors was confirmed by the small magnitudes of the least-squares deviations in fitting the results to quartic polynomials, as described in the next section.

The need for high precision and freedom from random errors ruled out the use of configuration selection schemes to reduce the computational effort of the CI treatment, though one series of calculations was carried out to assess the effect of freezing the oxygen inner-shell electrons (such an SD-FC calculation[1] would reduce the number of CF's for the symmetric points from 4120 to 2587, and would reduce the computational effort in the CI stage by about a factor of 2). This question was examined using the 35-CGTO basis set[1] in all-electron (SD) and frozen-core (SD-FC) CI calculations for five symmetric geometries involving a single step in δR or $\delta\theta$ in each direction from point 1. The results are given in Table II and show a variation of 100 μhartree in the core contribution to the correlation energy over this range. While small for most purposes, such variation can significantly affect the quartic potential coefficients, and it was decided not to freeze the core electrons in the final CI calculations.

In addition to the SCF and SD calculations, another potential surface (but no property surfaces) was generated using Davidson's formula[9] for estimating the contribution of quadruple excitations to the CI energy of a closed-shell state. This formula gives the quadruple excitations contribution ΔE_Q in terms of the double excitations contribution ΔE_D and the coefficient C_0 of the

TABLE II. Examination of the frozen core approximation, using a 35-CGTO basis set.[a]

Point	$R_1=R_2$	θ	$-E$(SCF)	$-E$(SD)[b]	$-E$(SD-FC)[c]	E(SD-FC) − E(SD)
1	1.811096	104.45	76.050698	76.297392	76.278910	0.018482
2	1.761096	104.45	76.051015	76.296182	76.277650	0.018532
3	1.861096	104.45	76.047565	76.295798	76.277368	0.018430
4	1.811096	101.45	76.050268	76.297107	76.278631	0.018476
5	1.811096	107.45	76.050628	76.297201	76.278712	0.018489

[a] Bond lengths in bohrs, angles in degrees, and energies in hartrees. See Paper I for a description of the basis set.

[b] CI with all single and double excitations.

[c] Frozen-core CI, containing all single and double excitations in which the $1a$ MO is doubly occupied.

SCF configuration in the normalized all-doubles CI expansion,

$$\Delta E_Q = (1 - C_0^2)\Delta E_D. \qquad (2)$$

In the present application C_0 was taken from the SD wavefunction, and the corresponding correlation energy was used instead of ΔE_D, but the very small contribution of single excitation configurations is not expected to have a noticeable effect on the corrections. The energies obtained by adding ΔE_Q to the SD results are shown in the last column of Table I under the heading SDQ.

Davidson's formula was expected to produce an important correction to the SD potential surface, since the latter, being limited to single and double excitations from the SCF function, is likely to retain some of the SCF bias towards too short a bond length and incorrect asymptotic behavior. In fact, symmetric dissociation to three separate ground-state atoms cannot be correctly described by the SD wavefunction without the addition of at least one quadruply excited configuration (in which all four bonding electrons are excited into antibonding orbitals). This expectation was indeed justified by the subsequent results. Furthermore, the corrections produced by the formula varied smoothly over the surface, and while they resulted in some increase in the least-squares deviation in the fitting process, the root-mean-square fitting error was still only 0.07 μhartree (compared to 0.02 μhartree for the SCF and SD surfaces).

In assessing the quality of the calculations, we conclude that the 39-STO basis set is highly adequate for describing the SCF wavefunction of the molecule, as it leads to an SCF energy within 3 mhartree of the estimated Hartree–Fock limit,[1] but is not quite as satisfactory for the CI calculation. The present SD wavefunction accounts for 75% of the estimated correlation energy,[1] with the quadruple excitations estimated to account for an additional 4%. Another 1% is probably due to triple excitations, while the remaining 20% discrepancy must be attributed to incompleteness of the basis set. The 25% deficiency in the total correlation energy is also found at the dissociation limit (see the oxygen atom results in Paper I), with about 70% of the correlation energy, as well as 70% of the deficiency, being attributable to atomic contributions.

III. POTENTIAL ENERGY SURFACES

The computed SCF, SD, and SDQ energies were used to determine the corresponding equilibrium geometries by means of an iterative regression and steepest-descent procedure, as described by Ermler and Kern.[2] The resulting geometries are compared with other calculations[3,10,11] and with experimentally derived data[12-14] in Table III, and the systematic improvement from SCF through SD to SDQ is strikingly evident. It is also seen that the various determinations of the geometry from experimental data are not consistent with each other. The error limits quoted for these determinations reflect statistical uncertainties only and do not include possible systematic errors.

