

## A Configuration Interaction Study of the Water Molecule and Interpretation of the Walsh Diagram

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Large scale *ab initio* SCF and CI calculations are used to investigate the bond angle dependence of the energy and one-electron properties of the water molecule. The SCF wave functions are used to reinvestigate the Hellmann–Feymann force interpretation of Walsh diagrams. The results are much closer to the ideas of Walsh than those obtained by Coulson and Deb.

**Key words:** SCF and CI calculation – water molecule – Hellmann–Feynman forces.

### 1. Introduction

Two main aims underline the present series of computations of the extensively studied water molecule. The first was to investigate the bond angle dependence of a number of one-electron properties using both SCF and large scale CI wave functions. The results both confirm and complement the only previous study [1] using wave functions of this quality in that, whilst Rosenberg et al. [1] considered the effects of varying the bond length, our results cover a wider range of bond angles. The second aim was to test the interpretation of Walsh diagrams, whose ultimate theoretical basis is still unclear, proposed by Coulson and Deb [2]. Since this explanation, which appears to us to be most promising, is based on the Hellmann–Feynman theorem, it should be tested using SCF wave functions of near Hartree–Fock quality rather than with the minimal basis set functions employed hitherto [2].

## 2. Choice of Basis Set and Calculations

Large scale SCF and CI calculations were performed on the H<sub>2</sub>O molecule at a fixed O—H separation over a range of angles. The primitive gaussian (10s6p/5s) basis of Huzingaga [3] was contracted according to the Dunning [4] (6,2,1,1, $\frac{1}{3}$ ,1,1, $\frac{1}{3}$ ,1,1) scheme and augmented by polarization functions to produce a (5s4p2d/3s1p) basis function set. A scale factor of 1.49 was used for the H atom functions. Polarization functions consisted of the Dunning [5] (3d)→(2d) contraction with a scale factor of 1.99 on the O atom and an uncontracted 2p function on the H atom with a scale factor of 2.15.

It was decided to adopt such a basis on the evidence of previous calculations performed by Newmann and Moskowitz [6], Dunning, Pitzer and Aung [7], Rosenberg, Ermler and Shavitt [1], and Ermler and Kern [8]. These calculations showed that although this basis obtains a Hartree–Fock energy of  $-76.05886$  Hartrees at the approximate equilibrium geometry compared with an estimated Hartree–Fock limit energy of  $-76.067$  [9], it was still of a reasonably tractable size for use in a subsequent full singles plus doubles CI calculation. Although the largest basis reported to date consisted of the 77 contracted gaussian type orbitals (CGTO's) used by Popkie, Kistenmacher and Clementi [10] who obtained a Hartree–Fock energy of  $-76.06598$  Hartrees, the most extensive series of computations on the water molecule are those of Rosenberg et al. [1]. They adopted a 39 STO basis (molecule optimized) to produce a set of SCF and CI property surfaces.

The calculations of Rosenberg and Shavitt [11], comparing both CGTO and STO bases at extended zeta plus polarization level, showed that, whereas SCF and core correlation energies were described much better in an STO basis (due largely to the presence of inner core *p* functions providing angular correlation), both predict virtually identical valence shell correlation energies. Furthermore, the one-electron properties predicted by our basis are very similar to those of Rosenberg et al. [11].

Rosenberg et al. [1] did, however, find that the Hellmann–Feynman forces, the primary consideration of our calculation, were very basis set dependent, greatly supporting our own findings. These inadequacies in the basis become apparent in the size of the electric field present at the oxygen nucleus at near equilibrium geometry, the total force on the molecule at equilibrium geometry and the electric field gradients at the hydrogen nuclei. The faults were evident at both SCF and CI level in both our calculations and in those of Rosenberg et al.

