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Point Charge Models for LiH, CH_4, and H_2O

A. D. Tait and G. G. Hall

Department of Mathematics, University of Nottingham, Nottingham, NG7 2RD, England

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Point charge models for LiH, CH_4, and H_2O are presented. The models preserve the correct total charge and dipole moment of the molecules. Relations between spherical Gaussian wave function values and point charge model values of a variety of one-electron molecular properties are derived. The errors inherent in some of the point charge model values are of two types: those which may be large but are easily evaluated and those which are small and diminish rapidly as the distance from the molecule increases. The models are shown to be a reliable means of calculating one-electron properties and possible uses of the models are suggested.

Key words: Point charge models – One-electron properties

1. Introduction

In a recent paper Hall [1] has proposed a point charge model for molecules. The model preserves the correct total charge of the molecule and the dipole moment. The model also gives a good approximation to the electrostatic potential outside of the shell of the molecule. In this paper we examine the point charge model as a means of calculating a variety of one-electron properties. As examples the results for LiH, CH_4, and H_2O are presented. Lithium hydride was chosen as a very simple ionic system, methane because of its high symmetry, and water because of the presence of lone pairs.

The electron density in a closed shell molecule is defined by

$$\varrho(\boldsymbol{r}) = 2\sum_{st} p_{st}\,\varphi_s(\boldsymbol{r})\,\varphi_t(\boldsymbol{r})\,, \tag{1}$$

where p_{st} is an element of the density matrix and is calculated here from an SCF wave function. The factor of two appears as a result of summing over the two spins. $\varphi_s(\boldsymbol{r})$ is an orbital with centre $\boldsymbol{r}_s$, exponent α_s and normalized to 1. If φ_s and φ_t are spherical Gaussian orbitals then their product is a spherical Gaussian with centre at

$$\boldsymbol{r}_{st} = (\alpha_s \boldsymbol{r}_s + \alpha_t \boldsymbol{r}_t)/(\alpha_s + \alpha_t)\,,$$

and exponent

$$\alpha_{st} = (\alpha_s + \alpha_t)\,.$$

Thus ϱ is a sum of spherical Gaussians. The basis of the point charge model is an approximation to $\varrho(\boldsymbol{r})$, namely

$$\varrho^*(\boldsymbol{r}) = 2\sum_{st} p_{st}\,S_{st}\,\delta(\boldsymbol{r} - \boldsymbol{r}_{st})\,, \tag{2}$$

where S_{st} is the overlap integral. The total number of electrons N, is found by integrating ϱ over all space:

$$N = \int \varrho(r)\,dr = 2\sum_{st} p_{st} \int \varphi_s(r)\,\varphi_t(r)\,dr = \int \varrho^*(r)\,dr\,.$$

The electronic dipole moment is

$$\boldsymbol{\mu} = \int \boldsymbol{r}\,\varrho(r)\,dr = 2\sum_{st} p_{st} S_{st} \boldsymbol{r}_{st} = \int \boldsymbol{r}\,\varrho^*(r)\,dr\,.$$

The total charge is thus divided into charges of known magnitude and position. These charges satisfy the essential conservation laws that the values of N and $\boldsymbol{\mu}$ are preserved.

For the purpose of the following discussion we assume a set of point charges $Z_{st} = 2p_{st}S_{st}$. In practice since $Z_{st} = Z_{ts}$ and $\boldsymbol{r}_{st} = \boldsymbol{r}_{ts}$ the number of charges in the model can be reduced.

2. The Point Charge Model and One-Electron Properties

When discussing one-electron properties it is convenient to select as origin the point, at which the porperties are evaluated. For a system of point charges Z_k situated at points (x_k, y_k, z_k), the following properties may be defined:

Multiple moments

$$M = \sum_k Z_k x_k^u y_k^v z_k^w\,, \tag{3}$$

Potential

$$V = \sum_k{}' Z_k/|r_k|\,, \tag{4}$$

Electric field

$$E_\lambda = -\sum_k{}' Z_k \lambda_k/|r_k|\,, \tag{5}$$

Electric field gradient

$$q_{\lambda\sigma} = -\sum_k{}' Z_k(3\lambda_k\sigma_k - \delta_{\lambda\sigma} r_k^2)/|r_k^5|\,. \tag{6}$$

In (4)–(6) $r_k^2 = (x_k^2 + y_k^2 + z_k^2)$ and the primed summation indicates that any term with $r_k = 0$ is omitted. λ or σ in (5) and (6) may each be x, y, or z. The dipole, second and third moments are obtained from (3) by setting $u+v+w$ to 1, 2, and 3 respectively (u, v, and w are integers).

The general expression for the electronic multipole moment at the origin is

$$M_e = 2\sum_{st} p_{st} \langle \varphi_s | x^u y^v z^w | \varphi_t \rangle\,. \tag{7}$$

If φ_s and φ_t are spherical Gaussian orbitals we may rewrite (7) using standard formulae [2] as

$$\begin{aligned} M_e = 2\sum_{st} p_{st} S_{st} &\sum_{i=0}^{[u/2]} \binom{u}{2i} x_{st}^{u-2i} \frac{(2i-1)!!}{(2\alpha_{st})^i} \\ &\cdot \sum_{j=0}^{[v/2]} \binom{v}{2j} y_{st}^{v-2j} \frac{(2j-1)!!}{(2\alpha_{st})^j} \sum_{k=0}^{[w/2]} \binom{w}{2k} z_{st}^{w-2k} \frac{(2k-1)!!}{(2\alpha_{st})^k}\,. \end{aligned} \tag{8}$$

