

Field and field-gradient polarizabilities of H₂O

David M. Bishop* and Janusz Pipin

Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 9B4

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Using a charge-perturbation approach, all components of the polarizability tensors α , β , A , B , and C for H₂O have been evaluated at the SCF level and, with the exception of β and B , at the MC SCF level of approximation. This is the first such comprehensive evaluation of the electrical properties of water.

Key words: Water — Polarizabilities — Hyperpolarizabilities

1. Introduction and theory

Recently we have reported MC SCF (multiconfigurational self consistent field) calculations of the independent components of the α , β , A , C , and B polarizability tensors for LiH [1] and BeH, BH and CH⁺ [2]. In this article we describe similar calculations for H₂O, and the aim, as before, is not to provide an arbitrary set of properties but rather a complete description of the electric polarizability tensors. The method we once again use (though for the first time for a polyatomic molecule) is that of charge perturbation; that is to say a charge is placed some distance from the molecule and from the calculated multipole moments the tensors are deduced. There are three distinct advantages to doing things this way: (a) all tensor components are obtained from a few calculations on the molecule-charge system and any standard SCF or MC SCF programme may be used without modification, (b) by using linear combinations of the moments, contributions from tensors of immediately higher rank are eliminated, (c) we obtain a complete theoretical and true reference description.

* Member of the Ottawa-Carleton Chemistry Institute

Following Buckingham [3] and McLean and Yoshimine [4] we write the energy, dipole and quadrupole moment of a molecule in a general static electric field as

$$E = E^0 - \mu_\alpha^0 F_\alpha - \frac{1}{3} \Theta_{\alpha\beta}^0 F_{\alpha\beta} - \frac{1}{15} \Omega_{\alpha\beta\gamma}^0 F_{\alpha\beta\gamma} - \frac{1}{105} \Phi_{\alpha\beta\gamma\delta}^0 F_{\alpha\beta\gamma\delta} + \dots$$

$$- \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{3} A_{\alpha,\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{6} C_{\alpha\beta,\gamma\delta} F_{\alpha\beta} F_{\gamma\delta}$$

$$- \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{6} B_{\alpha\beta,\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots \quad (1)$$

$$\mu_\alpha = \mu_\alpha^0 + \alpha_{\alpha\beta} F_\beta + \frac{1}{3} A_{\alpha,\beta\gamma} F_\beta F_\gamma + \frac{1}{2} \beta_{\alpha\beta\gamma} F_\beta F_\gamma$$

$$+ \frac{1}{3} B_{\alpha\beta,\gamma\delta} F_\beta F_\gamma F_\delta + \dots \quad (2)$$

$$\Theta_{\alpha\beta} = \Theta_{\alpha\beta}^0 + A_{\gamma,\alpha\beta} F_\gamma + C_{\alpha\beta,\gamma\delta} F_\gamma F_\delta + \frac{1}{2} B_{\gamma\delta,\alpha\beta} F_\gamma F_\delta + \dots, \quad (3)$$

where E^0 , μ^0 , Θ^0 , Ω^0 are the energy and permanent multipole moments of the free molecule and α , β , γ , A , C , and B the static molecular polarizabilities. F_α , $F_{\alpha\beta}$, etc. are the electric field, field gradient etc. at the origin. The greek subscripts denote cartesian tensor components; a repeated subscript denotes a summation over all three cartesian coordinates x , y and z .

Water has C_{2v} symmetry and if the centre of mass is placed at the origin of a cartesian coordinate system with the C_2 axis along the z axis and the molecule in the xz plane (see Table 1), then we may specify the *independent* components by μ_z^0 (dipole moment); Θ_{xx}^0 , Θ_{zz}^0 (quadrupole moment); α_{xx} , α_{yy} , α_{zz} (dipole polarizability); β_{xxz} , β_{yyz} , β_{zzz} (first dipole hyperpolarizability); $A_{x,zx}$, $A_{y,zy}$, $A_{z,xx}$, $A_{z,zz}$ (dipole-quadrupole polarizability); $C_{xy,xy}$, $C_{xz,xz}$, $C_{yz,yz}$, $C_{xx,xx}$, $C_{yy,yy}$, $C_{zz,zz}$ (quadrupole-quadrupole polarizability); $B_{xy,xy}$, $B_{xz,xz}$, $B_{yz,yz}$, $B_{xx,xx}$, $B_{xx,zz}$, $B_{yy,xx}$, $B_{yy,zz}$, $B_{zz,xx}$, $B_{zz,zz}$ (dipole-dipole-quadrupole polarizability).