SCF calculations were performed using the ATMOL3 program suite [12]. CI calculations used the direct CI approach [13] with a program written by one of us (WIF). These included all singles plus doubles excitations from the ground state Hartree–Fock wavefunction into all virtual orbitals. The CI calculations generated 4864 spin/symmetry adapted configuration state functions in the C<sub>2v</sub> point group. The energy and one-electron property expectation values were computed at fixed bond length (R(OH) = 1.8111 bohr) for 17 bond angles in the

**Table 1.** Energies (SCF  $\propto$  CI) and resolved Hellmann–Feynman forces ( $F_1$ ) for H<sub>2</sub>O (atomic units)

$\alpha$ /deg	$E_{\text{SCF}}$ /Hartree	$E_{\text{CI}}$ /Hartree	$F_1(\text{SCF})$ /a.u.	$F_1(\text{CI})$ /a.u.
0°	-76.0393088	-76.2872417	-0.0296	-0.0281
100°	-76.0519169	-76.2928651	-0.0102	-0.0085
104.45°	-76.0588612	-76.2929736	-0.0058	-0.0012
110.0°	-76.0583699	-76.2922477	0.0064	+0.0072
120.0°	-76.0537951	-76.2875015	0.0201	+0.01981
135.0°	-76.0403136	-76.2742047	0.0329	0.0347
150.0°	-76.0234465	-76.2578481	0.0340	0.0326
160.0°	-76.0133000	-76.2480657	0.0273	0.0208
170.0°	-76.0062010	-76.2412226	0.0153	0.0130

range 80° to 180°. Energy and total Hellmann–Feynman forces  $F_1$  (at the H nucleus) perpendicular to the OH bond are presented in Table 1. The CI predictions of some electric and magnetic one-electron properties for geometries in the region of the minimum energy are presented in Table 2 (atomic units).

As observed earlier, the values obtained compare very favourably with those of Rosenberg et al. [1]. The predictions at the equilibrium geometry of the one-electron properties are compared with those of the above authors and with experimentally obtained values in Table 3. The percentage corrections (Table 3) calculated by Ermler and Kern [8] enable the computed values to be compared with experiment to some extent. In the scheme used by Ermler and Kern reduced normal coordinates harmonic and anharmonic force constants were first calculated from the SCF potential energy hypersurface and subsequently used to vibrationally average the one-electron properties by fitting the property surfaces within the normal coordinate frame of reference. Although there is no theoretical justification for applying such zero-point corrections to our computed values they provide an estimate which is not expected to be unreasonable. As can be seen from Table 3, the zero-point vibrational corrections are in general negligible, being the order of 1%, although Ermler and Kern did find a 20% correction necessary for the electric field gradient at the O nucleus. Table 3 shows that the present values for the quadrupole components,  $r^2$  and electric field gradient components at the O nucleus agree extremely well with both experiments and those of Rosenberg et al. The dipole moment deviates very slightly from experiment, a feature common to calculations using CGTO's rather than STO's. Although the electric field gradients at the H nuclei agree poorly with experiment, they are very similar to those reported by Rosenberg et al. This deficiency is almost certainly caused by deficiencies in the basis and may be further compounded by failure to average over excited rotational states. Rosenberg et al. suggested that  $d$  functions would have to be included on the H nuclei if deuteron nuclear quadrupole coupling constants are to be accurately predicted. Average diamagnetic shielding constants also agree well with those of Rosenberg et al. and with experiment. Lastly, the first derivatives of the properties, calculated with respect to the bond angle were computed and are compared with those obtained by