In (8) $[u/2]$ is the largest integer $\leq u/2$, and x_{st}, y_{st}, z_{st} are the components of r_{st}. From this latter equation we see that the components of the dipole moment have the form

$$\mu_x = 2\sum_{st} p_{st} S_{st} x_{st} = \sum_{st} Z_{st} x_{st} = \mu_x^* . \tag{9}$$

We will use symbols superscripted with an asterisk to represent point charge model values. The diagonal elements of the second moment tensor are of the same form as Q_{xx}, namely

$$\begin{aligned} Q_{xx} &= 2\sum_{st} p_{st} S_{st}\left(x_{st}^2 + \frac{1}{2\alpha_{st}}\right) \\ &= \sum_{st} Z_{st} x_{st}^2 + \tfrac{1}{2}\sum_{st} Z_{st}/\alpha_{st} \\ &= Q_{xx}^* + \tfrac{1}{2}\sum_{st} Z_{st}/\alpha_{st} . \end{aligned} \tag{10}$$

The off-diagonal elements of this tensor are of the form

$$Q_{xy} = 2\sum_{st} p_{st} S_{st} x_{st} y_{st} = \sum_{st} Z_{st} x_{st} y_{st} = Q_{xy}^* . \tag{11}$$

The third moments are of three types of which R_{xxx}, R_{xyy} and R_{xyz} will serve as examples.

$$\begin{aligned} R_{xxx} &= 2\sum_{st} p_{st} S_{st}(x_{st}^3 + 3x_{st}/(2\alpha_{st})) \\ &= \sum_{st} Z_{st} x_{st}^3 + \tfrac{3}{2}\sum_{st} Z_{st} x_{st}/\alpha_{st} \\ &= R_{xxx}^* + \tfrac{3}{2}\sum_{st} Z_{st} x_{st}/\alpha_{st} \end{aligned} \tag{12}$$

$$\begin{aligned} R_{xyy} &= 2\sum_{st} p_{st} S_{st}(y_{st}^2 + 1/2\alpha_{st}) x_{st} \\ &= \sum_{st} Z_{st} y_{st}^2 x_{st} + \tfrac{1}{2}\sum Z_{st} x_{st}/\alpha_{st} \\ &= R_{xyy}^* + \tfrac{1}{2}\sum Z_{st} x_{st}/\alpha_{st} . \end{aligned} \tag{13}$$

$$R_{xyz} = 2\sum_{st} p_{st} S_{st} x_{st} y_{st} z_{st} = \sum_{st} Z_{st} x_{st} y_{st} z_{st} = R_{xyz}^* . \tag{14}$$

The formulae for the potential, electric fields and electric field gradients involve the function $F_m(a)$ defined as follows

$$F_m(a) = \int_0^1 u^{2m} \exp(-au^2) du .$$

Useful related functions are

$$\bar{F}_m(a) = \int_1^\infty u^{2m} \exp(-au^2) du ,$$

and

$$\int_0^\infty u^{2m} \exp(-au^2) du = \frac{(2m-1)!!}{2(2a)^m}\left(\frac{\pi}{a}\right)^{\frac{1}{2}} .$$

Thus

$$F_m(a) = \frac{(2m-1)!!}{2(2a)^m}\left(\frac{\pi}{a}\right)^{\frac{1}{2}} - \bar{F}_m(a) .$$

For large values of a $\bar{F}_m(a)$ is approximately $\exp(-a)/2a$.

The electronic part of the potential is

$$\begin{aligned}
V &= 2\sum_{st} p_{st}\left\langle \varphi_s \left| \frac{1}{r} \right| \varphi_t \right\rangle \\
&= 2\sum_{st} p_{st} 2S_{st}\left(\frac{\alpha_{st}}{\pi}\right)^{\frac{1}{2}} F_0(\alpha_{st} r_{st}^2) \\
&= 2\sum_{st} \frac{p_{st}S_{st}}{|r_{st}|} - 4\sum_{st} p_{st}S_{st}\left(\frac{\alpha_{st}}{\pi}\right)^{\frac{1}{2}} \bar{F}_0(\alpha_{st} r_{st}^2) \\
&= \sum_{st} Z_{st}/|r_{st}| - \frac{2}{\sqrt{\pi}}\sum_{st} Z_{st}\sqrt{\alpha_{st}}\,\bar{F}_0(\alpha_{st} r_{st}^2) \\
&= V^* - \frac{2}{\sqrt{\pi}}\sum_{st} Z_{st}\sqrt{\alpha_{st}}\,\bar{F}_0(\alpha_{st} r_{st}^2)\,.
\end{aligned} \tag{15}$$

The x component of the electric field is typical of the three components and is defined as

$$\begin{aligned}
E_x &= 2\sum_{st} p_{st}\left\langle \varphi_s \left| \frac{x}{r^3} \right| \varphi_t \right\rangle \\
&= 2\sum_{st} p_{st}S_{st}4\alpha_{st}x_{st}\left(\frac{\alpha_{st}}{\pi}\right)^{\frac{1}{2}} \bar{F}_1(\alpha_{st} r_{st}^2) \\
&= \sum_{st} Z_{st}x_{st}/|r_{st}^3| - \frac{4}{\sqrt{\pi}}\sum_{st} Z_{st}\alpha_{st}^{\frac{3}{2}}x_{st}\bar{F}_1(\alpha_{st} r_{st}^2) \\
&= E_x^* - \frac{4}{\sqrt{\pi}}\sum_{st} Z_{st}x_{st}\alpha_{st}^{\frac{1}{2}}\bar{F}_1(\alpha_{st} r_{st}^2)\,.
\end{aligned} \tag{16}$$