We have calculated all of these components at the SCF level and the α , A and C tensors at the MC SCF level as well; the purpose of the latter study being to investigate the importance of electron correlation rather than to produce definitive values. Several, but not all, of these tensors have been calculated before at both the SCF and post-SCF levels. Of the more recent publications we draw attention to the following: Purvis and Bartlett [5] (α and β using many body perturbation theory), Werner and Meyer [6] (α using coupled-electron-pair approximation), Reinsch [7] (α using MC SCF theory), Lazzarotti and Zanasi [8] (α and β using SCF theory), Dacre [9] (α , β , A and C using SCF theory), John et al [10] (α and A using SCF and CI theory).

Table 1. Geometry and axes for the H₂O molecule in atomic units ($r_{\text{OH}} = 1.8111$ and $\Theta = 104.45^\circ$)^a

Atom	x	y	z
O	0	0	-0.124144
H ₁	-1.43153	0	0.985266
H ₂	1.43153	0	0.985266

^a Experimental geometry; taken from Ermiler WC, Kern CW, (1971) J Chem Phys 55:4851. The origin of the axes is at the centre of mass

Throughout this paper atomic units are used; for distance: 1 bohr $\approx 0.52918 \times 10^{-10}$ m, for energy: 1 hartree $\approx 4.3598 \times 10^{-18}$ J, for μ : 1 au $\approx 8.4784 \times 10^{-30}$ C m, for Θ : 1 au $\approx 4.4866 \times 10^{-40}$ C m², for α : 1 au $\approx 0.16488 \times 10^{-40}$ C² m² J⁻¹, for β : 1 au $\approx 0.32063 \times 10^{-52}$ C³ m³ J⁻², for A : 1 au $\approx 8.7250 \times 10^{-52}$ C² m³ J⁻¹, for C : 1 au $\approx 4.6171 \times 10^{-62}$ C² m⁴ J⁻¹, for B : 1 au $\approx 1.6967 \times 10^{-63}$ C³ m⁴ J⁻².

2. Method

The method we have used has been described in detail for a diatomic molecule in [1] and [11], all that is now new is the set of equations for abstracting the polarizabilities from the perturbed multipole moments. For a molecule of C_{2v} symmetry these are

$$\begin{aligned} \alpha_{zz} &= [\mu_z(-Q, 0, 0) + \mu_z(Q, \pi, 0) - \mu_z(Q, 0, 0) - \mu_z(-Q, \pi, 0)](R^2/4Q) \\ \alpha_{xx} &= \left[\mu_x\left(-Q, \frac{\pi}{2}, 0\right) - \mu_x\left(Q, \frac{\pi}{2}, 0\right) \right](R^2/2Q) \\ \alpha_{yy} &= \left[\mu_y\left(-Q, \frac{\pi}{2}, \frac{\pi}{2}\right) - \mu_y\left(Q, \frac{\pi}{2}, \frac{\pi}{2}\right) \right](R^2/2Q) \\ \beta_{zzz} &= \left[\mu_z\left(Q, \frac{\pi}{2}, 0\right) + \mu_z\left(-Q, \frac{\pi}{2}, 0\right) - 2\mu_z^0 \right](R^4/Q^2) \\ \beta_{zyy} &= \left[\mu_z\left(Q, \frac{\pi}{2}, \frac{\pi}{2}\right) + \mu_z\left(-Q, \frac{\pi}{2}, \frac{\pi}{2}\right) - 2\mu_z^0 \right](R^4/Q^2) \\ \beta_{zzz} &= [\mu_z(Q, 0, 0) + \mu_z(-Q, 0, 0) + \mu_z(Q, \pi, 0) + \mu_z(-Q, \pi, 0) - 4\mu_z^0](R^4/2Q^2) \\ A_{x,zx} &= \left[\Theta_{xz}\left(-Q, \frac{\pi}{2}, 0\right) - \Theta_{xz}\left(Q, \frac{\pi}{2}, 0\right) \right](R^2/2Q) \\ A_{y,zy} &= \left[\Theta_{yz}\left(-Q, \frac{\pi}{2}, \frac{\pi}{2}\right) - \Theta_{yz}\left(Q, \frac{\pi}{2}, \frac{\pi}{2}\right) \right](R^2/2Q) \\ A_{z,xx} &= \left[\mu_z\left(-Q, \frac{\pi}{2}, 0\right) - \mu_z\left(Q, \frac{\pi}{2}, 0\right) \right](R^3/2Q) \\ A_{z,zz} &= [\mu_z(-Q, 0, 0) - \mu_z(Q, 0, 0) + \mu_z(-Q, \pi, 0) - \mu_z(Q, \pi, 0)](R^3/4Q) \\ C_{xx,xx} &= \left[\Theta_{xx}\left(-Q, \frac{\pi}{2}, 0\right) - \Theta_{xx}\left(Q, \frac{\pi}{2}, 0\right) \right](R^3/6Q) \\ C_{yy,yy} &= \left[\Theta_{xx}(-Q, 0, 0) + \Theta_{xx}(-Q, \pi, 0) - \Theta_{xx}(Q, 0, 0) - \Theta_{xx}(Q, \pi, 0) \right. \\ &\quad \left. + \frac{6Q}{R^3}(C_{xx,xx} + C_{zz,zz}) \right](R^3/6Q) \\ C_{zz,zz} &= [\Theta_{zz}(-Q, 0, 0) + \Theta_{zz}(-Q, \pi, 0) - \Theta_{zz}(Q, 0, 0) - \Theta_{zz}(Q, \pi, 0)](R^3/12Q) \\ C_{xy,xy} &= \left[\Theta_{xy}\left(-Q, \frac{\pi}{2}, \frac{\pi}{4}\right) - \Theta_{xy}\left(Q, \frac{\pi}{2}, \frac{\pi}{4}\right) \right](R^3/6Q) \end{aligned}$$

