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FSGO Point Charge Models—Their Accuracy and Extension to Higher Gaussians

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An FSGO model of ethane demonstrates how currently used point charge models can give the wrong sign for the potential. The Hall point charge potential on the other hand is asymptotically accurate.

An extension of the Hall point charge model to higher Gaussians is demonstrated. This extended model potential is shown to be of comparable accuracy to that of the spherical Gaussian model.

Key words: Point charge models – Higher-Gaussians.

1. Introduction

The calculation of electrostatic interactions between two or more molecules can be simplified. This involves replacing the continuous distribution of charge in each molecule by a set of point charges. Integrals over charges are then replaced by sums over point charges.

The number of point charges required will depend on the molecular species involved, their distance apart, their relative orientation and finally on the accuracy of the approximation desired. In general, for the same degree of approximation, the charge regions of closest approach will need more charges. In practice, however, calculations are performed at a range of molecular orientations and thus no uneven distribution of charges is called for. It is difficult to assess the accuracy of a given modelling scheme, this can only be done through a consideration of conserved molecular properties such as total charge and dipole moment [1], and electric field [2] or through the study of a number of examples.

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We demonstrate using an FSGO model of ethane how the standard Mulliken [3] and Shipman [6] point charge models can give the opposite sign for the potential while the Hall [1] model gives the required asymptotic accuracy. Further, in the Hall model it is shown how higher Gaussians may be included.

2. The Nature of the Molecular Charge Density

The molecular charge density is observable, in principle, since it can be deduced from X-ray Crystallographic experiments. In practice, however, the M.O. one electron density $\rho(\boldsymbol{r})$ is a more convenient, readily available, *ab initio* form. It expresses the density as a linear combination of products of well-known basis functions $\{\psi_s(\boldsymbol{r})\}$

$$\rho(\boldsymbol{r}) = 2 \sum_{s,t} P_{st} \psi_s(\boldsymbol{r}) \psi_t(\boldsymbol{r}). \tag{1}$$

These product functions $\psi_s(\boldsymbol{r})\psi_t(\boldsymbol{r})$ have a simple form in the case of Gaussian basis sets. Here the product Gaussian is again a Gaussian, and

$$\rho(\boldsymbol{r}) = 2 \sum_{\alpha} a_\alpha \phi_\alpha(\boldsymbol{r})$$

where

$$\phi_\alpha(\boldsymbol{r}) = \sum_{i,j,k} a_{ijk} (x - x_\alpha)^i (y - y_\alpha)^j (z - z_\alpha)^k \chi_\alpha(\boldsymbol{r})$$

and

$$\chi_\alpha(\boldsymbol{r}) = \left(\frac{\beta_\alpha}{\pi}\right)^{3/2} \exp\left[-\beta_\alpha(\boldsymbol{r} - \boldsymbol{r}_\alpha)^2\right].$$

is a spherical Gaussian. (This unique property of the product makes the Gaussian the only suitable M.O. basis for non-linear molecules.)

The higher Gaussians are not essential as they can be simulated by lobe functions, that is by linear combinations of close spherical Gaussians. This follows from the statement of Boys [4] that each single centred, single exponent Gaussian $\phi_\alpha(\boldsymbol{r})$ can be obtained by acting with a differential operator $D_\alpha(\nabla_{r_\alpha})$ on the centre $\boldsymbol{r}_\alpha$ of a spherical Gaussian namely

$$\phi_\alpha(\boldsymbol{r}) = D_\alpha(\nabla_{r_\alpha}) \chi_\alpha(\boldsymbol{r}).$$

For lobe functions this operator is replaced by a finite difference operator. It is noted then that integrals over lobe functions are linear combinations of integrals over spherical Gaussian functions. There is, however, the problem in using lobe functions, of defining a suitable separation between the close spherical Gaussians making up the function [5]. This problem apart they remain a convenient form for performing integrals over various symmetry types using the simple code of the spherical Gaussian program.