**Table 2.** (Atomic Units) Electric and Magnetic Properties of H<sub>2</sub>O (CI)

	$\mu$	$\theta_{zz}$	$\theta_{yy}$	$q_{yy}(O)$	$q_{zz}(O)$	$q_{aa}(H_1)$	$q_{bb}(H_1)$	$\langle \frac{1}{R}(O) \rangle$	$\langle \frac{1}{R}(H_1) \rangle$	$F_z(O)$	$\langle R^2 \rangle$
90°	0.8502	1.2478	0.5441(5)	-1.2655(5)	-0.6064	-0.53037	0.22645	-23.4359	-5.7919(5)	-0.03267	-19.5014
100.0°	0.7966	1.7088	0.1243	-1.4918(5)	-0.3265	-0.52552	0.22725	-23.4373	-5.7638	-0.03244	-19.5326
102.5°	0.7817	1.8226	0.0200	-1.5415	-0.2614(5)	-0.5402	0.22757	-23.4377	-5.7571	-0.03247	-19.5404
104.45°	0.7697	1.9057	-0.0675	-1.5801	-0.2001	-0.52350	0.22803	-23.4380(5)	-5.7539	-0.03251(5)	-19.5463
107.5°	0.7506(5)	2.0483	-0.1865	-1.6339	-0.1358	-0.52258	0.22874	-23.4385	-5.7437	-0.03261	-19.5557
110.0°	0.7343	2.1596(5)	-0.2883(5)	-1.6771	-0.0748	-0.52249	0.22992	-23.4389	-5.7371	-0.03269(5)	-19.5633
120.0°	0.6646(5)	2.5946	-0.6835(5)	1.8334(5)	0.1067(5)	-0.52320	0.23558	-23.4406	-5.7113	-0.03297	-19.5925

Conversion Factors:

Dipole moment: 1 a.u. = 2.541770 Debye

Quadrupole moment: 1 a.u. = 1.345046 Buckingham

Electric field gradient/Nuclear quadrupole coupling constant: 1 a.u. = 234.9648 MHz/Barn (<sup>17</sup>O = 0.026 barns <sup>2</sup>H = 0.0028 barns)

Diamagnetic shielding: 1 a.u. = 17.749666 ppm

Force/Electric field: 1 a.u. = 8.238879 dyne

Distance: 1 a.u. = 0.52917 Bohr

$\langle r^2 \rangle$ : 1 a.u. = 0.2800285 × 10<sup>-16</sup> cm<sup>2</sup>

**Table 3.** Comparison of Results for Properties of Water

Property/Units	This calc. (CI)	Rosenberg <i>et al.</i> (CI)	Experiment	Estimated zero point corrections [8]
$E_{\text{min}}/\text{Hartree}$	-76.292975	-76.3398025	-76.4	
$\theta_e/\text{deg}$	104.90	104.93	105.019 <sup>a</sup> 103.89 <sup>b</sup> 104.52 <sup>c</sup>	
$r_e/\text{\AA}$	-	0.9527	0.9574 <sup>a</sup> 0.9587 <sup>b</sup> 0.9572 <sup>c</sup>	
<b>Quadrupole moment</b>				
$\theta_{yy}/\text{Buckingham}$	2.6013	2.6197	2.63 ± 0.02	2.15%
$\theta_{zz}/\text{Buckingham}$ (with respect to centre of mass)	-0.1433	-0.1199	-0.13 ± 0.03 <sup>f</sup>	10.5%
$\sigma_{aa}^{(d)}(0)/\text{ppm}$	416.02	416.42	416.1	—
$\sigma_{aa}^{(d)}(\text{H}_1)/\text{ppm}$	102.07	102.83	102.4 [9]	+1%
<b>Electric field gradient (at O)</b>				
$(eqQ/h)^{(^{17}\text{O})_{zz}}$ (MHz)	-1.1447	-1.085	-1.28 ± 0.01	+22.7%
$(eqQ/h)^{(^{17}\text{O})_{yy}}$	-8.9775	-9.724	-8.89 ± 0.03 <sup>h</sup>	0.4%
<b>Electric field gradient (at H)</b>				
$(eqQ/h)^{(^2\text{H})_{aa}}$ (KHz)	350.00	362.46	307.95 ± 0.14	
$(eqQ/h)^{(^2\text{H})_{bb}}$	-150.09	-157.70	-133.13 ± 0.14 <sup>h</sup>	1%
$\langle r^2 \rangle / 10^{16} \text{ cm}^2$ (with respect to centre of mass)	-5.4758	-5.4590	± 5.1 ± 0.7 <sup>e</sup>	0.1(5)%
<b>Dipole moment</b>				
$\mu_z/\text{Debye}$	1.9523	1.9070	± 1.8546 <sup>d,e</sup>	0.3%

<sup>a</sup> See ref. 15.<sup>b</sup> See ref. 16.<sup>c</sup> See ref. 17.<sup>d</sup> See ref. 18.<sup>e</sup> See ref. 19.<sup>f</sup> See ref. 20.<sup>g</sup> See ref. 21.<sup>h</sup> See ref. 22.