The molecular force field was determined for each potential surface by least-squares fitting of the computed energies to a quartic polynomial in displacement coordinates, relative to the equilibrium geometry on that surface. The minimum energies obtained for the three surfaces (at the respective geometries of Table III) were −76.064977 (SCF), −76.339867 (SD), and −76.354795 (SDQ) hartree. The force constants obtained are compared with several sets of experimentally derived force constants[15-18] in Table IV. They are given relative to the energy expression [equivalent to Eq. (4) of Ref. 17]

TABLE III. Computed and experimentally derived equilibrium geometry and some force constants of the water molecule.[a]

			Meyer[d]		This work			Experimental[e]		
	DPA[b]	KEK[c]	SCF	CEPA	SCF	SD	SDQ			
R_e	0.941	0.9413	0.9405	0.9550	0.9398	0.9527	0.9573	0.9572(3),[f]	0.95748(2),[g]	0.9587(1)[h]
θ_e	106.6	106.11	106.41	105.07	106.08	104.93	104.58	104.52(5),[f]	105.019(13),[g]	103.89(6)[h]
f_{RR}	9.83	9.866	9.684	8.642	9.7934	8.8757	8.539	8.454[f]		
$f_{\theta\theta}$	0.867	0.8815	0.850	0.789	0.8751	0.8135	0.801	0.761[f]		
$f_{RR'}$	−0.078	−0.069	−0.061	−0.096	−0.0662	−0.0829	−0.085	−0.101[f]		
$f_{R\theta}$	0.249	0.2575	0.248	0.254	0.2576	0.2708	0.274	0.228[f]		
f_{RRR}		−10.508	−10.27	−9.37	−10.36	−9.70	−9.50	−9.5[i]		
$f_{\theta\theta\theta}$		−0.1451	−0.144	−0.123	−0.1492	−0.1302	−0.126	−0.16[i]		
f_{RRRR}		15.3	13.6	14.3	13.6	14.0	15.3	14.7[i]		

[a] Bond length in angstroms, angle in degrees. For force constant units see Ref. a, Table IV.

[b] Dunning, Pitzer, and Aung, Ref. 10.

[c] Krohn, Ermler, and Kern, Ref. 3.

[d] Reference 11.

[e] The numbers in parentheses are the uncertainties in the last digit, as quoted by the authors.

[f] Benedict, Gailar, and Plyler, Ref. 12, from ir spectra of H_2O, HDO, and D_2O.

[g] Hoy and Bunker, Ref. 13, from ir spectra of H_2O and D_2O.

[h] Cook, De Lucia, and Helminger, Ref. 14, from microwave spectra of H_2O, D_2O, and T_2O.

[i] Hoy, Mills, and Strey, Ref. 15.

TABLE IV. Computed and experimentally derived force constants for the water molecule.[a]

Constant	SCF	SD	SDQ	SO[b]	KM(I)[c]	KM(II)[c]	HMS[d]	SS[e]
f_{RR}	9.7934(9)	8.8757(4)	8.539(5)	8.435(30)	8.454	8.454	8.454	8.454
$f_{\theta\theta}$	0.87515(6)	0.81351(8)	0.8011(9)	0.810(39)	0.761	0.761	0.761	0.760
$f_{RR'}$	−0.0662(7)	−0.0829(3)	−0.085(3)	−0.118(39)	−0.101	−0.101	−0.101	−0.101
$f_{R\theta}$	0.25764(6)	0.27076(7)	0.2741(8)	0.50(15)	0.228	0.228	0.228	0.219
f_{RRR}	−10.356(16)	−9.703(6)	−9.50(3)	−9.16(66)	−9.55(9)	−10.18(68)	−9.47(48)	−9.40
$f_{\theta\theta\theta}$	−0.1492(4)	−0.1302(2)	−0.1261(16)	−0.22(1)	−0.14(2)	−0.13(3)	−0.160(18)	−0.15
$f_{RRR'}$	0.001(13)	−0.021(5)	−0.004(26)	−0.17(54)	−0.32(24)	0.48(71)	0.12(72)	−0.49
$f_{RR\theta}$	− 0.033(14)	−0.039(5)	−0.016(29)	−0.59(57)	0.16(5)	0.22(9)	0.20(10)	0.29
$f_{RR'\theta}$	−0.535(25)	−0.510(10)	−0.55(5)	−0.62(36)	−0.66(2)	−0.46(6)	−0.40(28)	−0.53
$f_{R\theta\theta}$	−0.1584(9)	−0.1560(4)	−0.159(3)	−0.44(3)	0.15(30)	0.31(39)	−0.12(5)	−0.35
f_{RRRR}	13.58(17)	13.97(21)	15.3(22)	14.0(36)	15.4(5)	18.5(23)	14.7(24)	14.8
$f_{\theta\theta\theta\theta}$	−0.047(3)	−0.033(3)	−0.052(33)	−0.04(13)	0.0(3)	0.0(3)	−0.003(9)	−0.010
$f_{RRRR'}$	−0.09(12)	−0.03(15)	−1.2(17)	1.2(17)	0.8(9)	−2.8(30)	−0.8(27)	1.22
$f_{RRR'R'}$	0.13(16)	0.12(20)	−1.4(21)	2.0(23)	1.3(17)	0.1(60)	0.1(17)	1.58
$f_{RRR\theta}$	−0.21(32)	−0.26(39)	−2.3(42)	−6.6(65)	...[f]	...[f]	...[f]	−0.94
$f_{RRR'\theta}$	0.17(30	0.17(36)	2.3(39)	−6.5(106)	...[f]	...[f]	...[f]	0.22
$f_{RR\theta\theta}$	−0.080(53)	−0.075(63)	0.00(68)	−1.2(21)	−1.7(12)	−2.7(21)	−0.35(3)	0.33
$f_{RR'\theta\theta}$	0.29(10)	0.32(11)	0.2(12)	−0.9(31)	−0.5(26)	−1.5(42)	0.31(25)	1.40
$f_{R\theta\theta\theta}$	0.126(5)	0.109(6)	0.095(65)	−0.5(9)	...[f]	...[f]	...[f]	0.11

[a] See Eq. (3) for the definition of the constants. All constants are in 10^5 dyn/cm, with angles measured in radians. The units and the definitions of the constants (except for minor changes in notation) are the same as those in Ref. 2 (Table IV) and Ref. 17. Except in the HMS column, the numbers in parentheses are statistical uncertainties in the least significant digit quoted, given as three times the least-squares standard deviation, and do not reflect uncertainties in the data or in the formalism. (The HMS uncertainties are determined differently; see Ref. 15.)