$$\begin{aligned}
C_{xz,xz} &= \left[\Theta_{xz} \left(-Q, \frac{\pi}{4}, 0 \right) - \Theta_{xz} \left(Q, \frac{\pi}{4}, 0 \right) - \frac{\sqrt{2}Q}{R^2} A_{x,zx} \right] (R^3/6Q) \\
C_{yz,yz} &= \left[\Theta_{yz} \left(-Q, \frac{\pi}{4}, \frac{\pi}{4} \right) - \Theta_{yz} \left(Q, \frac{\pi}{4}, \frac{\pi}{4} \right) - \frac{Q}{R^2} A_{y,zy} \right] (R^3/3\sqrt{2}Q) \\
B_{xx,xx} &= \left[\mu_x \left(-Q, \frac{\pi}{2}, 0 \right) + \mu_x \left(Q, \frac{\pi}{2}, 0 \right) \right] (R^5/2Q^2) \\
B_{xx,zz} &= \left[\Theta_{zz} \left(Q, \frac{\pi}{2}, 0 \right) + \Theta_{zz} \left(-Q, \frac{\pi}{2}, 0 \right) - 2\Theta_{zz}^0 \right] (R^4/Q^2) \\
B_{yy,xx} &= - \left[\mu_y \left(Q, \frac{\pi}{2}, \frac{\pi}{2} \right) + \mu_y \left(-Q, \frac{\pi}{2}, \frac{\pi}{2} \right) + \frac{2Q^2}{R^5} B_{yy,zz} \right] (R^5/2Q^2) \\
B_{yy,zz} &= \left[\Theta_{zz} \left(Q, \frac{\pi}{2}, \frac{\pi}{2} \right) + \Theta_{zz} \left(-Q, \frac{\pi}{2}, \frac{\pi}{2} \right) - 2\Theta_{zz}^0 \right] (R^4/Q^2) \\
B_{zz,xx} &= [\Theta_{xx}(Q, 0, 0) + \Theta_{xx}(-Q, 0, 0) + \Theta_{xx}(Q, \pi, 0) \\
&\quad + \Theta_{xx}(-Q, \pi, 0) - 4\Theta_{xx}^0] (R^4/2Q^2) \\
B_{zz,zz} &= [\mu_z(Q, 0, 0) + \mu_z(-Q, 0, 0) - \mu_z(Q, \pi, 0) - \mu_z(-Q, \pi, 0)] (R^5/4Q^2) \\
B_{xy,xy} &= \left[\Theta_{xy} \left(Q, \frac{\pi}{2}, \frac{\pi}{4} \right) + \Theta_{xy} \left(-Q, \frac{\pi}{2}, \frac{\pi}{4} \right) \right] (R^4/Q^2) \\
B_{xz,xz} &= \left[\Theta_{xz} \left(Q, \frac{\pi}{4}, 0 \right) + \Theta_{xz} \left(-Q, \frac{\pi}{4}, 0 \right) \right] (R^4/Q^2) \\
B_{yz,yz} &= \left[\Theta_{yz} \left(Q, \frac{\pi}{4}, \frac{\pi}{4} \right) + \Theta_{yz} \left(-Q, \frac{\pi}{4}, \frac{\pi}{4} \right) \right] (\sqrt{2}R^4/Q^2).
\end{aligned}$$

In these equations, $\mu_z(Q, \theta, \phi)$, for example, represents the z component of the dipole moment when a charge Q is placed at a distance R from the origin, with polar angles of θ and ϕ . A charge of $\pm e$ was used and values of the tensors found with $R=30, 32$, and $34 a_0$. As a refinement, these values were plotted against R^{-2} and those reported are from an extrapolation of R to infinity.

