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A Point-Charge Representation of Frost-Model Wave Functions

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A point-charge representation of Frost-model wave functions is derived from a symmetry-adapted perturbation theoretic expansion. The new point-charge model is simpler than those suggested previously yet gives good estimates of first-order molecular properties. The treatment can easily be extended to deal with second-order properties and, when this is done, formulae similar to those of the Drude theory are obtained. Using these formulae, theoretical expressions for the refractive indices of methane, ethane and water are computed and are in reasonable accord with experiment for the two hydrocarbons but less satisfactory for water.

Key words: Frost-model wave functions – Point-charge models – Refractive indices

1. Introduction

Symmetry-adapted perturbation theory has been used in a number of contexts for several years now [1–5]. Recently we have shown how it can be extended to deal with two perturbations [6] and how the extended theory can be applied to Frost-model wave functions [7]. This last application leads to almost trivially simple methods for computing first and second-order properties of molecules; such computed values are in quite satisfactory agreement with experimental values.

For calculating the electrostatic potential due to a molecule and the electrostatic interaction between pairs of molecules there are great advantages to be gained by replacing the electronic charge distribution by a number of point charges. The most elegant treatment of this procedure has been given by Hall [8] who showed that from Hartree-Fock wave functions based on a basis set of floating spherical Gaussian orbitals (FSGOs) an extremely accurate point-charge model could be set up. The disadvantage of Hall's method is that a large number of point charges are needed but Shipman [9] has introduced what can be considered as an approximate version of Hall's theory which reduces the number of point charges to manageable proportions.

Both Shipman's and Hall's methods begin with the conventional expression for the molecular first-order density matrix. If, however, the symmetry-adapted perturbation theory referred to above is applied to Frost-model wave functions the leading term in the first-order density matrix is much simpler than the conventional expression. The main purpose of this paper is to show that, as a consequence, it is possible to obtain from this a much simpler point-charge model.

Aside from its simplicity, the new point-charge model based on the symmetry-adapted perturbation expansion has the advantage that classical mechanics can be used to determine the effect of external perturbations on the charges. This allows second-order properties in addition to first-order ones to be considered. As will be seen, the extended model is very similar in form to the Drude model [10] but, unlike the Drude method itself, the parameters involved are obtained from *ab initio* wave functions and do not have to be found empirically.

2. First-Order Molecular Properties

Suppose W is a symmetric operator whose expectation value with respect to the molecular wave function Ψ gives the required first-order property W_1:

$$W_1 = \langle \Psi | W | \Psi \rangle \tag{1}$$

so that, for example, if W represents the effect of a static electric field on the molecule, W_1 will be the molecular dipole moment. The Frost-model [11] for a $2n$-electron molecule assumes that Ψ can be adequately approximated by an antisymmetrized product of n Gaussian functions i.e.

$$\Psi \approx \psi = A\Phi \tag{2}$$

where the antisymmetrizer, A, is defined so that $A^2 = A$ and Φ is the product function

$$\Phi = \prod_{i=1}^{n} \phi_i(2i)\phi_i(2i-1)\alpha(2i)\beta(2i-1) \tag{3}$$

with ϕ_i the ith Gaussian. In the conventional approach, W_1 in (1) is replaced by the expectation value of W with respect to ψ i.e.

$$W_1 \approx W_{01} = \langle \psi | W | \psi \rangle / \langle \psi | \psi \rangle = \langle \Phi | WA | \Phi \rangle / \langle \Phi | A | \Phi \rangle \tag{4}$$