[b] Smith and Overend, Ref. 16. The force constants listed are taken from column (iii) of their Table 2.

[c] Kuchitsu and Morino, Ref. 17. Columns KM(I) and KM(II) list the force constants derived from the H_2O and D_2O spectral data, respectively, of Ref. 12.

[d] Hoy, Mills, and Strey, Ref. 15.

[e] Speirs and Špirko, Ref. 18. Taken from solution 1 (V.H.F.F.) of their Table IV.

[f] These force constants were arbitrarily set to zero.

$$E=E_e+\tfrac{1}{2}f_{RR}(\Delta_1^2+\Delta_2^2)+\tfrac{1}{2}f_{\theta\theta}\Delta_3^2+f_{RR'}\Delta_1\Delta_2+f_{R\theta}(\Delta_1+\Delta_2)\Delta_3+(1/R_e)[f_{RRR}(\Delta_1^3+\Delta_2^3)+f_{\theta\theta\theta}\Delta_3^3+f_{RRR'}(\Delta_1+\Delta_2)\Delta_1\Delta_2$$
$$+f_{RR\theta}(\Delta_1^2+\Delta_2^2)\Delta_3+f_{RR'\theta}\Delta_1\Delta_2\Delta_3+f_{R\theta\theta}(\Delta_1+\Delta_2)\Delta_3^2]+(1/R_e^2)[f_{RRRR}(\Delta_1^4+\Delta_2^4)+f_{\theta\theta\theta\theta}\Delta_3^4+f_{RRRR'}(\Delta_1^2+\Delta_2^2)\Delta_1\Delta_2$$
$$+f_{RRR'R'}\Delta_1^2\Delta_2^2+f_{RRR\theta}(\Delta_1^3+\Delta_2^3)\Delta_3+f_{RRR'\theta}(\Delta_1+\Delta_2)\Delta_1\Delta_2\Delta_3+f_{RR\theta\theta}(\Delta_1^2+\Delta_2^2)\Delta_3^2+f_{RR'\theta\theta}\Delta_1\Delta_2\Delta_3^2+f_{R\theta\theta\theta}(\Delta_1+\Delta_2)\Delta_3^3], \quad (3)$$

where $\Delta_i=\Delta R_i=R_i-R_e$ $(i=1,\ 2)$ and $\Delta_3=R_e\Delta\theta=R_e(\theta-\theta_e)$. The root-mean-square fitting errors for the theoretical surfaces were 0.018 (SCF), 0.021 (SD), and 0.073 μhartree (SDQ).

As in the case of the computed equilibrium geometry, there is considerable improvement in the quadratic force constants in going from SCF through SD to SDQ. The situation for the higher-order constants is less clear because of the large statistical uncertainties in both the theoretical and empirical values and because of the lack of agreement between the different empirical determinations. In general, the statistical uncertainties in the cubic and diagonal quartic constants are considerably smaller for the theoretical than for the empirical values, but for most of the quartic constants the uncertainties are so large as to leave little if any significance in either the theoretical or the empirical values (with the notable exception of the theoretical f_{RRRR} and $f_{\theta\theta\theta\theta}$ values). Note that the uncertainties in Table IV, except for those of Hoy *et al.*[15] (HMS), are quoted as three times the standard deviations; the HMS uncertainties are derived from estimated uncertainties in the input data.

Rather large differences, including even the quadratic constants (see particularly $f_{R\theta}$) are found between the results of Smith and Overend[16] (SO) and those of the other workers, but all sets of empirical constants, including the two sets KM(I) and KM(II) of Kuchitsu and Morino[17] (derived from H_2O and D_2O data, respectively) differ significantly from each other. Essentially all the empirical determinations are based on the infrared spectroscopic data and analysis of Benedict *et al.*[12] (BGP). The sets KM(I), KM(II), and HMS were derived by relating the harmonic frequencies, anharmonicity constants, and vibration-rotation constants of BGP to force constants defined in terms of normal coordinates, with the arbitrary constraint (due to insufficient data) that three of the quartic valence-field constants, $f_{RRR\theta}$, $f_{RRR'\theta}$, and $f_{R\theta\theta\theta}$ be equal to zero. The SO values were derived from observed vibrational energies and from rotational constants of different vibrational states (taken mostly, but not exclusively, from the BGP data), without use of the BGP harmonic frequencies and anharmonicity constants. They derived three different sets of force constants based on different selections of the input data, the third set (excluding HDO rotational data) being quoted in Table IV. The Speirs and Špirko[18] (SS) data in Table IV is one of three different solutions they obtained by using different procedures and constraints.

