

Hartree–Fock energy derivatives with respect to basis set exponents. Integral derivatives using Rys polynomials

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(Received 11 December 1986; accepted 24 March 1987)

The Rys polynomial method has been used to evaluate the first derivatives of the two electron integrals and the nuclear electron attraction integrals with respect to the Gaussian exponents. Gradients for the sulfur 6-31 G(*d*) basis set in HS⁻, H₂S, H₃S⁺, H₂S₂, H₃CSH, H₂CS, CS, H₂SO, SO₂ and SO₃ have been evaluated to illustrate the effect of charge, multiple bonding and hypervalency on the basis set exponents.

I. INTRODUCTION

Currently available basis sets are generally determined by optimizing the exponents and contraction coefficients of the primitive Gaussian functions for selected atomic spectroscopic states.^{1–5} Standard scaling factors for a few of the basis functions may sometimes be determined as an average of values optimized in different molecular environments.¹ Similarly, when polarization functions are added, they are usually optimized for selected molecular systems and then a standard value is suggested. Depending on the systems compared, the shortcomings of a particular basis set can be more or less pronounced. For example, in dealing with neutral and charged species, or comparing normal and hypervalent molecules, the computations could provide somewhat biased results depending on how the basis set was constructed.¹

Deficiencies in a basis set are difficult to assess. One could improve the basis set, and determine if the properties or energy differences of interest are changed significantly. A basis set can be improved by extending it, e.g., adding in more functions of *s* and *p* type (possibly diffuse functions in the description of anions or of Rydberg states), or adding extra *d* functions or functions with higher angular quantum number to provide a more flexible description of polarization. Another way of improving a basis set is to optimize some or all of its parameters (exponents, contraction coefficients, scale factors, positions of the functions) not just for atoms but each particular molecular system^{6,7} (this approach might be feasible if analytical derivatives are used). Both expansion and optimization of basis sets can be costly. Alternatively, deficiencies in a basis set for a particular molecule could be assessed by examining the derivatives of the energy with respect to the basis set parameters.

Integrals involving *s*- and *p*-type Gaussians are fairly simple⁸ and analytical gradients of the Hartree–Fock energy with respect to basis set parameters are available for molecular wave functions.⁹ However, these integral derivative formulas and the associated computer code cannot be extended easily to include *d*-type Gaussians. The Rys polynomial method¹⁰ has proved to be a practical technique for comput-

ing integrals¹⁰ and integral derivatives with respect to atom positions^{10,11} for higher angular momentum Gaussians. In the present paper, the Rys polynomial method is used to compute integral derivatives with respect to orbital exponents. The computational examples have been chosen to demonstrate the effect of charge, multiple bonding and hypervalency on the 6-31 G(*d*) basis set for sulfur.

II. THEORY

The first derivatives of the SCF and MSCSF energies can be expressed in terms of the derivatives of the one and two electron integrals:

$$\frac{\partial E}{\partial \alpha_i} = \sum_{\mu\nu} D_{\mu\nu} \frac{T_{\mu\nu}}{\partial \alpha_i} + \sum_{\mu\nu} D_{\mu\nu} \frac{\partial V_{\mu\nu}^{NE}}{\partial \alpha_i} - \sum_{\mu\nu} L_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial \alpha_i} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} D_{\mu\nu\lambda\sigma} \frac{\partial \langle \mu\nu | \lambda\sigma \rangle}{\partial \alpha_i}, \quad (1)$$

where $T_{\mu\nu}$ are the kinetic energy integrals, $V_{\mu\nu}^{NE}$ are the nuclear-electron attraction integrals, $S_{\mu\nu}$ are the overlap integrals, and $\langle \mu\nu | \lambda\sigma \rangle$ are the two-electron integrals; $D_{\mu\nu}$ is the one particle density matrix, $D_{\mu\nu\lambda\sigma}$ is the two particle density matrix and $L_{\mu\nu}$ is the Lagrangian in the AO basis. The evaluation of the density matrix or MO coefficient derivatives can be avoided because the energy is a minimum with respect to variations in the MO coefficients, provided orthonormality is maintained.¹²