Rosenberg *et al.* in Table 4. Again they show good agreement with the values reported by the above authors, with the exception of the  $\partial(q_{xx})/\partial\alpha$  values at the H nuclei.

The CI calculations in general provide strong support for the computed properties of Rosenberg *et al.* and in general agree very well with experimental values.

### 3. Interpretation of Walsh Diagrams

The diagrams, now called Walsh diagrams, introduced by Mulliken [22] and extensively refined and applied by Walsh [23] display the variation with molecular geometry of a loosely defined orbital energy called the Walsh ordinate. Although

**Table 4.** First Derivatives of One Electron Properties (atomic units per radian) ( $\partial Pe/\partial\alpha$ ) at Equilibrium Position

Property		This work	Rosenberg <i>et al.</i> [1]
1. Dipole/ $\mu_z$	$\mu_z$	-0.356933	-0.3668455
2. Quadrupole	$\theta_{zz}$	2.584756	—
	$\theta_{yy}$	2.365061	—
3. Electric field gradients (at oxygen)	$q_{xx}$	-0.380616	-0.3822994
	$q_{zz}$	-1.44073	-1.4490063
4. $\langle r^2 \rangle$		-0.17561	—
5. $\langle 1/R(0) \rangle$		0.00895724	—
6. $\langle 1/R(H_1) \rangle$		-0.15344	—
7. Electric field gradients (at $H_1$ )	$q_{xx}(H_1)$	-0.030025	-0.03408(2)
	$q_{zz}(H_1)$	0.297795	0.30958
	$q_{yz}(H_1)$	0.087778	0.088904

these diagrams have greatly deepened our understanding of the shapes of small molecules in both their ground and excited states, their theoretical basis is still uncertain. Although many workers have attempted to identify the Walsh ordinate precisely the recent review [24] shows both that none of the early attempts can be regarded as satisfactory and that no single explanation is yet accepted universally. Recently, Stenkamp and Davidson [25] have made the interesting suggestion that the Walsh ordinate is the eigenvalue of a new Fock Hamiltonian (the ICSCF operator) which has the property that the total molecular energy exactly equals the sum of the energies of the occupied orbitals. This explanation is not altogether convincing firstly because the physical significance of the orbital energies is not entirely clear since they differ so greatly from Hartree-Fock ones and more importantly because the equilibrium bond angles of several  $AB_2$  species are significantly over-estimated unless the core orbitals are included. Indeed  $NH_2^+$  is predicted to be linear if the  $1a_1$  (N 1s core orbital) is omitted. Mehrotra and Hoffman [26] have recently defined tempered orbitals which minimize the average of the energies of all the low lying levels. They showed computationally for ground states that the sum of the energies of the occupied tempered orbitals approximates closely the SCF energy (including internuclear repulsion) for the geometries of interest. On this basis they suggested that the Walsh ordinate should be identified with the tempered orbital energy and that internuclear repulsion plays no role in Walsh diagrams. Although this work clearly merits further development it can not be regarded as definite in the absence of theoretical reasons why the sum of the tempered orbital energies should approximate the molecular energy.