The large statistical uncertainties in the theoretical off-diagonal quartic force constants may be due in large measure to having an inadequate number of computed potential surface points (36, compared to 75 used by Krohn *et al.*[3]), and particularly to these points all lying quite deep in the potential well. Additional points with larger displacements from equilibrium are clearly desirable,[19] but the high cost involved precluded such an extension of the calculations at this time (it is hoped that it will be possible to carry out such additional calculations in the near future).

The deficiencies of the SCF potential surface, particularly in terms of equilibrium geometry and quadratic force constants (see also the comparison of several force constants with previous theoretical results in Table III), are as expected, reflecting the incorrect dissociation behavior of the SCF wavefunction and the concomitant underestimation of the bond length and overestimation of the harmonic force constants. This is rectified to a very large extent by the SD wavefunction, but as noted previously, even this function lacks one of the configurations, $(1b_2)^2(3a_1)^2 \rightarrow (4a_1)^2(2b_2)^2$, required for proper dissociation to $O(^3P) + 2H(^2S)$. Further improvement is indeed obtained in the SDQ surface, which gives an equilibrium geometry in excellent agreement with experiment (Table III), and as far as the disparities between the various sets of experimentally derived force constants allow us to deduce, a rather good force field. Meyer's CEPA results[11] (Table III) are mostly similar to our SDQ values. It is clear that the effects of incorrect dissociation of the SCF wavefunction, and to a lesser extent, of the SD wavefunction extend all the way to the bottom of the potential well. An alternative way to rectify this defect, without resorting to *post facto* corrections, is to use an appropriate multiconfigurational SCF function as the zero-order wavefunction, and then include all single and double excitations relative to all the configurations in this function in the final CI calculations. However, for a basis set of the size used here, this procedure would involve more laborious calculations than we can undertake at present.

IV. BINDING ENERGY

The theoretical binding energy is obtained as the difference between the calculated energy of the molecule at the bottom of its potential well and the sum of the energies of the constituent atoms in their ground state, calculated with the same type of wavefunction and using the appropriate parts of the same molecular basis set. Paper I presented SCF and CI(SD) calculations for the ^3P state of the oxygen atom with the oxygen part of the 39-STO basis set. Using these results together with an energy of -0.5 hartree for each hydrogen atom, and the calculated molecular energies of the SCF and SD wavefunctions at the single unoptimized geometry of Paper I, binding energies of 6.94 eV (SCF) and 9.245 eV (SD) were obtained, compared to an experimental estimate[1] of (10.085 ± 0.030) eV. If the interpolated SCF energy at the minimum of the SCF potential surface is used instead of the Paper I geometry, this leads to an SCF binding energy of 6.96 eV, an increase of only 0.02 eV. The increase is an order of magnitude smaller for the SD case, since the optimum SD geometry (point 36) is quite close to that used in Paper I, resulting in an SD binding energy of 9.246 eV. An SDQ binding energy is rather difficult to estimate from our results, since the oxygen atom is an open-shell system and since single excitations make a significant contribution to its SD wavefunction.

V. PROPERTIES

Expectation values of various one-electron operators were computed for the SCF and SD wavefunctions at each of the 36 points of Table I. (No SDQ property values could be obtained, since Eq. (2) is only valid for the energy.) The resulting values (which are given in a technical report[20]) were used in a least-squares procedure to derive quartic or cubic polynomial expansions for each of the properties in terms of the displacement coordinates, relative to the computed equilibrium geometry on each of the two surfaces. The SCF property values at the SCF equilibrium geometry (obtained from the least-squares fitting) and at the SD equilibrium geometry (point 36), as well as the SD property values at the SD equilibrium geometry, are given in Table V, together with experimental values where available (the notation and units are the same as in Paper I).

Three different types of polynomial expansions were used for the properties, depending on the symmetry characteristics of the corresponding operators.[3] The quartic expansion for type-A properties, those which are symmetric in R_1 and R_2, is

$$\begin{aligned}\mathcal{P}_A = {} & \mathcal{P}_E + K_2(\Delta_1 + \Delta_2) + K_3\Delta\theta + K_4(\Delta_1^2 + \Delta_2^2) + K_5\Delta\theta^2 + 2K_6\Delta_1\Delta_2 + 2K_7(\Delta_1 + \Delta_2)\Delta\theta + K_8(\Delta_1^3 + \Delta_2^3) + K_9\Delta\theta^3 + 3K_{10}(\Delta_1 + \Delta_2)\Delta_1\Delta_2 \\ & + 3K_{11}(\Delta_1^2 + \Delta_2^2)\Delta\theta + 6K_{12}\Delta_1\Delta_2\Delta\theta + 3K_{13}(\Delta_1 + \Delta_2)\Delta\theta^3 + K_{14}(\Delta_1^4 + \Delta_2^4) + K_{15}\Delta\theta^4 + 4K_{16}(\Delta_1^2 + \Delta_2^2)\Delta_1\Delta_2 + 6K_{17}\Delta_1^2\Delta_2^2 + 4K_{18}(\Delta_1^3 + \Delta_2^3)\Delta\theta \\ & + 12K_{19}(\Delta_1 + \Delta_2)\Delta_1\Delta_2\Delta\theta + 6K_{20}(\Delta_1^2 + \Delta_2^2)\Delta\theta^2 + 12K_{21}\Delta_1\Delta_2\Delta\theta^2 + 4K_{22}(\Delta_1 + \Delta_2)\Delta\theta^3 \qquad (4)\end{aligned}$$