As a rule W will be the sum of one-electron spin-independent operators:

$$W = \sum_{i=1}^{2n} w(\mathbf{r}_i) \tag{5}$$

It then follows that W_{01} can be expressed in terms of the electron density $\rho(\mathbf{r})$ of ψ:

$$\rho(\mathbf{r}) = 2 \sum_{s,t} T_{st}\phi_s(\mathbf{r})\phi_t(\mathbf{r}) \tag{6}$$

where, if $\mathbf{S}$ is the matrix whose r,s element S_{rs} is the overlap integral between the two Gaussians ϕ_s and ϕ_t, then $\mathbf{T} = \mathbf{S}^{-1}$. The result is

$$W_{01} = \int w(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \tag{7}$$

Recently [7] we have shown how symmetry-adapted perturbation theory can be used with Frost-model wave functions to calculate molecular properties. When the method is applied to first-order properties, the leading term in the perturbation expansion of W_1 is given by the expectation value of W with respect to the product function Φ. If the higher-order terms can be ignored, we have that:

$$W_1 \approx \overline{W}_{01} = \langle \Phi | W | \Phi \rangle \tag{8}$$

In the case when W takes the form of Eq. (5), $\overline{W}_{01}$ can be written in a form similar to W_{01}. To do this we introduce the electron density $\bar{\rho}(\mathbf{r})$ associated with Φ and defined by

$$\bar{\rho}(\mathbf{r}) = 2 \sum_s \phi_s(\mathbf{r}) \phi_s(\mathbf{r}) \tag{9}$$

and $\overline{W}_{01}$ is then given by

$$\overline{W}_{01} = \int w(\mathbf{r}) \bar{\rho}(\mathbf{r}) d\mathbf{r} \tag{10}$$

One interpretation of Eqs. (9) and (10) is that they are obtained from (6) and (7) by assuming that it is a reasonable approximation to replace the overlap matrix **S** and, hence, **T** by the unit matrix. This is not an interpretation we would wish to encourage but it is of some practical use to note that any formulae derived from (7) can be made to apply to (10) simply by replacing **S** with the unit matrix. For example, Tait and Hall [12] give an extensive set of formulae for calculating first-order molecular properties from Gaussian wave functions. Putting their P_{st} equal to T_{st} gives the formulae relevant to Frost-model wave functions, the property being computed via Eq. (7). By putting $P_{st} S_{st} = \delta_{st}$ the results obtainable via Eq. (10) can be found. It follows from this, of course, that W_{01} and $\overline{W}_{01}$ will give similar values if $T_{st} S_{st} \approx \delta_{st}$. But this is not a necessary condition, we suspect that more often than not the near equality of W_{01} and $\overline{W}_{01}$ is due to partial cancellation of the non-zero off-diagonal terms.

Neither $\overline{W}_{01}$ nor the more conventional expression W_{01} will actually equal W_1 and both ought to be corrected by the addition of extra terms. For W_{01} these must correct for the fact that ψ is only an approximation to the true molecular wave function Ψ. For $\overline{W}_{01}$ two types of correction must be applied, the first repairs the lack of antisymmetry in Φ and the second allows for the fact that the zero-order Hamiltonian used in the perturbation theory is not the molecular Hamiltonian. Of course it is not a practical possibility to calculate these correcting terms either for W_{01} or $\overline{W}_{01}$ so that the utility of both methods depends on whether or not (7) or (10) are reasonable approximations to W_1.

To examine this we can take the value of W_1 to be the same as the experimental value of the particular property where accurate experimental values are available. Alternatively W_1 can be assumed to be the same as the most accurate theoretical value, found, as a rule, from good quality Hartree-Fock wave functions.

In Table 1 we compare values of dipole and quadrupole moments of a few small molecules found by using (7) and (10) with the best estimates of W_1. It might have been expected that (7) would always give more satisfactory results than (10) but this is by no means the case. For in most cases the results using W_{01} and $\overline{W}_{01}$ are comparable and for those that are not $\overline{W}_{01}$ is as likely to be the more accurate as W_{01} is. Thus it would seem that we do as well by using the unconventional formula (10) as by using the conventional one (7).