For molecular calculations, the integrals usually involve basis functions constructed from a linear combination of Cartesian Gaussian functions. The derivative of a Gaussian function with respect to its exponent is again a Gaussian with an angular quantum number incremented by 2:

$$\begin{aligned} \frac{\partial}{\partial \alpha_i} g_a(l_A, \mathbf{r}_A, \alpha_i) &= \frac{\partial}{\partial \alpha_i} x_A^{l_A} y_A^{m_A} z_A^{n_A} \exp(-\alpha_i |\mathbf{r}_A|^2) \\ &= -x_A^{l_A+2} y_A^{m_A} z_A^{n_A} \exp(-\alpha_i |\mathbf{r}_A|^2) \\ &\quad - x_A^{l_A} y_A^{m_A+2} z_A^{n_A} \exp(-\alpha_i |\mathbf{r}_A|^2) \\ &\quad - x_A^{l_A} y_A^{m_A} z_A^{n_A+2} \exp(-\alpha_i |\mathbf{r}_A|^2), \end{aligned} \quad (2)$$

where $\mathbf{r}_A = \mathbf{r} - \mathbf{A} = (x_A, y_A, z_A)$, \mathbf{r} is the electron coordinate, $l_A = (l_A, m_A, n_A)$ and $\mathbf{A} = (A_x, A_y, A_z)$ the Gaussian center. The integral derivatives are, therefore, equivalent to integrals over Gaussian functions of angular quantum number higher by two (e.g., $s \rightarrow d$; $p \rightarrow f$; $d \rightarrow g$).

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A. Two electron integrals

The two electron integrals $\langle \mu\nu | \lambda\sigma \rangle$ over contracted Gaussians appearing in Eq. (1) can be expressed as linear

combinations of two-electron integrals over primitive Gaussians. The integrals over the primitives can be evaluated using a numerical quadrature based on Rys polynomials¹⁰:

$$\begin{aligned} (g_a g_b | r_{12}^{-1} | g_c g_d) &= \int \int x_A^{l_A}(1) y_A^{m_A}(1) z_A^{n_A}(1) \exp(-\alpha |r_A(1)|^2) \cdot x_B^{l_B}(1) y_B^{m_B}(1) z_B^{n_B}(1) \exp(-\beta |r_B(1)|^2) \cdot r_{12}^{-1} \\ &\quad \times x_C^{l_C}(2) y_C^{m_C}(2) z_C^{n_C}(2) \exp(-\gamma |r_C(2)|^2) \cdot x_D^{l_D}(2) y_D^{m_D}(2) z_D^{n_D}(2) \exp(-\delta |r_D(2)|^2) d\tau_1 d\tau_2 \\ &= \sum_{\alpha=1}^N I_x(t_\alpha) I_y(t_\alpha) I_z^*(t_\alpha), \\ I_z^* &= 2\rho^{1/2} \pi^{-1/2} I_z(t_\alpha) W_\alpha. \end{aligned} \quad (3)$$

The t_α are the positive zeroes of the N th Rys polynomial $R_N(t, X)$ and W_α are quadrature weight factors [$N > (\sum |l_i|)/2$]. For spherical Gaussians the two dimensional integral is

$$I_x(0,0,0,0,t) = \pi(\alpha + \beta)^{-1/2} (\gamma + \delta)^{-1/2} \exp \left[-\rho t^2 (P_x - Q_x)^2 - \frac{\alpha\beta}{\alpha + \beta} (A_x - B_x)^2 - \frac{\gamma\delta}{\gamma + \delta} (C_x - D_x)^2 \right] \quad (4)$$

where

$$\rho = \frac{(\alpha + \beta)(\gamma + \delta)}{\alpha + \beta + \gamma + \delta}, \quad P_x = \frac{\alpha A_x + \beta B_x}{\alpha + \beta}, \quad \text{and} \quad Q_x = \frac{\gamma C_x + \delta D_x}{\gamma + \delta}.$$