(as before, $\Delta_i = \Delta R_i = R_i - R_e$, but note that $\Delta\theta = \theta - \theta_e$ is used, rather than $\Delta_3 = R_e\Delta\theta$). For type-B properties, those which are antisymmetric in the exchange of R_1 and R_2, the cubic expansion (the 14 asymmetric points are insufficient for an adequate characterization of a quartic expansion) is

$$\mathcal{P}_B = K_1(\Delta_1 - \Delta_2) + K_2(\Delta_1^2 - \Delta_2^2) + 2K_3(\Delta_1 - \Delta_2)\Delta\theta + K_4(\Delta_1^3 - \Delta_2^3) + 3K_5(\Delta_1 - \Delta_2)\Delta_1\Delta_2 + 3K_6(\Delta_1^2 - \Delta_2^2)\Delta\theta + 3K_7(\Delta_1 - \Delta_2)\Delta\theta^2. \qquad (5)$$

For type-C properties, those which possess no symmetry (such as origin-dependent properties centered on the hydrogen nuclei), the cubic expansion is

$$\mathcal{P}_c=\mathcal{P}_e+K_2\Delta_1+K_3\Delta_2+K_4\Delta\theta+K_5\Delta_1^2+K_6\Delta_2^2+K_7\Delta\theta^2+2K_8\Delta_1\Delta_2$$
$$+2K_9\Delta_1\Delta\theta+2K_{10}\Delta_2\Delta\theta+K_{11}\Delta_1^3+K_{12}\Delta_2^3+K_{13}\Delta\theta^3+3K_{14}\Delta_1^2\Delta_2+3K_{15}\Delta_1^2\Delta\theta+3K_{16}\Delta_1\Delta_2^2+3K_{17}\Delta_1\Delta\theta^2+3K_{18}\Delta_2^2\Delta\theta+3K_{19}\Delta_2\Delta\theta^2$$
$$+6K_{20}\Delta_1\Delta_2\Delta\theta. \tag{6}$$

Fifty data points are actually available for the determination of the expansion coefficients in Eq. (6), since each asymmetric geometry calculation provides two data points. Nevertheless, these are not enough for the adequate characterization of a quartic polynomial expansion for type-C properties.

The expansion coefficients for the correlation energy ΔE_{corr}(SD) and for components of the dipole moment vector μ and of the field gradient tensor q at the oxygen and hydrogen nuclei are given in Tables VI–VIII. Expansions for all the properties calculated are given in the above-mentioned technical report.[20]

TABLE V. Property values for the water molecule.

Property[a]	SCF[b]	SCF[c]	SD[d]	Experiment[e]
$-V/2T$		1.00025	1.00007	1.00000
$\mathfrak{F}_z$(O)	0.8897	1.0312	0.6532	0.
$\mathfrak{F}_z$(H)	−0.0236	−0.0564	0.0639	0.
$\mathfrak{F}_y$(H)	−0.0347	−0.0534	0.0898	0.
$\mathfrak{F}_z$(total)	0.8425	0.9184	0.7810	0.
μ	1.9484	1.9811	1.9070	1.8473 ± 0.0010
Θ_{xx}	−2.4658	−2.5063	−2.4998	−2.50 ± 0.02
Θ_{yy}	2.6511	2.6284	2.6197	2.63 ± 0.02
Θ_{zz}	−0.1853	−0.1221	−0.1199	−0.13 ± 0.03
$\langle r^2\rangle$	5.3308	5.3760	5.4590	5.1 ± 0.7
$\chi_{\mathrm{av}}^{\mathrm{d}}$	−15.0744	−15.2053	−15.4401	−14.6 ± 2.0
$\chi_{xx}^{\mathrm{d}}-\chi_{\mathrm{av}}^{\mathrm{d}}$	−0.9008	−0.9379	−0.9417	−1.06 ± 0.01
$\chi_{yy}^{\mathrm{d}}-\chi_{\mathrm{av}}^{\mathrm{d}}$	0.8719	0.8816	0.8868	0.95 ± 0.01
$\chi_{zz}^{\mathrm{d}}-\chi_{\mathrm{av}}^{\mathrm{d}}$	0.0289	0.0562	0.0549	0.11 ± 0.02
$\sigma_{\mathrm{av}}^{\mathrm{d}}$(O)	416.54	416.22	416.42	~414.6
σ_{xx}^{d}(O)	417.69	417.26	417.61	
σ_{yy}^{d}(O)	415.60	415.45	415.47	
σ_{zz}^{d}(O)	415.32	415.96	416.16	
$\sigma_{\mathrm{av}}^{\mathrm{d}}$(H)	104.07	102.92	102.83	102.4
σ_{aa}^{d}(H)	131.52	130.19	130.05	
σ_{bb}^{d}(H)	48.49	47.64	47.64	
σ_{xx}^{d}(H)	132.20	130.92	130.79	
α(H)	1.695	1.714	1.719	
$(eqQ/h)_{xx}(^{17}\mathrm{O})$	11.162	11.450	10.809	10.17 ± 0.07
$(eqQ/h)_{yy}(^{17}\mathrm{O})$	−10.374	−10.370	−9.724	−8.89 ± 0.03
$\eta(^{17}\mathrm{O})$	0.859	0.811	0.799	0.75 ± 0.01
$(eqQ/h)_{aa}$(D)	385.52	354.19	362.46	307.95 ± 0.14
$(eqQ/h)_{bb}$(D)	−168.51	−153.50	−157.70	−133.13 ± 0.14
η(D)	0.1258	0.1332	0.1298	0.1350 ± 0.0007
α(D)	0.761	0.870	0.984	−1.266

[a] Symbols and units as in Paper I.