Table 1. Comparison of some first-order properties computed from (7) and (10) with "exact" values

Molecule	Property	Theoretical value[a]		"exact"[a,b]
		W_{01}	$\overline{W}_{01}$	
LiH[c]	Dipole moment[d]	−6.28	−6.11	(−)5.88[e]
	Quadrupole moment[f] $Q_{\parallel}$	−5.42	−5.21	−7.34[g], −4.15[h], −4.35[i]
	$Q_{\perp}$	2.71	2.61	3.67[g], 2.08[h], 2.18[i]
C_2H_6[j]	Quadrupole moment[f] $Q_{\parallel}$	−0.95	−0.62	−0.8±0.1[k]
	$Q_{\perp}$	0.48	0.31	0.4±0.1[k]
$H_2O(C)$[l, m]	Dipole moment[m], μ_{zz}	1.83	1.58	(+)1.85[n]
	Quadrupole moment[m], Q_{xx}	3.01	2.93	2.63[p], 1.6±0.6[q]
	Q_{yy}	−3.45	−3.13	−2.50[p], −2.0±0.6[q]
	Q_{zz}	0.44	0.20	−0.13[p], 0.4±0.4[q]
$H_2O(S)$[l, m]	Dipole moment[m], μ_{zz}	2.27	1.85	(+)1.85[n]
	Quadrupole moment[m], Q_{xx}	3.23	3.05	2.63[p], 1.6±0.6[q]
	Q_{yy}	−3.59	−3.23	−2.50[p], −2.0±0.6[q]
	Q_{zz}	0.36	0.18	−0.13[p], 0.4±0.4[q]

[a] Dipole moments in debyes, quadrupole moments in buckinghams.

[b] Either experimental or accurate Hartree-Fock values.

[c] Wave function of Ref. [12].

[d] Positive direction Li to H.

[e] Experimental value, Ref. [14].

[f] $Q_{\parallel}$, $Q_{\perp}$ refer to components parallel and perpendicular to molecular axis, origin at centre of mass.

[g] Theoretical value, Ref. [15].

[h] Theoretical value, Ref. [16].

[i] Theoretical value, Ref. [17].

[j] Geometry: carbon atoms at (0, 0, ±1.4579) (units are bohrs), one hydrogen at (1.9616, 0, −2.157) the others being given by symmetry. Inner shell exponents, 9.30054 a.u.; CH bond exponents, 0.35511 a.u.; CC bond exponent, 0.35267 a.u. One of the CH bond orbitals centered at (1.2002, 0, −1.8815), the remainder being given by symmetry. Wavefunction of D. Martin.

[k] Experimental value, Ref. [18].

[l] For details of the Frost-model wave functions see the appendix.

[m] x and z axes in molecular plane. z axis bisects HOH angle with positive direction from O towards the H atoms. Quadrupole moments relative to centre of mass.

[n] Experimental value, Ref. [19].

[p] Experimental value, Ref. [20].

[q] Experimental value, Ref. [21].

A final point concerns the Frost-model wave functions for water. It is well-known that the Frost model does not work properly for water [13] owing to the propensity of the lone-pair orbitals to coalesce with the inner-shell oxygen orbital. Normally, therefore, the positions of the lone-pair FSGO's are fixed by some subjective criterion. Since we are mainly interested in electrical properties we choose to fix these positions so that a good molecular dipole moment is obtained. This, of course, gives two possible choices depending on whether (7) or (10) is used to compute the dipole moment. Thus we use two different Frost-model wave functions for water; the first, $H_2O(C)$, gives a good value of the dipole moment via the conventional formula (7) and the second $H_2O(S)$ gives a good dipole moment when the symmetry-adapted perturbation expansion formula (10) is used. Further details of these wave functions are given in the Appendix.