The energies and perturbed moments were found by using SCF and MC SCF wavefunctions given by the GAMESS system [12]. The experimental geometry was assumed (Table 1) and all properties were calculated at the centre of mass.

The largest Gaussian-type-orbital basis set used was the uncontracted (11s7p4d/5s2p1d) which was constructed on the principles of Werner and Meyer [6]. For oxygen the Huzinaga (10s6p) set [13] has the s and p orbitals of lowest-valued exponent replaced by a pair of such orbitals and four d orbitals added. For hydrogen, Huzinaga's 5s basis set was augmented by two p orbitals (exponents from [6]) and one d orbital (with $\xi_d=0.6$). We call this basis I. Computational constraints necessitated a smaller basis when carrying out the MC SCF calculations and for these we used the contracted [5s8p3d/2s2p] basis. This was obtained by adding to the [4s7p/2s] of Clementi and Popkie [14] a

Table 2. Total energy, dipole and quadrupole moments of H₂O (in atomic units)

Basis	Method	E_0	μ_z^0	Θ_{xx}^0	Θ_{zz}^0
I ^a	SCF	-76.060376	0.7803	1.8903	-0.1050
II ^b	SCF	-76.062269	0.7814	1.9145	-0.0621
II ^b	MC SCF	-76.157069	0.7111	1.9184	-0.0335

^a (11s7p4d/5s2p1d)^b [5s8p3d/2s2p]

further *s* and *p* orbital on O (exponents as in [9]) as well as three *d*-orbitals (exponents 0.25, 1.0, 2.0) on O and two *p*-orbitals on H (exponents 0.2, 1.5). We call this basis II.

For the MC SCF calculations (using the GAMESS system) our choice of configurations was based on the GUGA method [15]. The configuration space employed consisted of 490 configurations which were generated from one reference configuration built from five doubly-occupied and three vacant molecular orbitals. The excitation level of six was assumed.

3. Results and discussion

In Table 2 we show our results for the unperturbed molecule for the total energy, and the dipole and quadrupole moments. In Table 3 our values for μ_z^0 , the α

Table 3. Energies dipole moments and polarizabilities for H₂O (atomic units)

Ref.	Energy	μ_z^0	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	β_{xxz}	β_{yyz}	β_{zzz}	$\bar{\beta}$
SCF calculations										
LZ ^a	-76.066390	0.7836	9.033	7.575	8.271	8.293	-10.581	1.098	-3.574	-7.834
WM ^b	-76.0553	0.782	9.04	7.99	8.47	8.50				
PB ^c	-76.05443	0.784	9.18	7.95	8.47	8.53	-9.63	-0.48	-5.22	-9.20
This work ^d	-76.06038	0.7803	9.24	7.91	8.55	8.53	-7.87	1.41	-4.68	-6.68
This work ^e	-76.06227	0.7814	8.83	7.45	8.06	8.11	-16.33	-2.76	-9.00	-16.85
Beyond SCF calculations										
WM ^b	-76.2799	0.723	9.81	9.59	9.64	9.68				
PB ^c	-76.29898	0.735	9.87	9.30	9.46	9.54	-10.0	-3.7	-9.2	-13.7
This work	-76.15707	0.7111	9.25	9.06	8.50	8.94				
Experiment ^f										
	-76.459	0.724				9.82				-21.8±0.9

^a [8]^b [6]^c [5]^d Basis I: (11s7p4d/5s2p1d)^e Basis II: [5s8p3d/2s2p]