As in the case of the derivatives with respect to the function positions, the derivatives with respect to the exponents could be expressed in terms of the exponent derivatives of the two dimensional integrals.¹¹ However this is complicated by the fact that t depends on the exponents. Alternatively, the exponent derivatives can be expressed as integrals over higher angular momentum Gaussians, as indicated by Eq. (2):

$$\begin{aligned} \frac{\partial}{\partial \alpha_i} (g_a g_b | r_{12}^{-1} | g_c g_d) &= - \sum_{\alpha=1}^N I_x(l_A + 2, l_B, l_C, l_D, t_\alpha) I_y(m_A, m_B, m_C, m_D, t_\alpha) I_z^*(n_A, n_B, n_C, n_D, t_\alpha) \\ &\quad + I_x(l_A, l_B, l_C, l_D, t_\alpha) I_z(m_A + 2, m_B, m_C, m_D, t_\alpha) I_z^*(n_A, n_B, n_C, n_D, t_\alpha) \\ &\quad + I_x(l_A, l_B, l_C, l_D, t_\alpha) I_y(m_A, m_B, m_C, m_D, t_\alpha) I_z^*(n_A + 2, n_B, n_C, n_D, t_\alpha). \end{aligned} \quad (5)$$

The I 's over higher angular momentum Gaussians needed for the integral derivatives can be obtained by extending the recurrence relations used to calculate the I 's for the integrals.¹⁰ Alternatively the additional I 's can be generated by using the raising operators employed for the integral derivatives with respect to position.¹¹

For spherical Gaussians

$$\frac{\partial I_x(0,0,0,0,t)}{\partial A_x} = \Lambda_A \cdot I_x(0,0,0,0,t) = \left[-2\rho t^2 \frac{\alpha}{\alpha + \beta} (P_x - Q_x) - 2 \frac{\alpha\beta}{\alpha + \beta} (A_x - B_x) \right] \cdot I_x(0,0,0,0,t), \quad (6)$$

where Λ_A is a linear function of the coordinates. For higher angular momentum Gaussians, the derivatives are given by

$$\begin{aligned} \frac{\partial I_x(l_A, l_B, l_C, l_D, t)}{\partial A_x} &= \Lambda_A \cdot I_x(l_A, l_B, l_C, l_D, t) + \frac{l_A}{2\alpha} \Lambda_{AA} I_x(l_A - 1, l_B, l_C, l_D, t) + \frac{l_B}{2\beta} \Lambda_{AB} I_x(l_A, l_B - 1, l_C, l_D, t) \\ &\quad + \frac{l_C}{2\gamma} \Lambda_{AC} I_x(l_A, l_B, l_C - 1, l_D, t) + \frac{l_D}{2\delta} \Lambda_{AD} I_x(l_A, l_B, l_C, l_D - 1, t), \end{aligned} \quad (7)$$

where $\Lambda_{AB} = \partial \Lambda_A / \partial B_x$, etc. The two dimensional integrals over higher Gaussians can be obtained from integrals and derivatives over lower angular momentum Gaussians:

$$I_x(l_A + 1, l_B, l_C, l_D, t) = \frac{1}{2\alpha} \left[\frac{\partial I_x(l_A, l_B, l_C, l_D, t)}{\partial A_x} + l_A I_x(l_A - 1, l_B, l_C, l_D, t) \right]. \quad (8)$$

Substitution of Eq. (7) into Eq. (8) yields

$$\begin{aligned}
I_x(l_A + 1, l_B, l_C, l_D, t) &= \frac{1}{2\alpha} \Lambda_A I_x(l_A, l_B, l_C, l_D, t) + \frac{l_A}{2\alpha} \left(\frac{1}{2\alpha} \Lambda_{AA} + 1 \right) I_x(l_A - 1, l_B, l_C, l_D, t) \\
&+ \frac{1}{2\alpha} \frac{l_B}{2\beta} \Lambda_{AB} I_x(l_A, l_B - 1, l_C, l_D, t) + \frac{1}{2\alpha} \frac{l_C}{2\gamma} \Lambda_{AC} I_x(l_A, l_B, l_C - 1, l_D, t) \\
&+ \frac{1}{2\alpha} \frac{l_D}{2\delta} \Lambda_{AD} I_x(l_A, l_B, l_C, l_D - 1, t). \quad (9)
\end{aligned}$$