Finally the electronic components of the electronic field gradient tensor are

$$\begin{aligned}
q_{\lambda\sigma} &= 2\sum_{st} p_{st}\left\langle \varphi_s \left| \frac{3\lambda\sigma - \delta_{\lambda\sigma}r^2}{r^5} \right| \varphi_t \right\rangle \\
&= 2\sum_{st} p_{st}S_{st}\frac{4}{3}\left(\frac{\alpha_{st}^3}{\pi}\right)^{\frac{1}{2}} \{6\lambda_{st}\sigma_{st}\alpha_{st}\bar{F}_2(\alpha_{st} r_{st}^2) \\
&\quad - \delta_{\lambda\sigma}(3\bar{F}_1(\alpha_{st} r_{st}^2) - \exp(-\alpha_{st} r_{st}^2))\} \\
&= \sum \frac{Z_{st}}{|r_{st}^5|}(3\lambda_{st}\sigma_{st} - \delta_{\lambda\sigma}r_{st}^2) \\
&\quad - \frac{4}{3}\sum_{st} Z_{st}\alpha_{st}\left(\frac{\alpha_{st}}{\pi}\right)^{\frac{1}{2}} \{6\lambda_{st}\sigma_{st}\alpha_{st}\bar{F}_2(\alpha_{st} r_{st}^2) \\
&\quad - \delta_{\lambda\sigma}(3\bar{F}_1(\alpha_{st} r_{st}^2) - \exp(-\alpha_{st} r_{st}^2))\}\,. \\
&= q_{\lambda\sigma}^* - \frac{4}{3\sqrt{\pi}}\sum Z_{st}\alpha_{st}^{\frac{3}{2}} \{6\lambda_{st}\sigma_{st}\alpha_{st}\bar{F}_2(\alpha_{st} r_{st}^2) \\
&\quad - \delta_{\lambda\sigma}(3\bar{F}_1(\alpha_{st} r_{st}^2) - \exp(-\alpha_{st} r_{st}^2))\}\,.
\end{aligned} \tag{17}$$

In (17) λ and σ can each be x, y, or z. Examination of (9)–(17) shows that each one-electron property can be expressed as the point charge model value plus a correction. This correction is zero for the dipole moment, off-diagonal elements of the second moment tensor and for R_{xyz}. The correction is obviously the error obtained by using only the point charge value. The error in $Q^*_{\lambda\lambda}$ is constant. The errors in the remaining multipole moments are related in that the error in $R^*_{\lambda\lambda\lambda}$ is exactly three times the error in $R^*_{\lambda\sigma\sigma}$. Naturally if the evaluation of a third moment produces zero then the point charge model also gives zero and the error is zero. In general the error in these third moments increases with distance.

Inspection of (15)–(17) shows that the error involved in the point charge model decreases exponentially at large distances. The error decreases more rapidly than the actual value. The exponential term which appears in the correction to the diagonal term $q_{\lambda\lambda}$ is the contribution from the singularity at $r_{st} = 0$, and cannot be represented by the point charge model.

3. Examples of Point Charge Models

In this section we present the results obtained from simple spherical Gaussian wave functions for LiH, CH_4, and H_2O. We have used the smallest basis sets compatible with quantum mechanical principles and chemical intuition. All of the values are in atomic units and in the Tables powers of 10 are represented by numbers in parenthesis. The contribution from the nuclei of each molecule is included in each property.

Lithium Hydride

The nuclear geometry for LiH is Li at (0, 0, 0) and H at (0, 0, 3.02). The basis set consists of two spherical Gaussian orbitals which give a minimum energy when placed at (0, 0, −0.008251) and (0, 0, 2.72101) with exponents 2.00085 and 0.178880 respectively. The density matrix has diagonal elements of 1.01454 and off-diagonal elements of −0.121437. The point charge model is given in Table 1. The dipole moment has a non-zero z-component of −2.47184. The value of Q_{xx} and Q_{yy} is −3.07599 whereas Q^*_{xx} and Q^*_{yy} are both zero. The value of Q_{zz} is −8.97608 and that of Q^*_{zz} is −5.90008. The error in Q^*_{xx} is thus −3.07599. These values are constant along the x- and y-axes. The values of Q_{xz} at points on the

Table 1. Point charge model for LiH. All the charges are on the z-axis

Charge	z
3.00000 (0)	0.00000 (0)
1.00000 (0)	3.02000 (0)
−2.02907 (0)	−8.25054 (−3)
5.81430 (−2)	2.15726 (−1)
−2.02907 (0)	2.72101 (0)

Table 2. Q_{xz} for LiH at points along the x-axis

x	Q_{xz}	Q^*_{xz}
0.0	0.00000 (0)	0.00000 (0)
1.2	2.96621 (0)	2.96621 (0)
2.4	5.93242 (0)	5.93242 (0)
3.6	8.89863 (0)	8.89863 (0)
4.8	1.18648 (+1)	1.18648 (+1)
6.0	1.48311 (+1)	1.48311 (+1)
7.2	1.77973 (+1)	1.77973 (+1)

Table 3. Potential at points on the x-axis of LiH

x	V	V^*
1.2	4.91008 (−1)	4.82258 (−1)
2.4	1.29874 (−1)	1.28673 (−1)
3.6	4.90567 (−2)	4.89960 (−2)
4.8	2.29694 (−2)	2.29683 (−2)
6.0	1.23908 (−2)	1.23907 (−2)
7.2	7.38334 (−3)	7.38334 (−3)

x-axis are presented in Table 2, and although we have given them to only six significant digits the agreement is to ten digits which, in our case, is machine accuracy. Of the third moments R_{yyy}, R_{xxy}, R_{yzz}, and R_{xyz} are zero. As R^*_{xxx} and R^*_{xyy} are zero R_{xxx} and R_{xyy} represent the errors in the point charge model values, the error in R^*_{xxx} being three times that in R_{xyy} and R_{xzz}. The value of the latter is in general non-zero; inspection of (13) shows that at points on the x-axis R_{xzz} has a linear dependence on x, hence it is zero at the origin. At $x = 1.2$ R_{xzz} is 10.7713 and R^*_{xzz} is 7.08010. The error in R^*_{xzz} is 3.69119 at this point.