3. FSGO Point Charge Models – Their Accuracy

The FSGO point charge models considered differ only in their placement of the total charge associated with each product Gaussian. We consider the models of Hall [1], Shipman [6] and Mulliken [3]. In the Hall model, each product Gaussian charge (P.G.C.) is placed at the product Gaussian centre. In other models the PGC is divided and placed on the two Gaussian centres involved in the product. In the Shipman model, the charge is divided so as to conserve dipole moment, while in an application of the Mulliken population analysis, the PGC is equally divided between the two centres. Thus all models conserve the total charge of the PGC while only the Hall and Shipman models conserve the dipole moment. Further the Gaussian centres of charge are only conserved in the Hall model. An ordering of accuracy of models is thus expected to be Hall, Shipman and finally Mulliken.

We shall demonstrate the relative accuracies of these models using a simple FSGO basis of just over minimal size [7] in which, except for LiH, two Gaussians are fixed on each heavy (non hydrogen) nucleus, and one is placed on each bond. In LiH the Gaussian model consists of two spherical Gaussians along the LiH bond. Optimisation of both the Gaussian exponents and non-nucleus-fixed positions is performed by the Opit program [8]. The molecular properties given by an accurate analysis of the FSGO one-electron density are in no way close to experiment but the FSGO one-electron density is a particularly compact form on which to compare the various point charge models.

Table 1. The molecular geometries in Bohr (as used by Snyder and Basch [10]) with axis of symmetry along the z axis and, in the case of the water molecule, in the $y-z$ plane with the oxygen atom at the origin

Molecule			
LiH	RLiH = 3.0200		
H_2O	ROH = 1.8088	$\mathrm{H\hat{O}H} = 104.5230$	
C_2H_2	RCC = 2.2734	RCH = 2.0030	
BF	RBF = 2.3905		
C_2H_6	RCC = 2.9159	RCH = 2.0825	$\mathrm{C\hat{C}H} = 109.6407$

Table 2. The floating Gaussian basis set with the atom, bond or axis on which each Gaussian lies (O^2 denotes two basis functions at centre O)

Molecule	Basis $[s][P_x][P_y][P_z]$
LiH	$[(\mathrm{Li{-}H})^2]$
H_2O (s Gaussian)	$[\mathrm{O}^2$, O—H, z axis, x axis fixed ±0.05 Bohr]
H_2O ($s+p$ Gaussian)	$[\mathrm{O}^2$, O—H][O][−][O]
C_2H_2	$[\mathrm{C}^2$, C—C, C—H][C][C]
BF	$[\mathrm{F}^2$, B^2, F—B][F][F][F, B]
C_2H_6	$[\mathrm{C}^2$, C—C, C—H]

The H_2O ($s+p$ Gaussian) model does not contain a P_y Gaussian.

FSGO calculations on LiH, H_2O and C_2H_6 are presented in Table 3. The accurate electrostatic potentials on various exit lines from a heavy nucleus are compared with those calculated from each of the Hall, Shipman and Mulliken point charges.

Table 3. The spherical Gaussian point charge model potentials of Hall V_H, Shipman V_S and Mulliken V_M compared with the wavefunction potential V, $\varepsilon V_H = (V - V_H)/V$

LiH

The potential along the perpendicular to Li—H through Li where x = distance from Li.

xBohr	V	εV_H	εV_S	εV_M
2.0	1.92168 (−1)	1.34 (−2)	1.76 (−2)	4.34 (−2)
4.0	3.73619 (−2)	4.79 (−4)	5.44 (−3)	3.36 (−2)
6.0	1.23907 (−2)	0	5.22 (−3)	3.44 (−2)

0 denotes accurate to six significant figures, that is $\varepsilon V < 1.00$ (−5).