The expressions multiplying the various I_x 's are

$$\begin{aligned}
\frac{1}{2\alpha} \Lambda_A &= \frac{-\rho t^2}{\alpha + \beta} (P_x - Q_x) - \frac{\beta}{\alpha + \beta} (A_x - B_x), \\
\frac{1}{4\alpha^2} \Lambda_{AA} + \frac{1}{2\alpha} &= \frac{1}{4\alpha\beta} \Lambda_{AB} = \frac{1}{2} \left(\frac{1}{\alpha + \beta} - \frac{\rho t^2}{(\alpha + \beta)^2} \right), \\
\frac{1}{4\alpha\gamma} \Lambda_{AC} &= \frac{1}{4\alpha\delta} \Lambda_{AD} = \frac{1}{2} \frac{\rho t^2}{(\alpha + \beta)(\gamma + \delta)}. \quad (10)
\end{aligned}$$

A second application of this procedure generates $I_x(l_A + 2, l_B, l_C, l_D, t)$. The two electron integral derivatives can then be evaluated using Eq. (5).

B. One electron integrals

The nuclear electron attraction integrals over Gaussian primitives can be calculated in a manner analogous to the two electron repulsion integrals:

$$\begin{aligned}
V_{AB}^{\text{NE}} &= (g_a | r_{1C}^{-1} | g_b) \\
&= 2\pi^{-1/2} \int \int x_A^{l_A}(1) y_A^{m_A}(1) z_A^{n_A}(1) \exp(-\alpha r_A^2) \\
&\quad \times \exp(-u^2 r_{1C}) x_B^{l_B}(1) y_B^{m_B}(1) z_B^{n_B}(1) \exp(-\beta r_B^2) \\
&\quad \times d\tau_1 du \\
&= 2(\alpha + \beta)^{1/2} \pi^{-1/2} \sum_{\alpha=1}^N I_x^{\text{NE}}(t_\alpha) I_y^{\text{NE}}(t_\alpha) I_z^{\text{NE}}(t_\alpha) W_\alpha. \quad (11)
\end{aligned}$$

The integral and integral derivative for spherical Gaussians are

$$\begin{aligned}
I_x^{\text{NE}}(0,0,t) &= \exp \left[-\frac{\alpha\beta}{\alpha + \beta} (A_x - B_x)^2 \right] \\
&\quad \times \exp \left[-(\alpha + \beta) t^2 (P_x - C_x)^2 \right] \cdot \pi^{1/2} (\alpha + \beta)^{-1/2}, \\
\frac{\partial I_x^{\text{NE}}(0,0,t)}{\partial A_x} &= \left[-2 \frac{\alpha\beta}{\alpha + \beta} (A_x - B_x) - 2\alpha t^2 (P_x - C_x) \right] \\
&\quad \cdot I_x^{\text{NE}}(0,0,t) = \Lambda_A \cdot I_x^{\text{NE}}(0,0,t). \quad (12)
\end{aligned}$$

For higher angular momentum Gaussians, the derivatives are

$$\begin{aligned}
\frac{\partial I_x^{\text{NE}}(l_A, l_B, t)}{\partial A_x} &= \Lambda_A \cdot I_x^{\text{NE}}(l_A, l_B, t) \\
&+ \frac{l_A}{2\alpha} \Lambda_{AA} \cdot I_x(l_A - 1, l_B, t) \\
&+ \frac{l_B}{2\beta} \Lambda_{AB} \cdot I_x(l_A, l_B - 1, t). \quad (13)
\end{aligned}$$

$$\begin{aligned}
I_x^{\text{NE}}(l_A + 1, l_B, t) &= \frac{1}{2\alpha} \left[\frac{\partial I_x^{\text{NE}}(l_A, l_B, t)}{\partial A_x} + l_A I_x(l_A - 1, l_B, t) \right]. \quad (14)
\end{aligned}$$

Substitution into Eq. (13) gives:

$$\begin{aligned}
I_x^{\text{NE}}(l_A + 1, l_B, t) &= \frac{1}{2\alpha} \Lambda_A I_x^{\text{NE}}(l_A, l_B, t) + \frac{l_A}{2\alpha} \\
&\quad \times \left(\frac{1}{2\alpha} \Lambda_{AA} + 1 \right) \cdot I_x^{\text{NE}}(l_A - 1, l_B, t) \\
&\quad + \frac{1}{2\alpha} \frac{l_B}{2\beta} \Lambda_{AB} \cdot I_x(l_A, l_B - 1, t). \quad (15)
\end{aligned}$$