In 1971, Coulson and Deb [2] suggested that the Walsh ordinate is the integral over the appropriate parameter describing molecular geometry of the orbital contribution to the Hellman-Feynman force. Not only is this idea immediately appealing because the total electronic contribution to the force is the sum of contributions from each occupied molecular orbital but it is also unaffected by any

of the difficulties besetting the other explanations. Furthermore, the idea has been extensively applied [27, 28] qualitatively because simple physical arguments can be used to predict the sign and geometry dependence of the orbital force contributions. However, the only computational tests of the Coulson–Deb explanation reported so far [2] both used minimal basis set SCF wave functions which do not obey the Hellmann–Feynman theorem [29] whilst the water wave function [30] used [2] predicts an equilibrium inter-bond angle of approximately  $120^\circ$ . In this paper large basis set SCF wavefunctions which can be expected to satisfy the Hellmann–Feynman theorem are used to repeat the Coulson–Deb calculation of the  $\text{H}_2\text{O}$  Walsh diagram. Although the computed diagram would not depend on the model used to describe the bending of the molecule if the wavefunction satisfied the Hellmann–Feynman theorem exactly, those derived from SCF wavefunctions not at the Hartree–Fock limit will be model dependent. Coulson and Deb pointed out that the model (model a of [2]) in which the oxygen atom is considered fixed in space and the bending considered to arise from motion of the two protons along directions perpendicular to the bonds would be expected to be least sensitive to wavefunction errors. The total energy of the molecule relative to that of the linear geometry is, in the notation of [2],

$$E(\alpha) = (\text{cosec}(\alpha/2) - 1)/(2\lambda) + 2\sum_j w^j(\alpha).$$

The first term is the nuclear repulsion contribution whilst the quantities  $w^j(\alpha)$ , those plotted in the Walsh diagram are integrals over the orbital contributions  $f_{y_1}^j(\alpha)$  to the Hellmann–Feynman force. The values of the latter quantities (Table 5) derived from the present near Hartree–Fock wavefunctions are surprisingly similar to the previous ones [2] in view of the simplicity of the Ellison–Shull wavefunction [30]. The  $1a_1$  contributions are not presented because they are all less than  $7 \times 10^{-5}$  a.u. in magnitude. The present results greatly strengthen ones confidence in the Coulson and Deb explanation because whilst their  $2a_1$  and  $1b_2$  contributions are very similar to ours, the present  $3a_1$  contributions favour the bent geometry much more than those of Coulson and Deb. They found that the  $2a_1$  and  $3a_1$  orbitals favoured bending to an equal extent. Furthermore, the  $1b_1$  contributions which vanish identically for a minimal basis set wavefunction are indeed found to be very small. The Walsh diagram calculated by integrating these forces, which is compared with that of Coulson and Deb in the figure, accords much more with the argument of Walsh that it is the  $3a_1$  orbital which is the dominant driving force behind the bending of the molecule. Confidence in this Walsh diagram is reinforced by the close agreement (Table 1) between the total Hellmann–Feynman forces on nucleus  $\text{H}_1$  in the  $y_1$  direction predicted by the SCF wavefunctions with those predicted by the CI wavefunctions. Furthermore the equilibrium interbond angle ( $106.2^\circ$ ) for which the  $F_1$  force vanishes agrees closely with that ( $104.0^\circ$ ) which minimizes the total SCF energy.

It should be pointed out that inclusion of the internuclear repulsion term in [1] is essential because the sum of the orbital contributions by itself predicts no minimum in the energy. This clearly shows that those portions of the internuclear

**Table 5.** Orbital Contributions  $f_{y_1}^g$  to the Hellmann–Feynman Force (a.u.) Acting on the Hydrogen Atom in the Direction  $y_1$  Perpendicular to the OH Bond

## (a) Present Results:

	80°	90°	100°	102°30'	104°27'	107°30'	110°
2a <sub>1</sub>	0.0463	0.0391	0.0334	0.0321	0.0311	0.0296	0.0285
1b <sub>2</sub>	-0.0762	-0.0687	-0.0604	-0.0583	-0.0566	-0.540	-0.0519
3a <sub>1</sub>	0.0702	0.0640	0.0591	0.0581	0.0572	0.0560	0.0549
1b <sub>1</sub>	0.0049	0.0047	0.0045	0.0045	0.0044	0.0043	0.0043