H_2O (s Gaussian)

The potential along a O—H bond (in that direction) where x = distance from 0.

xBohr	V	εV_H	εV_S	εV_M
2.0	4.14645 (0)	1.51 (−1)	6.84 (−2)	7.34 (−2)
4.0	4.39221 (−2)	1.30 (−3)	−4.10 (−1)	−3.30 (−1)
6.0	1.07969 (−2)	0	−3.52 (−1)	−2.19 (−1)

H_2O (s Gaussian)

The potential along the bisector of H$\hat{O}$H (away from H) where x = distance from 0.

x Bohr	V	εV_H	εV_S	εV_M
2.0	−6.16993 (−2)	−7.69 (−1)	7.24 (−1)	1.01 (0)
4.0	−2.06098 (−2)	−1.94 (−5)	4.75 (−1)	6.97 (−1)
6.0	−8.64897 (−3)	0	3.01 (−1)	5.38 (−1)

C_2H_6

The potential along the reflected C—H bond (i.e. a line in an HCC plane at 70° to CC axis) where x = distance from C.

x Bohr	V	εV_H	εV_S	εV_M
2.0	6.09720 (−2)	3.90 (0)	4.99 (0)	5.00 (0)
4.0	−8.57218 (−3)	−2.09 (−2)	−1.84 (0)	−1.87 (0)
6.0	−1.90016 (−3)	0	−2.04 (0)	−2.06 (0)

C_2H_6

The potential perpendicular to a HCC plane through a C where x = distance from C.

x Bohr	V	εV_H	εV_S	εV_M
2.0	9.58996 (−2)	3.37 (0)	3.35 (0)	3.35 (0)
4.0	−2.73851 (−3)	−9.37 (−2)	−1.37 (0)	−1.38 (0)
6.0	1.37290 (−4)	0	1.01 (1)	1.02 (1)

The results quoted are the relative errors εV_A of the approximate potential V_A to the accurate potential V, namely we quote $\varepsilon V_A = (V - V_A)/V_A$. Note that $\varepsilon V_A > 1$ implies that the accurate potential V and the approximate potential V_A have opposite signs. We quote $|\varepsilon V_A|$ in the script.

In the cases considered, the Hall model potential is consistently better than the Shipman and Mulliken model potentials at distances of 4 Bohr and 6 Bohr from a heavy nucleus. Further, the Hall model potential gives a relative error at 6 Bohr (4 Bohr) from a heavy nucleus of $1.00E-5(1.00E-1)$ or better, while at 6 Bohr the Shipman and Mulliken models may give the wrong sign (see $C_2H_6 \perp$ HCC plane).

4. Extension of the FSGO Point Charge Models to Higher Gaussians – the Accuracy

A method of extension of the point charge models to higher Gaussians can be illustrated by reference to the Hall model.

For FSGO's the electron density

$$\rho(\boldsymbol{r}) = 2 \sum_{\alpha} a_\alpha \chi_\alpha(\boldsymbol{r})$$

is approximated by

$$\rho_H(\boldsymbol{r}) = 2 \sum_{\alpha} a_\alpha \delta(\boldsymbol{r} - \boldsymbol{r}_\alpha).$$

We suggest for higher Gaussians that the electron density

$$\rho(\boldsymbol{r}) = 2 \sum_{\alpha} a_\alpha D_\alpha(\nabla_{\boldsymbol{r}_\alpha}) \chi_\alpha(\boldsymbol{r}) \tag{2}$$

is approximated by

$$\rho_H(\boldsymbol{r}) = 2 \sum_{\alpha} a_\alpha D_\alpha(\nabla_{\boldsymbol{r}_\alpha}) \delta(\boldsymbol{r} - \boldsymbol{r}_\alpha) \tag{3}$$