The potential at points along the x-axis is given in Table 3. The value of E_y is zero on the x-axis and as the value of the y co-ordinate of each point charge is zero E^*_y is zero. The x- and z-components of the electric field on the x-axis are presented in Table 4. Non-zero electric field gradients are shown in Table 5.

Table 4. Electric field at points on the x-axis of LiH

x	E_x	E^*_x	E_z	E^*_z
1.2	6.73672 (−1)	6.55240 (−1)	8.57307 (−2)	1.05315 (−1)
2.4	1.20862 (−1)	1.18394 (−1)	5.80802 (−2)	6.08786 (−2)
3.6	3.47653 (−2)	3.45886 (−2)	3.02142 (−2)	3.03477 (−2)
4.8	1.29986 (−2)	1.29944 (−2)	1.60428 (−2)	1.60452 (−2)
6.0	5.80397 (−3)	5.80393 (−3)	9.20809 (−3)	9.20810 (−3)
7.2	2.93884 (−3)	2.93884 (−3)	5.68425 (−3)	5.68425 (−3)

Table 5. Electric field gradients for LiH at points on the x-axis

x	q_{xx}	q^*_{xx}	q_{yy}	q^*_{yy}
1.2	−1.27896 (0)	−1.20748 (0)	6.08082 (−1)	5.46033 (−1)
2.4	−1.39458 (−1)	−1.38217 (−1)	5.33014 (−2)	4.93308 (−2)
3.6	−3.15923 (−2)	−3.13441 (−2)	9.88093 (−3)	9.60795 (−3)
4.8	−9.56834 (−3)	−9.55963 (−3)	2.71412 (−3)	2.70716 (−3)
6.0	−3.56406 (−3)	−3.56412 (−3)	9.67387 (−4)	9.67322 (−4)
7.2	−1.54122 (−3)	−1.54122 (−3)	4.08172 (−4)	4.08172 (−4)

x	q_{zz}	q^*_{zz}	q_{xz}	q^*_{xz}
1.2	6.70882 (−1)	6.61451 (−1)	3.66529 (−3)	−1.44757 (−2)
2.4	8.61564 (−2)	8.88862 (−2)	−2.92345 (−2)	−3.51444 (−2)
3.6	2.17113 (−2)	2.17361 (−2)	−1.67120 (−2)	−1.71060 (−2)
4.8	6.85439 (−3)	6.85247 (−3)	−7.95850 (−3)	−7.96738 (−3)
6.0	2.59686 (−3)	2.59680 (−3)	−3.96437 (−3)	−3.96437 (−3)
7.2	1.13305 (−3)	1.13305 (−3)	−2.13352 (−3)	−2.13352 (−3)

Methane

The geometry of the methane molecule is close to that of Arrighini, Guidotti, Maestro, Moccia, and Salvetti [3]. The protons are situated at (a, a, a), $(a, -a, -a)$ $(-a, a, -a)$, and $(-a, -a, a)$, the value of 1.19350 for 'a' corresponds to a C–H bond length of 2.0672. The basis set consists of five spherical Gaussians; one on the carbon nucleus with an exponent of 9.30694 and one in each C–H bond at 1.23654 from the carbon nucleus. The exponents of the bond orbitals are 0.356102.

Table 6. Point charge model for methane

Charge	x	y	z
1.00000 (0)	1.19350 (0)	1.19350 (0)	1.19350 (0)
1.00000 (0)	1.19350 (0)	−1.19350 (0)	−1.19350 (0)
1.00000 (0)	−1.19350 (0)	1.19350 (0)	−1.19350 (0)
1.00000 (0)	−1.19350 (0)	−1.19350 (0)	1.19350 (0)
3.93691 (0)	0.00000 (0)	0.00000 (0)	0.00000 (0)
−3.11650 (0)	7.13916 (−1)	7.13916 (−1)	7.13916 (−1)
7.33820 (−1)	7.13916 (−1)	0.00000 (0)	0.00000 (0)
−3.11650 (0)	7.13916 (−1)	−7.13916 (−1)	−7.13916 (−1)
7.33820 (−1)	0.00000 (0)	7.13916 (−1)	0.00000 (0)
7.33820 (−1)	0.00000 (0)	0.00000 (0)	−7.13916 (−1)
−3.11650 (0)	−7.13916 (−1)	7.13716 (−1)	−7.13916 (−1)
7.33820 (−1)	0.00000 (0)	0.00000 (0)	7.13916 (−1)
7.33820 (−1)	0.00000 (0)	−7.13916 (−1)	0.00000 (0)
7.33820 (−1)	−7.13916 (−1)	0.00000 (0)	0.00000 (0)
−3.11650 (0)	−7.13916 (−1)	−7.13916 (−1)	7.13916 (−1)
3.15441 (−2)	2.63092 (−2)	2.63092 (−2)	2.63092 (−2)
3.15441 (−2)	2.63092 (−2)	−2.63092 (−2)	−2.63092 (−2)
3.15441 (−2)	−2.63092 (−2)	2.63092 (−2)	−2.63092 (−2)
3.15441 (−2)	−2.63092 (−2)	−2.63092 (−2)	2.63092 (−2)

The density matrix for CH_4 has elements as follows: $p_{ii}(i<5)=1.55825$, $p_{55}=1.03154$, $p_{ij}=p_{ji}$ $(i<5, j<5, i\neq j)=-0.379159$, and the remaining elements are -0.0576041. The point charge model consists of the nineteen charges listed in Table 6.