	120°	127°30'	135°	142°30'	150°	160°	170°
2a <sub>1</sub>	0.0242	0.0212	0.0182	0.0154	0.0124	0.0084	0.0043
1b <sub>2</sub>	-0.0434	-0.0372	-0.0311	-0.0254	-0.0199	-0.0129	-0.0064
3a <sub>1</sub>	0.0507	0.0472	0.0431	0.0383	0.0326	0.0232	0.0121
1b <sub>1</sub>	0.0040	0.0037	0.0033	0.0030	0.0024	0.0018	0.0009

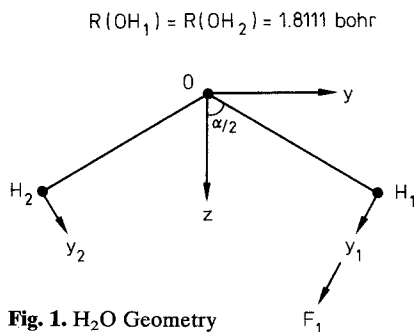
## (b) Coulson and Deb [2]:

	90°	100°	110°	120°
2a <sub>1</sub>	0.034	0.033	0.030	0.027
1b <sub>2</sub>	-0.062	-0.054	-0.050	-0.045
3a <sub>1</sub>	0.041	0.037	0.035	0.034

repulsion which can be associated with core electrons in more complicated systems should be identified because such nuclear repulsions are much larger than the interproton repulsions in AH<sub>2</sub> molecules. Thus using model a in an AB<sub>2</sub> molecule the sum of the contributions from all the B core electrons plus the repulsion calculated by placing on each B atom a positive charge equal to the number of core electrons on one B atom is clearly the total core contribution which would be expected to be small. The geometry is then determined by adding to the valence orbital contributions which are used to construct the Walsh diagram, that portion of the repulsion between the B nuclei which has not been included in the core term. Although no conceptual difficulties arise, the important computational testing of these ideas may be very difficult because it is hard to calculate reliably the Hellmann–Feynman force acting on a heavy nucleus. This is shown by the failure of the model for the bending of the water molecule which involves motion of the oxygen atom.

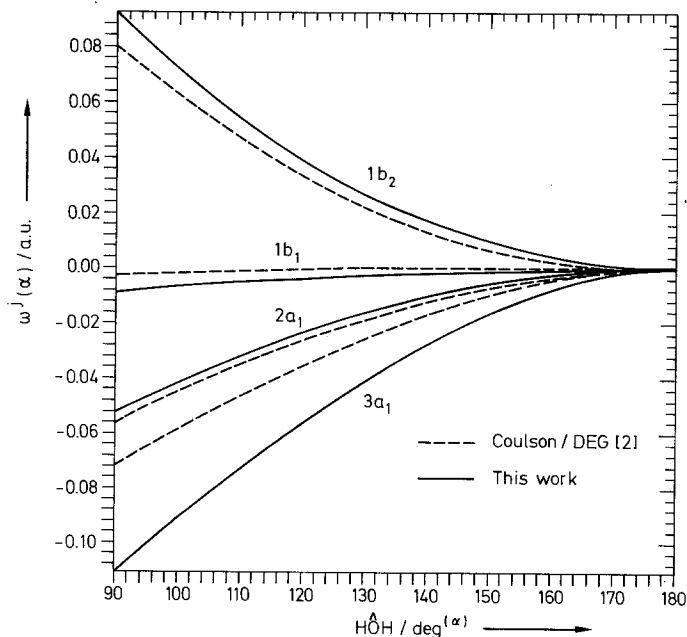
Finally, Coulson and Deb's [2] second model (model b) for the bending of water in which the expression for the electron nuclear force has to be augmented by further terms is considered. These further terms would vanish if the wavefunction satisfied the Hellmann–Feynman theorem exactly. Unfortunately the present results barely improve the previous ones because for a bond angle of 104° 27' we





find these further terms to be  $-0.011$ ,  $0.060$ ,  $0.032$ ,  $-0.087$  and  $0.012$  respectively, for the  $1a_1$ ,  $2a_1$ ,  $1b_2$ ,  $3a_1$  and  $1b$ , molecular orbitals. These difficulties can be traced almost certainly to basis set inadequacies because both the present SCF and CI calculations and those of Rosenberg and Shavitt [11] predict too large a force on the oxygen atom.