that is, in the case of s and p type basis sets, by point charges $\delta(\boldsymbol{r} - \boldsymbol{r}_\alpha)$, point dipoles $\partial/\partial x_\alpha \, \delta(\boldsymbol{r} - \boldsymbol{r}_\alpha)$ and point quadrupoles $\partial^2/\partial x_\alpha \partial y_\alpha \, \delta(\boldsymbol{r} - \boldsymbol{r}_\alpha)$, $\partial^2/\partial x_\alpha^2 \, \delta(\boldsymbol{r} - \boldsymbol{r}_\alpha)$. We note how this relates to the lobe functions in which, for example, the difference between two close spherical Gaussians simulates a p type Gaussian. The point charge component obtained from the square of this simulated Gaussian will consist of three equispaced charges $-q$, $2q + r$, $-q$, that is a quadrupole plus a charge. The above operator method would involve

$$\left(\frac{1}{2} \frac{\partial^2}{\partial x_\alpha^2} + \beta_\alpha\right) \chi_\alpha(\boldsymbol{r})$$

namely would give the quadrupole plus charge of

$$\left(\frac{1}{2} \frac{\partial^2}{\partial x_\alpha^2} + \beta_\alpha\right) \delta(\boldsymbol{r} - \boldsymbol{r}_\alpha)$$

Table 4. The *s* and *p* type Gaussian point pole model potentials of Hall V_H, Hall (just charges) V_{HC}, Shipman (just charges) V_{SC} and Mulliken (just charges) V_{MC} compared with the wavefunction potential V, $\varepsilon V_H = (V - V_H)/V$

H_2O (*s* and *p* Gaussian)
The potential along a O—H bond (in that direction) where x = distance from O.

x Bohr	V	εV_H	εV_{HC}	εV_{SC}	εV_M
2.0	4.38594 (0)	2.76 (−2)	7.23 (−2)	3.71 (−2)	3.56 (−2)
4.0	1.22787 (−1)	0	3.16 (−1)	2.06 (−1)	1.95 (−1)
6.0	3.86932 (−2)	0	4.09 (−1)	3.18 (−1)	3.03 (−1)

0 denotes accurate to six significant digits, that is $\varepsilon V < 1.00\,(-5)$

H_2O (*s* and *p* Gaussian)
The potential along the bisector of HÔH (away from H) where x = distance from O.

x Bohr	V	εV_H	εV_{HC}	εV_{SC}	εV_M
2.0	−2.89558 (−1)	−2.41 (−1)	9.53 (−1)	7.89 (−1)	7.66 (−1)
4.0	−8.98833 (−2)	0	7.47 (−1)	6.61 (−1)	6.41 (−1)
6.0	−4.04313 (−2)	0	6.68 (−1)	6.06 (−1)	6.86 (−1)

C_2H_2
The potential along a perpendicular to C—C through a C where x = distance from C.

x Bohr	V	εV_H	εV_{HC}	εV_{SC}	εV_M
2.0	1.29433 (−2)	4.86 (0)	5.85 (−1)	1.05 (0)	1.63 (0)
4.0	−2.25221 (−2)	−2.22 (−4)	5.57 (−1)	6.15 (−1)	5.34 (−1)
6.0	−9.20356 (−3)	0	5.12 (−1)	5.51 (−1)	4.76 (−1)

BF
The potential along a perpendicular to B—F through F where x = distance from F.

x Bohr	V	εV_H	εV_{HC}	εV_{SC}	εV_M
2.0	7.76544 (−2)	−3.70 (−1)	3.09 (0)	3.39 (0)	3.30 (0)
4.0	1.88715 (−2)	−5.25 (−4)	2.54 (0)	2.95 (0)	2.87 (0)
6.0	7.72418 (−3)	0	2.22 (0)	2.59 (0)	2.53 (0)

BF
The potential along a perpendicular to B—F through B where x = distance from B.

x Bohr	V	εV_H	εV_{HC}	εV_{SC}	εV_M
2.0	3.07576 (−1)	5.15 (−2)	2.92 (−1)	3.51 (−1)	3.75 (−1)
4.0	6.43236 (−2)	4.07 (−4)	2.51 (−1)	3.65 (−1)	3.88 (−1)
6.0	2.40465 (−2)	0	3.09 (−1)	4.25 (−1)	4.45 (−1)

as before. Indeed the large −196.987, 397.673, −196.987 charges of the Hall point charge model of water given by Tait and Hall [1] have exactly this property.