3. Point-Charge Models

Hall's point-charge model [8, 12] when applied to Frost-type wave functions consists of replacing (6) by

$$\rho^*(\mathbf{r}) = 2\sum_{s,t} S_{st}^{-1} S_{st}\,\delta(\mathbf{r}-\mathbf{R}_{st}) \tag{11}$$

where $\mathbf{R}_{st} = (\alpha_s\mathbf{R}_s + \alpha_t\mathbf{R}_t)/(\alpha_s+\alpha_t)$; α_s, α_t, $\mathbf{R}_s, \mathbf{R}_t$ being the exponents and centres of the Gaussians r and s. Eq. (11) represents the charge density as due to n point charges of magnitude $\{2S_{tt}^{-1}S_{tt}\}$ at the centres of the Gaussians and $\frac{1}{2}n(n-1)$ point charges of magnitude $\{4S_{st}^{-1}S_{st}\}$ positioned between the Gaussian centres. All told, therefore, there are $\frac{1}{2}n(n+1)$ point charges.

The main properties of this point-charge model are as follows:

a) The total electronic charge, $2n$, and the electronic dipole moment $\boldsymbol{\mu}_e$ are conserved i.e.

$$2n = \int \rho(\mathbf{r})d\mathbf{r} = \int \rho^*(\mathbf{r})d\mathbf{r}$$

$$\boldsymbol{\mu}_e = \int \mathbf{r}\rho(\mathbf{r})d\mathbf{r} = \int \mathbf{r}\rho^*(\mathbf{r})d\mathbf{r} = \boldsymbol{\mu}_e^*$$

where we follow Tait and Hall [12] in using symbols superscripted with an asterisk to represent point-charge model values.

b) Off-diagonal elements of the quadrupole tensor **Q** are of the form $Q_{xy} = Q_{xy}^*$, $Q_{xz} = Q_{xz}^*$, $Q_{yz} = Q_{yz}^*$ but there are significant differences between diagonal elements computed using (6) and (11) i.e. $Q_{xx} \neq Q_{xx}^*$ etc., however the error in Q_{xx}^*, Q_{yy}^*, Q_{zz}^* is constant. For higher moments, the use of (11) leads to quite large errors which in general increase with distance.

c) The electronic part of the potential $V(\mathbf{r})$, the components of the electric field $\mathbf{E}(\mathbf{r})$ and the components $\mathbf{q}(\mathbf{r})$ of the electronic field gradient tensor, all evaluated at the point $\mathbf{r}$, are such that the differences $V-V^*$, $\mathbf{E}-\mathbf{E}^*$, $\mathbf{q}-\mathbf{q}^*$ decrease exponentially at large distances. The error decreases more rapidly than the actual value.

Clearly we can make a similar point-charge approximation to $\bar{\rho}(\mathbf{r})$ by means of the following expression:

$$\bar{\rho}^*(\mathbf{r}) = \sum_s 2\delta(\mathbf{r}-\mathbf{R}_s) \tag{12}$$

which represents the charge density as due to n point charges of magnitude two units positioned at the Gaussian centres. We note that there is a considerable simplification in going from (11) to (12) since the number of charges is reduced from $\frac{1}{2}n(n+1)$ to n. It is easy to show that properties (a), (b), (c) of the point-charge model represented by Eq. (11) also apply to that represented by (12).

An alternative point-charge model, which also uses n charges positioned at each Gaussian centre has been introduced by Shipman [9]. Shipman's model, however, can be regarded as an approximation to Hall's model in which the $\frac{1}{2}n(n-1)$ off-centre charges are redistributed onto the Gaussian centres.

Since it is to be expected that the use of the point-charge density (12) for computing first-order properties will give the same qualitative agreement with the

Table 2. LiH potential from various models[a]

Distance from Lithium atom in bohrs	V	V^*	$\bar{V}$	$\bar{V}^*$	V^s
1.2	0.491008	0.482258	0.477708	0.468571	0.480649
2.4	0.129874	0.128673	0.125853	0.124670	0.128097
3.6	0.049057	0.048996	0.047451	0.047392	0.048757
4.8	0.022969	0.022968	0.022194	0.022193	0.022851
6.0	0.012391	0.012391	0.011964	0.011964	0.012326
7.2	0.007383	0.007383	0.007126	0.007126	0.007344

[a] Potential in atomic units. For explanation of symbols see text.

results found from expression (10) as Hall's point-charge model gives with respect to results found from expression (7), we see no advantage in making a large number of comparisons such as was done by Tait and Hall [12]. Instead we simply note that the conclusions reached by the latter authors will also hold for the new point-charge model.