[b] SCF values at the SCF equilibrium geometry (interpolated from polynomial fit).

[c] SCF values at the SD equilibrium geometry (point 36).

[d] SD values at the SD equilibrium geometry (point 36).

[e] See Paper I for references.

TABLE VI. Expansion coefficients for type-A properties.[a]

	μ_z		$q_{xx}(\mathrm{O})$		$q_{zz}(\mathrm{O})$		
	SCF	SD	SCF	SD	SCF	SD	$\Delta E_{\mathrm{corr}}(\mathrm{SD})$
φ_e	0.76656320(7)	0.75025479(1)	−1.8271900(4)	−1.76931751(6)	0.1290877(4)	0.17753357(5)	−0.27525766(0)
K_2	0.1006018(13)	0.0826377(3)	−0.789128(7)	−0.6807460(14)	0.366548(7)	0.3625877(12)	−0.01398654(7)
K_3	−0.3945783(16)	−0.3668455(3)	0.419565(9)	0.3822994(14)	−1.442162(8)	−1.4490063(12)	0.00216517(7)
K_4	0.01663(10)	0.009387(10)	0.0267(5)	0.05271(5)	0.1151(5)	0.09145(4)	−0.003139(2)
K_5	−0.10790(2)	−0.114763(6)	0.22369(11)	0.19988(3)	0.36171(11)	0.34826(2)	−0.0048543(14)
K_6	−0.02190(8)	−0.028360(7)	−0.0811(5)	−0.07040(3)	0.1325(4)	0.13296(3)	−0.0008827(17)
K_7	−0.034613(11)	−0.024184(3)	0.08744(6)	0.061745(14)	−0.19326(6)	−0.152090(12)	0.0010628(7)
K_8	−0.0314(19)	−0.03327(16)	0.162(11)	0.1326(8)	−0.012(10)	−0.0116(7)	0.00130(4)
K_9	−0.0388(3)	−0.02622(3)	−0.0106(15)	−0.00208(14)	−0.4174(14)	−0.38752(12)	0.001648(7)
K_{10}	−0.0015(6)	−0.00222(5)	0.001(3)	−0.0008(2)	−0.046(3)	−0.04121(19)	−0.000225(11)
K_{11}	0.0141(10)	0.01196(9)	−0.025(6)	−0.0336(4)	0.149(5)	0.1560(4)	−0.00005(2)
K_{12}	−0.0119(9)	−0.01101(8)	−0.028(5)	−0.0241(4)	−0.152(5)	−0.1247(3)	0.000293(18)
K_{13}	−0.00578(12)	−0.007610(12)	0.0485(6)	0.03540(6)	−0.0160(6)	−0.02149(5)	0.000232(3)
K_{14}	0.019(12)	0.010(3)	−0.12(7)	−0.117(14)	−0.03(6)	−0.006(12)	0.0003(7)
K_{15}	−0.0137(19)	−0.0176(5)	−0.036(10)	−0.037(2)	0.232(10)	0.1976(19)	0.00248(11)
K_{16}	−0.003(2)	−0.0002(6)	−0.008(12)	0.004(3)	0.014(12)	−0.004(2)	0.00029(13)
K_{17}	0.0061(19)	0.0034(5)	0.012(10)	0.005(2)	−0.009(10)	0.0050(19)	−0.00002(11)
K_{18}	0.003(10)	−0.003(3)	−0.03(5)	−0.017(12)	0.04(5)	0.042(10)	−0.0004(6)
K_{19}	−0.002(3)	−0.0014(8)	0.002(17)	−0.001(4)	0.008(16)	0.013(3)	0.00000(19)
K_{20}	−0.002(2)	−0.0029(5)	−0.017(11)	−0.011(2)	−0.031(10)	−0.039(2)	0.00005(12)
K_{21}	−0.0016(18)	0.0001(5)	−0.001(10)	−0.008(2)	0.059(9)	0.0539(18)	0.00019(11)
K_{22}	0.0120(5)	0.01272(13)	0.015(3)	0.0197(6)	−0.090(3)	−0.0763(5)	−0.00046(3)

[a] The coefficients are given in atomic units (angles in radians) relative to Eq. (4). Conversion factors to conventional units for φ_e are given in Paper I and Ref. 20. Statistical uncertainties (in parentheses) are three times the least-squares standard deviation in the last digit quoted. The molecule is in the *YZ* plane, with the *Z* axis bisecting the HOH angle; μ is the dipole moment vector, $q(\mathrm{O})$ is the field gradient tensor at the oxygen nucleus, and ΔE_{corr} is the correlation energy (which is expanded relative to the SD equilibrium geometry).