FGO (s and p Gaussian) calculations on H_2O, C_2H_2 and BF in Table 4 illustrate that the accuracy of the higher Gaussian Hall model is comparable to that of the spherical Gaussian one. Namely the potential V_H at a distance of 6 Bohr (4 Bohr) from a heavy nucleus gives a relative error of $1.00E-5(1.00E-3)$ or better. Further, we note that the charges on their own are insufficient for higher Gaussians as indicated by the potentials V_{HC}. We have also displayed the charge-only Shipman and charge-only Mulliken models for completeness.

5. Mathematical Analysis of the Extended Hall Model

We may illustrate the asymptotic accuracy of the extended Hall model potential or, indeed, that of the electric field or electric field gradient by an analysis little different from that given by Tait and Hall [1].

The accurate density is given by Eq. (2) and the approximate density is given by Eq. (3). We are thus interested in the error density

$$\varepsilon(\boldsymbol{r}) = 2\sum_{\alpha} a_\alpha D_\alpha(\nabla_{\boldsymbol{r}_\alpha})[\chi_\alpha(\boldsymbol{r}) - \delta(\boldsymbol{r}-\boldsymbol{r}_\alpha)]$$

which leads to an error in the moment $x^i y^j z^k$ of

$$\int x^i y^j z^k \varepsilon(\boldsymbol{r})\, d\boldsymbol{r} = 2\sum_{\alpha} a_\alpha D_\alpha(\nabla_{\boldsymbol{r}_\alpha})\left[1-\exp\left(\frac{1}{4\beta_\alpha}\nabla^2_{\boldsymbol{r}_\alpha}\right)\right] x^i_\alpha y^j_\alpha z^k_\alpha$$

(see Appendix A) namely to the conservation of total charge and dipole moment.

In general, the model preserves the moment $P(\boldsymbol{r})$ where $\nabla^2 P = 0$.

The error potential is

$$\int \frac{1}{r}\varepsilon(\boldsymbol{r})\, d\boldsymbol{r} = 2\sum_{\alpha} a_\alpha D_\alpha(\nabla_{\boldsymbol{r}_\alpha}) 2\sqrt{\frac{\beta_\alpha}{\pi}}\, \bar{F}_0(\beta_\alpha r^2_\alpha)$$

where

$$\bar{F}_n(a) = \int_1^\infty t^{2n} \exp(-at^2)\, dt$$

has an asymptotic form of $\exp(-a)/2a$ and

$$\frac{d}{da}\bar{F}_n(a) = -\bar{F}_{n+1}(a).$$

The error potential is thus seen to decay exponentially, and therefore at a faster rate than the potential itself which decays as an inverse power. The error electric field and error electric field gradient also decay at an exponential rate compared to the inverse power decay of the accurate value. Further, the error potential and error electric field are linear combinations of the $\bar{F}_n(a)$ terms and so available codes for the evaluation of the higher Gaussian basis potential and electric field may be used to calculate the point charge potential and electric field. Just replace a call of $\bar{F}_n(a)$ by zero. This may involve changing just one line of code.

6. Implementation of the Extended Hall Model

In the extended Hall model it is computationally more convenient to differentiate the basis Gaussians rather than their products.