As expected, the dipole moment for CH_4 is zero. The diagonal second moments $Q_{\lambda\lambda}$ are equal at -5.61731 and $Q^*_{\lambda\lambda}=0.0922448$. $Q_{\lambda\lambda}$ and $Q^*_{\lambda\lambda}$ are constant along the C–H bond direction. $Q_{\lambda\sigma}$ is zero. There are only three distinct values for the third moments. As a consequence of the symmetry of methane $R_{xxx}=R_{yyy}=R_{zzz}$, R_{xyz} is unique and the six remaining third moments are equal. Values of the third moments at points along a C–H bond are directly proportional to the distance from the carbon nucleus, with the exception of R_{xyz} which is constant at 2.26433. Thus only R_{xyz} is non-zero at the origin; at $(1, 1, 1)$ $R_{xxx}=16.8519$, and $R_{xxy}=5.61731$. The corresponding values of R^*_{xxx} and R^*_{xxy} are -0.276734 and -0.0922448 respectively. At $(1, 1, 1)|R^*_{xxy}|=|Q^*_{xx}|$ and $|R_{xxy}|=|Q_{\chi\chi}|$, although the dimensions differ.

The symmetry of CH_4 is reflected in the various electric field components and electric field gradients. At points along the C–H bond direction $E_x=E_y=E_z$,

Table 7. Potential, electric field and electric field gradient at points (a, a, a) for CH_4

a	V	V^*	E_x	E^*_x	q_{xz}	q^*_{xz}
1.5	9.70321 (−1)	7.38475 (−1)	1.83964 (0)	1.41718 (0)	−6.63272 (0)	−5.73344 (0)
2.0	1.14840 (−1)	1.04007 (−1)	1.23752 (−1)	9.88716 (−2)	−2.46351 (−1)	−1.86736 (−1)
2.5	3.22414 (−2)	3.20187 (−2)	2.17703 (−2)	2.11258 (−2)	−2.89986 (−2)	−2.71059 (−2)
3.0	1.34171 (−2)	1.34153 (−2)	6.89731 (−3)	6.89095 (−3)	−6.81782 (−3)	−6.79531 (−3)
3.5	6.67148 (−3)	6.67148 (−3)	2.82885 (−3)	2.82883 (−3)	−2.28453 (−3)	−2.28453 (−3)
4.0	3.70789 (−3)	3.70789 (−3)	1.34446 (−3)	1.34446 (−3)	−9.23878 (−4)	−9.23878 (−4)
4.5	2.22998 (−3)	2.22998 (−3)	7.07972 (−4)	7.07972 (−4)	−4.24609 (−4)	−4.24609 (−4)
5.0	1.42316 (−3)	1.42316 (−3)	4.02384 (−4)	4.02384 (−4)	−2.14474 (−4)	−2.14474 (−4)
5.5	9.51476 (−4)	9.51476 (−4)	2.42691 (−4)	2.42691 (−4)	−1.16529 (−4)	−1.16529 (−4)
6.0	6.60445 (−4)	6.60445 (−4)	1.53521 (−4)	1.53521 (−4)	−6.71104 (−5)	−6.71104 (−5)
6.5	4.72856 (−4)	4.72856 (−4)	1.00997 (−4)	1.00997 (−4)	−4.05391 (−5)	−4.05391 (−5)
7.0	3.47481 (−4)	3.47481 (−4)	6.86639 (−5)	6.86639 (−5)	−2.54851 (−5)	−2.54851 (−5)
7.5	2.61087 (−4)	2.61087 (−4)	4.80070 (−5)	4.80070 (−5)	−1.65737 (−5)	−1.65737 (−5)

Table 8. Spherical Gaussian basis set for water. The molecule lies in the xz-plane with O at the origin

Exponent	x	y	z
9.14599 (+1)	0.00000 (0)	0.00000 (0)	0.00000 (0)
1.34143 (+1)	0.00000 (0)	0.00000 (0)	0.00000 (0)
4.64512 (−1)	7.88531 (−1)	0.00000 (0)	6.05061 (−1)
4.64512 (−1)	−7.88531 (−1)	0.00000 (0)	6.05061 (−1)
4.74836 (−1)	0.00000 (0)	0.00000 (0)	−2.52360 (−1)
1.01826 (0)	0.00000 (0)	5.00000 (−2)	0.00000 (0)
1.01826 (0)	0.00000 (0)	−5.00000 (−2)	0.00000 (0)

the diagonal elements of the electric field gradient tensor are zero and the off diagonal elements are equal. The values of the non-zero properties are listed in Table 7.

Water

The geometry employed for the water corresponds to an internal $H\hat{O}H$ angle of 105° and an O–H bond length of 1.81417. The molecule lies in the *xz*-plane with the oxygen nucleus at the origin and the positive *z*-axis bisects the internal $H\hat{O}H$ angle. The basis set consists of seven spherical Gaussians and is defined in Table 8.

The density matrix and point charge model are given in Tables 9 and 10.