However, it does seem worthwhile to make at least one comparison between the various point-charge models. We do this for the popular example of the electrostatic potential of the LiH molecule at points on a line passing through the lithium atom and perpendicular to the molecular axis. The results are shown in Table 2. In the table V refers to the conventional potential obtained from $\rho(\mathbf{r})$, V^* is Hall's point-charge potential, $\bar{V}$ is the potential using $\bar{\rho}(\mathbf{r})$, $\bar{V}^*$ is the point-charge potential from $\bar{\rho}^*(\mathbf{r})$ (Eq. (12)) and V^S is Shipman's point-charge potential. As is to be expected V, V^* and V^S are in good agreement with V^* closer to V than V^S is. $\bar{V}^*$ is in good agreement with $\bar{V}$ again as expected. V and $\bar{V}$ differ by about 4%, $\bar{V}$ being smaller, and V^* and $\bar{V}^*$ differ by about the same amount. The potential obtained from Frost-model wave functions can hardly be very accurate but one hopes that the qualitative features of the potential are correct. As far as this is concerned we feel that V and $\bar{V}$ and, hence, V^* and $\bar{V}^*$ will usually exhibit the same qualitative behaviour so that whichever is found the most convenient can be used.

4. The Classical Equation of Motion

The purpose of this section is to relate the point-charge model represented by $\bar{\rho}^*$ to the classical theory of the electron. To do this we note that the product function Φ which is used as zero-order function in the symmetry-adapted perturbation theory is an eigenfunction of the Hamiltonian H_0,

$$H_0 = \sum_{s=1}^{n} \{h_s(2s) + h_s(2s-1)\} \tag{13}$$

which is a sum of one-electron harmonic oscillator Hamiltonians

$$h_s = -\tfrac{1}{2}\nabla^2 + 2\alpha_s^2 |\mathbf{r}_s|^2 \tag{14}$$

where $\mathbf{r}_s = \mathbf{r} - \mathbf{R}_s$.

The classical Hamiltonian which is the analogue of (14) will be just the sum of Hamiltonians for classical oscillators and, hence, for the $2s$-electron the classical path with zero phases will be given by

$$\mathbf{r}^c(2s)=\mathbf{R}_s+\mathbf{A}_s\cos\Omega_s t \tag{15}$$

where $\mathbf{A}_s$ is the amplitude of the oscillation and $\Omega_s=2\alpha_s$ is the frequency. The classical charge-density for the $2n$-electron system will be given by

$$\rho^c(\mathbf{r},t)=2\sum_s\delta(\mathbf{r}-\mathbf{R}_s-\mathbf{A}_s\cos\Omega_s t) \tag{16}$$

which, of course, is time dependent. This time dependence can be removed by setting $\mathbf{A}_s=0$ $s=1\ldots n$ which implies a set of stationary point charges. Not surprisingly this leads to $\rho^c=\bar{\rho}^*$, so that (12) is equivalent to the classical charge density of n stationary point charges.

5. Second-Order Properties

The symmetry-adapted perturbation theory which leads to Eq. (8) for the first-order property W_1 can also be applied to finding second-order properties. The result is that

$$W_2\approx\overline{W}_{02}=\tfrac{1}{2}\int w(\mathbf{r})\bar{\rho}'(\mathbf{r})d\mathbf{r} \tag{17}$$

where $\bar{\rho}'(\mathbf{r})$ represents the first-order change in $\bar{\rho}(\mathbf{r})$ due to the perturbation W. The classical equations of motion can be used to find $\bar{\rho}'(\mathbf{r})$ and thus the point-charge model can be extended so as to compute second-order properties.