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**Fig. 2.** Walsh diagrams for H<sub>2</sub>O

## References

1. Rosenberg, B. J., Ermler, W. C., Shavitt, I.: *J. Chem. Phys.* **65**, 4072 (1976)
2. Coulson, C. A., Deb, D. M.: *Int. J. Quant. Chem.* **5**, 411 (1971)
3. Huzinaga, S.: *J. Chem. Phys.* **42**, 1293 (1965)
4. Dunning, T. H.: *J. Chem. Phys.* **55**, 718 (1970)
5. Dunning, T. H.: *J. Chem. Phys.* **55**, 3958 (1971)
6. Newmann, D., Moskowitz, J. W.: *J. Chem. Phys.* **49**, 2056 (1968)
7. Dunning, T. H., Pitzer, R. M., Aung, S.: *J. Chem. Phys.* **57**, 5644 (1971)
8. Ermler, W. C., Kern, C. W.: *J. Chem. Phys.* **55**, 4851 (1971)
9. Ermler, W. C., Kern, C. W.: *J. Chem. Phys.* **61**, 3860 (1974)
10. Popkie, H., Kristenmacher, H., Clementi, E.: *J. Chem. Phys.* **59**, 1325 (1973).
11. Rosenberg, B. J., Shavitt, I.: *J. Chem. Phys.* **63**, 2162 (1975)
12. Saunders, V. R.: S.R.C. Daresbury Laboratory, Daresbury, Lancs., England
13. Roos, B. O., Siegbahn, P. in: *Electronic Structure Theory*, Vol. 3, edited by H. F. Schaefer III
14. Hoy, A. R., Bunker, P. R.: *J. Mol. Spectrosc.* **52**, 439 (1974); *ibid.* **59**, 159 (1975)
15. Cook, R. C., DeLucia, F. C., Helmonger, P.: *J. Mol. Spectrosc.* **53**, 62 (1974)
16. Benedict, W. S., Gailar, N., Plyler, E. K.: *J. Chem. Phys.* **24**, 1139 (1956)
17. Clough, S. A., Beers, Y., Klein, G. P., Rothman, L. S.: *J. Chem. Phys.* **59**, 2254 (1973)
18. Dyke, T. R., Muenter, J. S.: *J. Chem. Phys.* **59**, 3125 (1973)
19. Verhoeven, J., Dymanus, A.: *J. Chem. Phys.* **52**, 3222 (1970)
20. Eisenberg, D., Prochan, J. M. Flygare, W. H.: *J. Chem. Phys.* **43**, 4531 (1965)
21. Verhoeven, J., Dymanus, A., Bluysen, H.: *J. Chem. Phys.* **50**, 3330 (1969)
22. Mulliken, R. S.: *Rev. Mod. Phys.* **14**, 204 (1942).
23. Walsh, A. D.: *J. Chem. Soc.* 2260 (1953)
24. Buenker, R. J., Peyerimhoff, S. D.: *Chem. Rev.* **74**, 127 (1974)
25. Stenkamp, L. Z., Davidson, E. R.: *Theoret. Chim. Acta (Berl.)* **30**, 283 (1973)
26. Mehrotra, P. K., Hoffman, R. A.: *Theoret. Chim. Acta (Berl.)* **48**, 301 (1978)
27. Deb, B. M.: *J. Amer. Chem. Soc.*, **96**, 2030 (1974)
28. Deb, B. M., Sen, P. N., Bose, S. K.: *J.A.C.S.* **96**, 2044 (1974)
29. Stanton, R. E.: *J. Chem. Phys.* **36**, 1298 (1962)
30. Ellison, F. O., Shull, H.: *J. Chem. Phys.* **23**, 2348 (1955)

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