^f Energy taken from Pople JA, Binkley JS (1975) Mol Phys 29:599; dipole moment from McClellan AL (1963) Tables of experimental dipole moments, Freeman and Co., San Francisco; $\bar{\alpha}$ from Werner and Meyer, see foot-note b; $\bar{\beta}$ from Ward JF, Miller CK (1979) Phys Rev A19:826

and β tensors are compared with those of others. Our SCF energies with both basis sets are lower than Werner and Meyer's [6] and Purvis and Bartlett's [5] SCF values but not as good as Lazzeretti and Zanasi's [8]. Basis II though smaller than I gives a lower energy because of improved optimization of the exponents. However, the coupled-electron-pair approximation [6] and many-body-perturbation theory [5], as expected, capture more electron correlation than does our MC SCF calculation. For the latter, our value of $\mu_z^0 = 0.7111$ compares favourably with [5] and [6] and the experimental value of 0.724: correlation has reduced this value by 9%; Purvis and Bartlett found a reduction of 6.5%. Our SCF quadrupole moment Θ_{xx} (1.914) agrees well with the John et al. [10] value of 1.983. The other component, Θ_{zz} , is both small and extremely sensitive to the basis set size and the introduction of electron correlation. The experimental values [16] are $\Theta_{xx}^0 = 1.96 \pm 0.02$ and $\Theta_{zz}^0 = -0.10 \pm 0.02$.

Our reported SCF value of the mean polarizability $\bar{\alpha}$, 8.53 with basis I, agrees very well with [5] and [6], though the agreement with [6] is somewhat fortuitous since the components do not agree so well. Our MC SCF value of $\bar{\alpha}$ shows an increase due to correlation but not such a big increase as in [5]. Reinsch [7] also carried out an MC SCF evaluation of the α tensor and found a value of 9.210 for $\bar{\alpha}$, 3% larger than our value. This is due to his bigger basis set.

The SCF values of β were found to be extremely sensitive to basis-set size and consequently, since our MC SCF calculations had (because of computational restrictions) to use a limited basis, β was not calculated at this level of theory. This problem has been discussed previously by Purvis and Bartlett [5] and Lazzeretti and Zanasi [8]; our SCF values are of the same order as theirs.

The field gradient tensors A , B , C have until now received very little attention, which is unfortunate since they can play an important role in molecular-charge interactions. In Table 4 we give all the independent components. For the same reasons as for β , only SCF values were obtained for B . A finite-field treatment has been used by Dacre [9] at the SCF level for the A and C tensors, however his values are quite different from ours since his origin was taken to be at the O atom and these quantities are origin dependent. His values will also differ from ours due to his neglect of the B tensor in making his calculations. It appears

Table 4. Values of A , B and C tensor components in atomic units

Basis	Method	$A_{x,zx}$	$A_{y,zy}$	$A_{z,xx}$	$A_{z,zz}$	$C_{xy,xy}$	$C_{xz,xz}$	$C_{yz,yz}$	$C_{xx,xx}$	$C_{yy,yy}$	$C_{zz,zz}$
I	SCF	6.27	1.40	1.62	1.68	8.48	11.06	4.72	11.78	12.02	10.10
II	SCF	6.71	1.69	2.08	1.90	7.18	10.15	2.92	10.63	10.32	8.42
II	MC SCF	7.46	1.68	2.54	2.44	8.48	11.33	4.41	11.65	12.58	8.76
Basis	Method	$B_{xy,xy}$	$B_{xz,xz}$	$B_{yz,yz}$	$B_{xx,xx}$	$B_{xx,zz}$	$B_{yy,xx}$	$B_{yy,zz}$	$B_{zz,xx}$	$B_{zz,zz}$	
I	SCF	-83.61	-87.11	-80.54	-76.61	39.14	234.06	67.99	55.78	-90.91	
II	SCF	-56.95	-60.42	-45.38	-67.55	21.36	124.36	43.90	33.84	-66.83	

from Table 4 that electron correlation does not change the A and C tensors inordinately.

The only other work in which the A tensor has been calculated is that of John et al. [10]. Their SCF value of $A_{z,zz}$, 1.642, is in agreement with our value obtained with the bigger basis set I. Their CI value for this component is equal to 2.194 and is comparable with our MC SCF result. If we take into account that $A_{z,yy} = -A_{z,zz} - A_{z,xx}$ then their SCF and CI values for this component, which are -3.638 and -4.070 , respectively, can be compared with our SCF values of -3.29 and -3.98 and our MS SCF value of -4.98 . The last two independent components $A_{x,zx}$ and $A_{y,zy}$ according to John et al. [10] have values 6.570 and 1.161 and are in agreement with our results. Their CI value for $A_{x,zx}$ of 6.742 is of the same order as our MC SCF result and their CI value for $A_{y,zy}$ of 1.786 is in agreement with our MC SCF result.

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