We may express Eq. (1) as

$$\rho(\boldsymbol{r}) = 2 \sum_{s,t} P_{st} D_s(\nabla_{\boldsymbol{r}_s}) \chi_s(\boldsymbol{r}) D_t(\nabla_{\boldsymbol{r}_t}) \chi_t(\boldsymbol{r})$$

where $\psi_s(\boldsymbol{r})$ has been replaced by $D_s(\nabla_{\boldsymbol{r}_s})\chi_s(\boldsymbol{r})$. Thus

$$\rho(\boldsymbol{r}) = 2 \sum_{s,t} P_{st} D_s(\nabla_{\boldsymbol{r}_s}) D_t(\nabla_{\boldsymbol{r}_t}) [\chi_s(\boldsymbol{r}) \chi_t(\boldsymbol{r})].$$

The product spherical Gaussian $\chi_s(\boldsymbol{r})\chi_t(\boldsymbol{r})$ is itself a Gaussian of centre $\boldsymbol{r}_{st} = (\alpha_s \boldsymbol{r}_s + \alpha_t \boldsymbol{r}_t)/(\alpha_a + \alpha_t)$, exponent $2\alpha_{st} = (\alpha_s + \alpha_t)$ and of total charge $S_{st} = \int \chi_s(\boldsymbol{r})\chi_t(\boldsymbol{r})\, d\boldsymbol{r}$ (note that this is different from the overlap $T_{st} = \int \psi_s(\boldsymbol{r})\psi_t(\boldsymbol{r})\, d\boldsymbol{r}$ between the two basis functions $\psi_s(\boldsymbol{r})$ and $\psi_t(\boldsymbol{r})$).

Thus $\rho(\boldsymbol{r}) = 2 \sum_{s,t} P_{st} D_s(\nabla_{\boldsymbol{r}_s}) D_t(\nabla_{\boldsymbol{r}_t}) [S_{st} \chi_{st}(\boldsymbol{r})]$.

The extended Hall model replaces this continuous distribution by

$$\rho_H(\boldsymbol{r}) = 2 \sum_{s,t} P_{st} D_s(\nabla_{\boldsymbol{r}_s}) D_t(\nabla_{\boldsymbol{r}_t}) [S_{st} \delta(\boldsymbol{r} - \boldsymbol{r}_{st})]$$

which has charge component

$$\rho_{HC}(\boldsymbol{r}) = 2 \sum_{s,t} P_{st} [D_s(\nabla_{\boldsymbol{r}_s}) D_t(\nabla_{\boldsymbol{r}_t}) S_{st}] \delta(\boldsymbol{r} - \boldsymbol{r}_{st})$$

$$= 2 \sum_{s,t} P_{st} T_{st} \delta(\boldsymbol{r} - \boldsymbol{r}_{st})$$

and thus the form of the charge only component of the extended Hall model is exactly that of the original Hall model, as noted by Yoffe [9]. (This indeed follows for the Shipman and Mulliken models.)

For computational convenience we proceed as follows. The overlap S_{st} is a function of the displacement $\boldsymbol{d}_{st} = \boldsymbol{r}_s - \boldsymbol{r}_t$ between the two product Gaussian centres

$$\nabla_{\boldsymbol{r}_s} = \frac{\alpha_s}{2\alpha_{st}} \nabla_{\boldsymbol{r}_{st}} + \nabla_{\boldsymbol{d}_{st}}$$

$$\nabla_{\boldsymbol{r}_t} = \frac{\alpha_t}{2\alpha_{st}} \nabla_{\boldsymbol{r}_{st}} - \nabla_{\boldsymbol{d}_{st}}$$

thus

$$\rho_H(\boldsymbol{r}) = 2\sum_{s,t} P_{st} D_s\left(\frac{\alpha_s}{2\alpha_{st}}\nabla_{\boldsymbol{r}_{st}} + \nabla_{\boldsymbol{d}_{st}}\right) D_t\left(\frac{\alpha_t}{2\alpha_{st}}\nabla_{\boldsymbol{r}_{st}} - \nabla_{\boldsymbol{d}_{st}}\right)[S_{st}(\boldsymbol{d}_{st}) * \delta(\boldsymbol{r} - \boldsymbol{r}_{st})] \tag{4}$$