Examining the expansion for the correlation energy ΔE_{corr} (Table VI), it is seen that this property surface is relatively flat in the equilibrium region, with small values of the expansion coefficients relative to φ_e. Nevertheless, the variation in ΔE_{corr} with geometry is quite important and is responsible for the improved agreement of the SD equilibrium geometry and force constants with experiment compared to SCF. The correlation energy reflects two types of error in the SCF description of the wavefunction, the omission of dynamic (primarily short-range) electron correlation and the incorrect dissociation behavior (contributing primarily to long-range correlation). The first of these is expected to gain in importance as the atoms are brought closer together, while the second is responsible for the generally observed increase in the magnitude of ΔE_{corr} as the bonds are stretched. In the present results for the equilibrium region, the predominant effect is due to the long-range term, as reflected in the negative value of K_2 (Table VI), resulting in a lengthening of R_e on the SD surface compared to SCF. The short-range term may be responsible for the observed increase in $|\Delta E_{\mathrm{corr}}|$ whenever the bond angle is reduced, reflected in the positive value of K_3. A combination of both terms is probably responsible for the negative value of K_4, which results in a decrease in the bond-stretching force constant f_{RR} on the SD surface. These trends are reinforced on adding the quadruple-excitation correction, further improving agreement with experiment (Tables III, IV). As suggested by Pulay,[21] since the variation of ΔE_{corr} in the equilibrium region is very nearly linear in the displacement coordinates, a computation of the force constants from the corresponding derivatives of the energy at the *experimental* equilibrium geometry would bring the force constants of the different surfaces into much better agreement with each other and with experiment.

The expansions obtained for the dipole moment function are particularly interesting, since this function determines the infrared transition intensities. The integrated band intensities are proportional to the squares of the matrix elements of the dipole moment function between the corresponding vibrational wavefunctions, thus only the magnitudes of these elements are determined directly from the integrated intensity data. These matrix elements are closely related (through the Taylor series expansion of the dipole moment function) to the derivatives of the dipole moment function with respect to internal coordinates, and again, integrated intensities provide direct information only for the magnitudes of the derivatives, not for their signs. Indirect infor-

TABLE VII. Expansion coefficients for type-B properties.[a]

	μ_y		$q_{yz}(\mathrm{O})$	
	SCF	SD	SCF	SD
K_1	0.195026(3)	0.1655769(10)	1.071042(12)	0.932504(6)
K_2	−0.02286(7)	−0.034411(18)	−0.1214(3)	−0.15011(10)
K_3	0.15142(4)	0.143279(10)	−0.17036(17)	−0.13839(6)
K_4	−0.0208(5)	−0.0268(4)	−0.135(2)	−0.124(2)
K_5	−0.01428(11)	−0.01344(9)	0.0185(5)	0.0097(5)
K_6	0.0109(3)	0.0036(2)	0.0595(14)	0.0733(13)
K_7	0.03523(16)	0.02884(12)	0.0239(8)	0.0368(7)

[a] See Ref. a, Table VI. The coefficients are relative to Eq. (5). The H_1 atom and R_1 bond are in the first quadrant of the YZ plane.[26]

TABLE VIII. Expansion coefficients for type-C properties.[a]

	$q_{xx}(\mathrm{H})$		$q_{zz}(\mathrm{H})$		$q_{yz}(\mathrm{H})$	
	SCF	SD	SCF	SD	SCF	SD
P_e	0.3212475(11)	0.3031157(7)	−0.036582(3)	−0.039644(2)	−0.390866(2)	−0.3683812(16)
K_2	−1.06933(5)	−0.98130(3)	0.09914(14)	0.11312(8)	1.41130(11)	1.30107(7)
K_3	0.01031(5)	0.00973(3)	−0.02349(14)	−0.02321(8)	−0.01652(11)	−0.01426(7)
K_4	−0.033361(19)	−0.03408(2)	0.32530(5)	0.30958(5)	0.09720(4)	0.08890(4)
K_5	1.7233(15)	1.5785(5)	−0.173(4)	−0.1912(14)	−2.359(3)	−2.1730(11)
K_6	−0.0011(15)	−0.0003(5)	0.001(4)	0.0007(14)	0.005(3)	0.0047(11)
K_7	0.0104(3)	0.01334(13)	0.0122(7)	0.0090(3)	0.1051(5)	0.1024(3)
K_8	−0.0110(4)	−0.00917(16)	0.0168(10)	0.0156(4)	0.0083(8)	0.0072(3)
K_9	0.0160(7)	0.0171(3)	−0.6697(19)	−0.6209(7)	−0.1852(15)	−0.1622(6)
K_{10}	0.0136(7)	0.0128(3)	0.0064(19)	0.0080(7)	−0.0111(15)	−0.0107(6)
K_{11}	−1.748(12)	−1.732(12)	0.24(3)	0.24(3)	2.45(3)	2.44(3)
K_{12}	0.001(12)	0.000(12)	0.01(3)	0.01(3)	0.00(3)	0.00(3)
K_{13}	−0.025(2)	−0.025(2)	0.015(5)	0.005(5)	0.034(4)	0.031(4)
K_{14}	0.009(3)	0.007(3)	−0.008(7)	−0.007(7)	−0.000(6)	−0.001(6)
K_{15}	−0.002(7)	−0.002(7)	0.683(18)	0.680(18)	0.166(14)	0.165(14)
K_{16}	−0.000(3)	−0.000(3)	0.001(7)	0.001(7)	−0.004(6)	−0.004(6)
K_{17}	−0.001(3)	−0.002(3)	0.028(9)	0.031(9)	−0.176(7)	−0.177(7)
K_{18}	0.002(7)	0.002(7)	−0.004(18)	−0.003(18)	0.003(14)	0.003(14)
K_{19}	−0.007(3)	−0.007(3)	0.002(9)	0.001(9)	−0.000(7)	0.003(7)
K_{20}	−0.004(3)	−0.004(3)	−0.001(7)	−0.002(7)	−0.001(5)	−0.001(5)