As an example consider the case where the molecule is perturbed by a static electric field $\mathbf{E}$ so that the equation of motion of the $2s$ and $(2s-1)$ electrons is

$$\frac{d^2\mathbf{r}_s}{dt^2}+4\alpha_s^2\mathbf{r}_s=\mathbf{E} \tag{18}$$

so that

$$\mathbf{r}(2s)=\mathbf{R}_s+\frac{1}{4\alpha_s^2}\mathbf{E} \tag{19}$$

on setting the amplitude $\mathbf{A}_s$ for the harmonic terms equal to zero. The total density will therefore be

$$P(\mathbf{r})=2\sum_s\delta\left(\mathbf{r}-\mathbf{R}_s-\frac{1}{4\alpha_s^2}\mathbf{E}\right) \tag{20}$$

and hence

$$\bar{\rho}'(\mathbf{r})=P(\mathbf{r})-\bar{\rho}^*(\mathbf{r})=2\sum_s\left\{\delta\left(\mathbf{r}-\mathbf{R}_s-\frac{1}{4\alpha_s^2}\mathbf{E}\right)-\delta(\mathbf{r}-\mathbf{R}_s)\right\} \tag{21}$$

Since $w(\mathbf{r}) = -\mathbf{r}$ and the polarizability α satisfies $W_2 = -\frac{1}{2}\alpha\mathbf{E}$, it follows that

$$-\tfrac{1}{2}\alpha\mathbf{E} = -\tfrac{1}{2}\int \mathbf{r}\bar{\rho}'(\mathbf{r})d\mathbf{r} = -\sum_s \left\{\mathbf{R}_s + \frac{1}{4\alpha_s^2}\mathbf{E} - \mathbf{R}_s\right\} \tag{22}$$

$$\text{i.e. } \alpha = \tfrac{1}{2}\sum_s 1/\alpha_s^2 \tag{23}$$

This agrees with the result of Frost-model perturbation theory [7].

If the applied field is time dependent the equation of motion becomes

$$\frac{d^2\mathbf{r}_s}{dt^2} + 4\alpha_s^2\mathbf{r}_s = \mathbf{E}\cos\omega t \tag{24}$$

where ω is the frequency of the field. It follows that

$$\mathbf{r}(2s) = \mathbf{R}_s + \frac{1}{4\alpha_s^2 - \omega^2}\mathbf{E}\cos\omega t \tag{25}$$

Consequently the frequency-dependent polarizability is given by

$$\alpha(\omega) = 2\sum_s \frac{1}{\omega_s^2 - \omega^2} \tag{26}$$

where $\omega_s^2 = 4\alpha_s^2$. When $\omega = 0$, Eq. (26), naturally enough, reduces to the frequency independent case given by Eq. (23).

Both these examples are familiar. The equations correspond to those used in the Drude theory [10]. Thus we can conclude that when the point-charge model is extended to allow second-order properties to be computed one arrives naturally at the Drude model. However, there are important differences to be borne in mind. In the Drude theory, as usually presented, the oscillator potential is taken to be $-k\mathbf{r}_s$ where k is an empirical parameter. In the present treatment $k = 4\alpha_s^2$ where α_s is not an empirical parameter but an *ab initio* one obtained directly from the Frost-model wave function. Moreover, in the Drude theory, the oscillators are either the atoms in the molecule or, more usually, the molecule is assumed to oscillate as if it were a single particle, so that there is just one centre and one frequency of oscillation. The point-charge model has n particles oscillating with different frequencies (although some may be equal due to symmetry) about different centres whose positions are obtained from *ab initio* calculations. Thus the present interpretation is much less empirical than the Drude model itself.