while the one electron property

$$\int f(\boldsymbol{r})\rho_H(\boldsymbol{r})\, d\boldsymbol{r} = 2\sum_{s,t} P_{st} D_s\left(\frac{\alpha_s}{2\alpha_{st}}\nabla_{\boldsymbol{r}_{st}} + \nabla_{\boldsymbol{d}_{st}}\right) D_t\left(\frac{\alpha_t}{2\alpha_{st}}\nabla_{\boldsymbol{r}_{st}} - \nabla_{\boldsymbol{d}_{st}}\right)\left[S_{st}(\boldsymbol{d}_{st}) f(\boldsymbol{r}_{st})\right].$$

We may now expand these expressions in terms of derivatives of S_{st} and f.

Taking the example of the square of a p Gaussian we have, dropping the leading coefficient, the contribution $\delta\rho_H$ to the point charge model $\rho_H(\boldsymbol{r})$ is given by

$$\begin{aligned}\delta\rho_H &= \left(\frac{\alpha_s}{2\alpha_{st}}\frac{\partial}{\partial x_{st}} + \frac{\partial}{\partial u_{st}}\right)\left(\frac{\alpha_t}{2\alpha_{st}}\frac{\partial}{\partial x_{st}} - \frac{\partial}{\partial u_{st}}\right)\left[S_{st}(\boldsymbol{d}_{st})\delta(\boldsymbol{r} - \boldsymbol{r}_{st})\right] \\ &= \frac{\alpha_s\alpha_t}{(2\alpha_{st})^2} S_{st}\frac{\partial^2}{\partial x_{st}^2}\delta(\boldsymbol{r} - \boldsymbol{r}_{st}) + \frac{(\alpha_t - \alpha_s)}{2\alpha_{st}}\frac{\partial}{\partial u_{st}} S_{st}\frac{\partial}{\partial x_{st}}\delta(\boldsymbol{r} - \boldsymbol{r}_{st}) \\ &\quad - \frac{\partial^2}{\partial u_{st}^2} S_{st}\delta(\boldsymbol{r} - \boldsymbol{r}_{st})\end{aligned}$$

which, on setting $s = t$, eliminates the middle dipole term and gives a charge and quadrupole at the centre $\boldsymbol{r}_s$ as before.

7. Conclusion

Care must be exercised in using the Mulliken and Shipman point charge models to evaluate the molecular electrostatic potential since, in some important regions, they have poor accuracy and may give the wrong sign. On the other hand the Hall point charge model potential is asymptotically accurate and in the cases considered gives a relative error of $1.00E-5(1.00E-1)$ or better at 6 Bohr (4 Bohr).

An extension of the Hall model to higher Gaussians is made. There follows no loss in the asymptotic convergence of potential, electric field and electric field gradient and further, the same moments of charge are conserved.

Appendix A

$$\int_{-\infty}^{\infty} x^{2s}\exp(-\alpha x^2)\, dx = \frac{(2s)!}{(4\alpha)^s s!}\left(\frac{\pi}{\alpha}\right)^{1/2}. \tag{5}$$

Thus

$$\left(\frac{\alpha}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} x^i \exp(-\alpha(x-\beta)^2)\, dx = \left(\frac{\alpha}{\pi}\right)^{1/2}\int_{-\infty}^{\infty}(x+\beta)^i \exp(-\alpha x^2)\, dx$$

which, on expanding $(x+\beta)^i$ and using Eq. (5)

$$
\begin{aligned}
&= \sum_{s=0}^{[i/2]} \frac{i!}{(i-2s)!(4\alpha)^s s!} \beta^{i-2s} \\
&= \sum_{s=0}^{[i/2]} \frac{1}{s!} \left(\frac{1}{4\alpha} \frac{\partial^2}{\partial\beta^2} \right)^s \beta^i \\
&= \left[\exp\left(\frac{1}{4\alpha} \frac{\partial^2}{\partial\beta^2} \right) \right] \beta^i.
\end{aligned}
$$

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