Table 9. Density matrix for H_2O (lower triangle)

6.10934 (−2)						
2.07973 (−1)	7.14320 (−1)					
−5.16081 (−4)	1.60914 (−4)	2.12016 (0)				
−5.16081 (−4)	1.60914 (−4)	−1.58862 (−1)	2.12016 (0)			
−6.86706 (−2)	−2.93275 (−1)	−1.57053 (0)	−1.57053 (0)	3.09698 (0)		
1.42753 (−2)	3.53045 (−2)	7.11939 (−2)	7.11939 (−2)	−1.06664 (−2)	9.84933 (+1)	
1.42735 (−2)	3.53045 (−2)	7.11939 (−2)	7.11939 (−2)	−1.06664 (−2)	−9.84193 (+1)	9.84933 (+1)

Table 10. Point charge model for water

Charge	*x*	*y*	*z*
3.97673 (+2)	0.00000 (0)	0.00000 (0)	0.00000 (0)
1.00000 (0)	1.43928 (0)	0.00000 (0)	1.10440 (0)
1.00000 (0)	−1.43928 (0)	0.00000 (0)	1.10440 (0)
6.98333 (−5)	3.98460 (−3)	0.00000 (0)	3.05749 (−3)
−8.91195 (−5)	2.63915 (−2)	0.00000 (0)	2.02509 (−2)
−4.24031 (0)	7.88531 (−1)	0.00000 (0)	6.05061 (−1)
6.98333 (−5)	−3.98460 (−3)	0.00000 (0)	3.05749 (−3)
−8.91195 (−5)	−2.63915 (−2)	0.00000 (0)	2.02509 (−2)
3.56622 (−1)	0.00000 (0)	0.00000 (0)	6.05061 (−1)
−4.24031 (0)	−7.88531 (−1)	0.00000 (0)	6.05061 (−1)
1.44684 (−2)	0.00000 (0)	0.00000 (0)	−1.30342 (−3)
2.49613 (−1)	0.00000 (0)	0.00000 (0)	−8.62759 (−3)
4.56760 (0)	3.89932 (−1)	0.00000 (0)	1.71639 (−1)
4.57670 (0)	−3.89932 (−1)	0.00000 (0)	1.71639 (−1)
−6.19396 (0)	0.00000 (0)	0.00000 (0)	−2.52360 (−1)
−5.43072 (−3)	0.00000 (0)	5.50543 (−4)	0.00000 (0)
−5.16374 (−2)	0.00000 (0)	3.52766 (−3)	0.00000 (0)
−1.85512 (−1)	2.47025 (−1)	3.43364 (−2)	1.89549 (−1)
−1.85512 (−1)	−2.47025 (−1)	3.43364 (−2)	1.89549 (−1)
3.75393 (−2)	0.00000 (0)	3.40990 (−2)	−8.02557 (−2)
−1.96987 (+2)	0.00000 (0)	5.00000 (−2)	0.00000 (0)
−5.43072 (−3)	0.00000 (0)	−5.50543 (−4)	0.00000 (0)
−5.16374 (−2)	0.00000 (0)	−3.52766 (−3)	0.00000 (0)
−1.85512 (−1)	2.47025 (−1)	−3.43364 (−2)	1.89549 (−1)
−1.85512 (−1)	−2.47025 (−1)	−3.43364 (−2)	1.89549 (−1)
3.75393 (−2)	0.00000 (0)	−3.40990 (−2)	−8.02557 (−2)
−1.96987 (+2)	0.00000 (0)	−5.00000 (−2)	0.00000 (0)

It is important to note that this model of water differs markedly from all previous point charge models. The point charge corresponding to each lone pair has the value -197 whereas earlier models had a maximum value of -2 corresponding to the two electrons. This large charge is neutralized by the large charge of 398 on the oxygen nucleus. The result of this feature is that the electric field around the lone pair has a much stronger angular dependence than is given by earlier models.

Recent calculations on the water dimer [4–6] have shown that the most favourable configuration for the approach of the two monomers is along a line containing an O–H bond of one and which bisects the external $\hat{HOH}$ bond angle of the other. With these calculations in mind we have calculated one-electron properties along the line of an O–H bond and along the negative z-axis of our molecule.

The dipole moment for H_2O based on the present wave function is 0.275483. The low symmetry of the molecule dictates that Q_{xx} and Q_{yy} are constant, Q_{xy} and Q_{yz} are zero in the two directions investigated. Q_{xz} is also zero along the negative z-axis. The values of Q_{xx}, Q^*_{xx}, Q_{yy}, and Q^*_{yy} are -3.36956, 0.213646, -4.56893, and -0.985721 respectively, the error in the point charge values being -3.58321. As in the previous examples Q_{xz} in the O–H bond direction is proportional to the distance from the oxygen nucleus where it is zero. At a point P on the O–H bond, with co-ordinates (0.651613, 0.0, 0.5), Q^*_{xz} is -0.179508 and agrees exactly with Q_{xz}. Q_{zz} is non-zero at the origin and has a value of -4.26952 whilst $Q^*_{zz} = -0.686313$. However at P we find Q_{zz} and Q^*_{zz} have both decreased by 0.275483, which is the numerical value of the dipole moment, doubling the distance from O causes a drop in both properties of twice this value. The values of Q_{zz} and Q^*_{zz} along the z-axis are tabulated in Table 11.