To illustrate the use of Eq. (26) consider the refractive indices of water, methane and ethane. For small frequencies where $n \sim 1$ the Clausius-Mossotti relation simplifies to

$$n - 1 \approx 2\pi d\alpha(\omega) \tag{27}$$

where d is the number density of the gas. As a rule experimental values are fitted to an expression of the form

$$n - 1 = \frac{C}{\nu_0^2 - \nu^2} \tag{28}$$

Table 3. Values of C and v_0^2

Molecule	C^a This paper	Ref. [22]	Experiment[c]	v_0^{2b} This paper	Ref. [22]	Experiment[c]
CH_4	5.56	5.42	5.03	0.143	0.140	0.117
C_2H_6	9.73	10.28	8.49	0.142	0.148	0.114
$H_2O(C)$	5.56	3.07	2.63	0.335	0.153	0.107
$H_2O(S)$	5.55	3.07	2.63	0.338	0.153	0.107

[a] Units of 10^{27} cm^{-2}. [b] Units of 10^{22} cm^{-2}. [c] Ref. [23].

and empirical values of C and v_0^2 are given in Table 3. The frequency dependent polarizability $\alpha(\omega)$ is a sum of a number of terms like (28) but this sum can be approximated by just one term. The theoretical values of C and v_0^2 obtained in this way from Frost-model wave functions are given in Table 3, as also are values found from more accurate wave functions [22]. The table shows reasonable agreement between theory and experiment for methane and ethane but for water the Frost-model results appear to be wrong by a factor of two.

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Appendix: Frost Model for Water

To obtain Frost-model wave functions which give a good dipole moment for water we fix the nuclear geometry so that OH = 1.808 bohrs and the HOH angle is 104.5°. The lone-pair orbitals are centred on lines in the y–z plane passing through the oxygen atom, the angle between the two lines being 110° (for the x,y,z directions see footnote to Table 1; the origin, however, is taken at the oxygen nucleus). The lone-pair orbitals were fixed for various values of z and all the exponents together with the OH bonding orbital positions were optimized. As can be seen from the selection of results given in Table 4 the energies do not vary very much but the dipole moments do. The result using $\overline{W}_{01}$ (Eq. 10) is consistently closer to the experimental value than W_{01} except in the rather uncertain region very close to the origin, where the overlap matrix is nearly singular due to the lone pair orbitals almost coalescing with the oxygen inner-shell orbital. Because of this, near the origin the results do appear to be rather random and there are large changes in the dipole values for both $\overline{W}_{01}$ and W_{01} over small changes in z. Moreover, we have found difficulty in optimizing the wave function since the energy surface appears to be rather flat with a number of shallow minima.

In spite of these problems we find that when $z = -0.005$ bohrs we obtain a wave function for which

Table 4. Dipole moment and energy of H_2O

z-component of the lone pairs[a]	Dipole moment[b] W_{01}	 $\overline{W}_{01}$	Energy[c]
-0.05	2.42	2.10	-64.2314
-0.03	2.37	1.99	-64.2339
-0.01	2.27	1.85	-64.2345
-0.008	2.39	1.90	-64.2341
-0.005	1.83	1.58	-64.2382

[a] In bohrs.
[b] In debyes, experimental value = 1.85 (Ref. [19]).
[c] In hartrees, Hartree-Fock value = -76.06 (Ref. [24]).

Eq. (7) leads to a good dipole moment. We denote this wave function by $H_2O(C)$ and it has the following parameters:

Inner shell exponent, 17.31682; OH bond exponent, 0.55000; lone pair exponent, 0.54003; OH bond orbitals positioned at $(\pm 0.5202, 0, 0.4028)$ lone pair orbitals positioned at $(0, \pm 0.7140, -0.0050)$. The choice $z = -0.01$ bohrs gives a wave function from which a good dipole moment can be found by using Eq. (10). This wave function is denoted by $H_2O(S)$ and has the following parameters:

Inner shell exponent, 17.31272; OH bond exponent, 0.55793; lone pair exponent, 0.53857; OH bond orbitals positioned at $(\pm 0.4930, 0, 0.3817)$; lone pair orbitals positioned at $(0, \pm 0.0143, -0.0100)$.

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