[a] See Footnote a, Tables VI, VII. The coefficients are relative to Eq. (6). The H atom at which $q(\mathrm{H})$ is given is H_1 (in the first quadrant of the YZ plane).[26]

mation about the signs is obtained by comparing the data for different isotopic species, and additional information is obtained from a careful analysis of the rotational components of each band.[22] Difficulties in the experimental determination of absolute intensities, particularly when bands overlap, often result in considerable uncertainties in the magnitudes and signs of dipole moment derivatives, so that the theoretical determination of the dipole moment function is particularly important. A recent theoretical vibrational analysis by Carney[23] finds an inconsistency between the accepted experimental values of the integrated intensities for H_2O and HDO and the expected isotope effects, and concludes that the accepted value for the fundamental ν_1 band of H_2O (which is overlapped to some extent by ν_3) is in error by as much as a factor of 4. His revised value is in very good agreement with the dipole moment derivatives deduced from the present and previous *ab initio* calculations.[4,23,25]

Also given in Tables VI–VIII are expansions for several components of the field gradient tensor q at the oxygen and hydrogen nuclei, from which quadrupole coupling constants eqQ/h can be obtained (the missing yy components can be determined by the zero trace condition on the q tensor, while the xy and xz components vanish identically). These are reported as examples of properties that show large variations with molecular geometry.

Other calculations of the dependence of one-electron properties of the water molecule on the geometry include the work of Dixon, Claxton, and Smith,[24] of Smith, Jørgensen, and Öhrn,[25] and of Krohn, Ermler, and Kern.[2–4] These were all limited to SCF wavefunctions. Dixon *et al.* used a minimal set of contracted Gaussian basis functions chosen to fit oxygen atomic SCF orbitals and a scaled hydrogen 1s orbital, and studied 21 geometries, but did not generate polynomial expansions for the properties. Smith *et al.* used a 30-function CGTO basis and produced quadratic expansions for the energy and dipole moment (they also obtained energy surfaces for several positive ion states). Kern and co-workers[2,3] used a 35-function CGTO basis set, carried out the SCF calculations at 75 geometries, and obtained quartic and cubic polynomial expansions and vibrational corrections to the property values. The present study, while limited to 36 geometries, employed a considerably improved basis set (the present SCF energy is 14 mhartree lower than that of Ermler and Kern, and is only 3 mhartree above the estimated Hartree–Fock limit), and includes a determination of the effects of electron correlation. While the results of all studies show very similar trends,[26] the detailed differences are far from negligible and reflect the sensitivity of many of the property expectation values to the quality of the wavefunction.[1] It is also interesting to note that while there are many significant differences in the expansion coefficients for the property values in the present SCF and SD calculations, a preliminary analysis of computed vibrational corrections to the one-electron properties[27] shows that these corrections are generally very similar on the two surfaces, even in those cases in which the total SCF and SD values for a property may vary significantly. (Normal coordinate expansions and vibrational corrections for the properties will be described in the next paper in this series.)

VI. SUMMARY

Potential energy surfaces for the ground state of the water molecule were obtained by SCF and CI (SD) calculations. Energies were computed at 36 points (22 symmetric and 14 asymmetric geometries) and were used to derive quartic valence force field expansions.

The SCF results were similar to those of previous near-Hartree–Fock calculations,[2,3,10,11] and displayed the usual Hartree–Fock tendency to produce too short bond-lengths and too large harmonic force constants. Considerable improvement in these quantities was found in the SD calculations, and further improvement, producing excellent agreement with experiment, was obtained when a correction for quadruply excited configurations[9] was added to the SD energies. These corrected (SDQ) results are similar to Meyer's CEPA results.[11] The quality of the higher-order force constants is more difficult to assess because of the large statistical uncertainties in both the theoretical and experimentally derived force constants and because of the large disparities between the different experimental derivations.[12–18] The principal limitation in the present potential surface calculations appears to be the restriction to too small a region of the surface, with greater displacements from equilibrium being required for a more satisfactory characterization of the surface and for a more reliable derivation of the higher-order force constants.

The binding energy of the water molecule was computed with the SCF and SD wavefunctions, the result being too low by 31% and 8%, respectively, for these two cases. One-electron properties were computed and fitted to quartic and cubic polynomial expansions in internal displacement coordinates. Normal coordinate expansions, vibrational energies, and vibrational corrections to the properties will be presented in a forthcoming paper.

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