The third moments R_{xxy}, R_{yyy}, R_{yzz}, and R_{xyz} are all zero in the O–H bond direction, and, on the negative z-axis, only R_{yyz}, R_{zzz} and R_{xxz} are non-zero. R_{xxx} and R_{xyy} have a linear dependence on the distance from the oxygen nucleus along the O–H direction. Both are zero at the origin and at P have values of 6.58694 and 2.97717 respectively. R^*_{xxx} and R^*_{xyy} are -0.417643 and 0.642309 at the same

Table 11. Second moments for H_2O along the z-axis

z	Q_{zz}	Q^*_{zz}
0.0	−4.26952	−0.686313
−0.8	−3.82875	−0.245541
−1.6	−3.38797	0.195231
−2.4	−2.94720	0.636003
−3.2	−2.50643	1.07678
−4.0	−2.06566	1.51755
−4.8	−1.62489	1.95832
−5.6	−1.18411	2.39909
−6.4	−0.743341	2.83986
−7.2	−0.302569	3.28063
−8.0	0.138203	3.72141

Table 12. Third moments for H_2O at points in the O–H direction. Molecule is in the xz-plane

x	z	R_{zzz}	R^*_{zzz}	R_{xxz}	R^*_{xxz}	R_{xzz}	R^*_{xzz}
0.00000 (0)	0.00000 (0)	−2.07733 (0)	1.03513 (0)	5.77349 (−1)	1.61483 (0)	0.00000 (0)	0.00000 (0)
6.51613 (−1)	5.00000 (−1)	4.53356 (0)	2.27121 (0)	2.37910 (0)	1.62498 (0)	2.96158 (0)	6.26718 (−1)
1.30323 (0)	1.00000 (0)	1.15577 (+1)	3.92051 (0)	4.41479 (0)	1.86907 (0)	6.28218 (0)	1.61245 (0)
1.43928 (0)	1.10440 (0)	1.30764 (+1)	4.31702 (0)	4.86935 (0)	1.94955 (0)	7.02080 (0)	1.86357 (0)
1.95484 (0)	1.50000 (0)	1.89950 (+1)	5.98304 (0)	6.68441 (0)	2.34709 (0)	9.96179 (0)	2.95720 (0)
2.60645 (0)	2.00000 (0)	2.68456 (+1)	8.45879 (0)	9.18798 (0)	3.05906 (0)	1.40004 (+1)	4.66097 (0)
3.25806 (0)	2.50000 (0)	3.51094 (+1)	1.13478 (+1)	1.19255 (+1)	4.00496 (0)	1.83981 (+1)	6.72375 (0)

Table 13. Potential in H_2O

x	z	V	V^*
Points in the O–H direction			
1.95484 (0)	1.50000 (0)	6.31140 (−1)	5.12087 (−1)
2.60645 (0)	2.00000 (0)	1.05472 (−1)	1.02299 (−1)
3.25806 (0)	2.50000 (0)	3.96774 (−2)	3.96479 (−2)
3.90968 (0)	3.00000 (0)	2.04001 (−2)	2.04000 (−2)
4.56129 (0)	3.50000 (0)	1.22863 (−2)	1.22863 (−2)
5.21290 (0)	4.00000 (0)	8.17280 (−3)	8.17280 (−3)
Points on the z-axis			
	−2.4	−6.02108 (−2)	−6.78693 (−2)
	−3.2	−3.37610 (−2)	−3.38545 (−2)
	−4.0	−2.04351 (−2)	−2.04355 (−2)
	−4.8	−1.37399 (−2)	−1.37399 (−2)
	−5.6	−9.89456 (−3)	−9.89456 (−3)
	−6.4	−7.47303 (−3)	−7.47303 (−3)

Table 14. Non-zero components of the electric field in H_2O

x	z	E_x	E^*_x	E_z	E^*_z
Points in the O–H direction					
1.95484 (0)	1.50000	1.49387 (0)	1.12944 (0)	1.16073 (0)	8.83103 (−1)
2.60645 (0)	2.00000	1.26042 (−1)	1.13376 (−1)	1.01535 (−1)	9.18403 (−2)
3.25806 (0)	2.50000	2.90678 (−2)	2.89184 (−2)	2.39131 (−2)	2.37985 (−2)
3.90968 (0)	3.00000	1.10361 (−2)	1.10355 (−2)	8.98255 (−3)	8.98212 (−3)
4.56129 (0)	3.50000	5.29439 (−3)	5.29439 (−3)	4.17236 (−3)	4.17236 (−3)
5.21290 (0)	4.00000	2.94017 (−3)	2.94017 (−3)	2.21276 (−3)	2.21276 (−3)
Points on the z-axis					
	−2.4			3.42266 (−2)	7.13469 (−2)
	−3.2			2.39815 (−2)	2.45600 (−2)
	−4.0			1.12878 (−2)	1.12908 (−2)
	−4.8			6.15031 (−3)	6.15031 (−3)
	−5.6			3.73397 (−3)	3.73397 (−3)
	−6.4			2.44267 (−3)	2.44267 (−3)

point. At the origin R_{yyz} is -1.03766 and R^*_{yyz} is -0.000172836, at P the corresponding values are 1.24681 and 0.492688. The values of R_{zzz}, R_{xxz} and R_{xzz} and point charge values at points in the O–H direction are presented in Table 12. R_{yyz} has a linear dependence with distance along the negative z-axis as well as in the O–H bond direction, at $(0, 0, -0.8)$ R_{yyz} is -4.69280 and R^*_{yyz} is -0.788750, the non-zero values of both at the origin have been given above. In Tables 13–15 we give the values of the potential, non-zero electric fields and field gradients.

4. Discussion

For each of the molecules we have examined it is possible to derive the observed relationship between the various multipole moments from the definition given in (8). The relationship between Q_{zz} at points in the O–H direction for H_2O and the dipole moment, is perhaps fortuitous, but can be derived from the appropriate expression. Since the errors produced by the point charge model in the multipole moments are closely related it should be possible to construct the quadrupole and octupole moment tensors using Buckingham's definitions [7], with the knowledge that given elements are exact and the error in others is precisely known. Naturally, knowledge of the basis set and density matrix from which the point charge model was obtained permits the exact evaluation of the multipole moments from the point charge model. The advantage is that the calculation based on the point charge model is easier to perform than that based on the original wave function.

The results presented for the potential and its derivatives show that the error involved in the point charge model is small and diminishes rapidly. Whereas the multipole moments are, in most cases, well represented by the point charge model at any point in space whether or not that point is within the confines of the nuclear framework, the potential and its derivatives are only accurate outside the shell of the molecule [1]. A contributory factor to this feature is the inability of the point charge model to include terms which arise from the Dirac delta functions which appear in $q_{\lambda\lambda}$.

One question that must be answered concerns the accuracy to which molecular properties can be calculated using the spherical Gaussian model. Recent work by Dixon and Tait [8] suggests that even the simplest form of spherical Gaussian model provides reliable information about molecular structure. It is known that the Frost model [9] gives about 84% of the Hartree-Fock energy, and there is evidence [8] to support the thesis that one-electron properties can be obtained as a more-or-less constant percentage of the values obtained in more accurate calculations.

5. Conclusion

From the results presented in Tables 1–15 we conclude that the point charge model proposed by Hall [1] may be used to calculate one-electron properties with a high degree of accuracy. Where errors occur it is possible to evaluate them exactly without recourse to the complete spherical Gaussian wave function.

Table 15. Electric field gradients in H_2O

x	z	q_{xx}	q^*_{xx}	q_{yy}	q^*_{yy}
Points in the O–H direction					
1.95484 (0)	1.50000 (0)	−3.10260 (0)	−2.52093 (0)	3.51082 (0)	2.86440 (0)
2.60645 (0)	2.00000 (0)	−1.51141 (−1)	−1.26689 (−1)	1.76179 (−1)	1.48780 (−1)
3.25806 (0)	2.50000 (0)	−2.14951 (−2)	−2.11371 (−2)	2.61621 (−2)	2.57584 (−2)
3.90968 (0)	3.00000 (0)	−5.90026 (−3)	−5.89789 (−3)	7.36033 (−3)	7.35854 (−3)
4.56129 (0)	3.50000 (0)	−2.22498 (−3)	−2.22498 (−3)	2.78651 (−3)	2.78651 (−3)
5.21290 (0)	4.00000 (0)	−1.02391 (−3)	−1.02391 (−3)	1.26434 (−3)	1.26434 (−3)

x	z	q_{zz}	q^*_{zz}	q_{xz}	q^*_{xz}
1.95484 (0)	1.50000 (0)	−4.08224 (−1)	−3.43475 (−1)	−5.08212 (0)	−4.14661 (0)
2.60645 (0)	2.00000 (0)	−2.50364 (−2)	−2.20908 (−2)	−2.55363 (−1)	−2.15685 (−1)
3.25806 (0)	2.50000 (0)	−4.66504 (−3)	−4.62126 (−3)	−3.79656 (−2)	−3.73817 (−2)
3.90968 (0)	3.00000 (0)	−1.46130 (−3)	−1.46064 (−3)	−1.06463 (−2)	−1.06431 (−2)
4.56129 (0)	3.50000 (0)	−5.61523 (−4)	−5.61525 (−4)	−3.99915 (−3)	−3.99915 (−3)
5.21290 (0)	4.00000 (0)	−2.40437 (−4)	−2.40437 (−4)	−1.79536 (−3)	−1.75936 (−3)

z	q_{xx}	q^*_{xx}	q_{yy}	q^*_{yy}	q_{zz}	q^*_{zz}
Points on the z-axis						
−2.4	−1.07364 (−2)	−7.30841 (−2)	2.07224 (−2)	−4.08633 (−2)	−9.98668 (−3)	1.13947 (−1)
−3.2	−1.56998 (−2)	−1.69078 (−2)	−9.34760 (−3)	−1.05507 (−2)	2.50396 (−2)	2.74585 (−2)
−4.0	−5.71490 (−3)	−5.72222 (−3)	−3.84941 (−3)	−3.85673 (−3)	9.56008 (−3)	9.57895 (−3)
−4.8	−2.45546 (−3)	−2.45548 (−3)	−1.74199 (−3)	−1.74200 (−3)	4.19749 (−3)	4.19749 (−3)
−5.6	−1.23112 (−3)	−1.23112 (−3)	−9.04262 (−4)	−9.04262 (−4)	2.13538 (−3)	2.13538 (−3)
−6.4	−6.87201 (−4)	−6.87201 (−4)	−5.17403 (−4)	−5.17403 (−4)	1.20460 (−3)	1.20460 (−3)

A molecular dynamics study of liquid water by Rahman and Stillinger [10] has stimulated interest in point charge models. They have used a simple point charge model for the water molecule to provide the electrostatic contribution to the effective pair potential. The point charge model examined in the present paper offers the possibility of providing a highly accurate model from which this contribution may be calculated without substantially modifying the molecular dynamics program.

Another possible application of the present point charge model is the investigation of problems of chemical reactivity. Bonaccorsi, Pullman, Scrocco, and Tomasi [11] have shown that the study of isopotential curves for large heterocycles reveals a discrimination between the different possible sites of protonation on the same molecular skeleton. They suggest that such studies may provide a method of comparing protonation sites of different kinds and also sites on different molecules. The key to such investigations is an efficient means of calculating the potential at many points around the molecule; the point charge model is well suited to this task.

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Dr. A. D. Tait
Department of Mathematics
The University of Nottingham
University Park
Nottingham NG7 2RD, England