The constants multiplying the various integrals are

$$\begin{aligned}
\frac{1}{2\alpha} \Lambda_A &= -\frac{\beta}{\alpha + \beta} (A_x - B_x) - t^2 (P_x - C_x), \\
\frac{1}{4\alpha^2} \Lambda_{AA} + \frac{1}{2\alpha} &= \frac{1}{4\alpha\beta} \Lambda_{AB} = \frac{1 - t^2}{2(\alpha + \beta)}. \quad (16)
\end{aligned}$$

The kinetic energy integral over primitive Gaussians can be expressed in terms of overlap integrals. Since overlap integrals can be computed readily even for very high angular momentum Gaussians, exponent derivatives of overlap integrals and kinetic energy integrals are easy to calculate.

C. Invariance properties

Various relations between the derivatives of the integrals can be used to reduce the computational work significantly. For example, the two electron integrals are invariant to overall translation; hence, the derivatives with respect to position must obey

$$\frac{\partial \langle \mu\nu | \lambda\sigma \rangle}{\partial A_x} + \frac{\partial \langle \mu\nu | \lambda\sigma \rangle}{\partial B_x} + \frac{\partial \langle \mu\nu | \lambda\sigma \rangle}{\partial C_x} + \frac{\partial \langle \mu\nu | \lambda\sigma \rangle}{\partial D_x} = 0 \quad (17)$$

and similar expressions for y and z . Thus, only nine of the 12 position derivatives need to be calculated and the remaining three can be obtained by translational invariance. Rotational invariance is somewhat more difficult to apply, but can further reduce the computational effort.¹³

Other than virial scaling¹⁴ there is no general invariance property for the derivatives with respect to the exponents that can readily be exploited to improve the computational speed. However, some useful relations can be obtained for special cases. The product of two Gaussians describing the same electron on the same center is another Gaussian on the same center:

$$g_a(l_A, \mathbf{r}_p, \alpha) g_b(l_B, \mathbf{r}_p, \beta) = g_p(l_A + l_B, \mathbf{r}_p, \alpha + \beta). \quad (18)$$

For this product, the derivative with respect to α or β will be the same:

$$\begin{aligned} & \frac{\partial g_p(l_A + l_B, r_p, \alpha + \beta)}{\partial \alpha} \\ &= \frac{\partial g_p(l_A + l_B, r_p, \alpha + \beta)}{\partial \beta} \\ &= -x_p^{l_A + l_B + 2} y_p^{m_A + m_B} z_p^{n_A + n_B} \exp[-(\alpha + \beta)|r_p|^2] \\ & \quad - x_p^{l_A + l_B} y_p^{m_A + m_B + 2} z_p^{n_A + n_B} \exp[-(\alpha + \beta)|r_p|^2] \\ & \quad - x_p^{l_A + l_B} y_p^{m_A + m_B} z_p^{n_A + n_B + 2} \exp[-(\alpha + \beta)|r_p|^2]. \end{aligned} \quad (19)$$

Thus, if a two electron integral has g_a and g_b on the same center

$$\frac{\partial(g_a g_b |r_{12}^{-1}|g_c g_d)}{\partial \alpha} = \frac{\partial(g_a g_b |r_{12}^{-1}|g_c g_d)}{\partial \beta}; \quad \mathbf{A} = \mathbf{B} \quad (20)$$

and similarly for $\partial/\partial\gamma$ and $\partial/\partial\delta$ if $\mathbf{C} = \mathbf{D}$ (no simple relations exists for $\mathbf{A} = \mathbf{C}$). Equivalent expressions can be written for the one electron integrals.

III. RESULTS AND DISCUSSION

The first derivatives of the energy with respect to the primitive Gaussians exponents and contraction coefficients have been evaluated in a series of sulfur containing molecules with the 6-31G and 6-31G(*d*) basis sets.¹⁵ The latter basis set contains a set of six *d* functions on each nonhydrogen atom. The results are collected in Tables I and II. The

selected molecular systems illustrate sulfur atom in a number of different environments: (a) neutral, positively, or negatively charged; (b) single bonded to different atoms (H,C,S); (c) single, double, and triple bonds; and (d) normal and hypervalent species. The optimum geometries obtained at the HF/6-31G(*d*) level have been used throughout.¹⁶ The energies and the wave functions have been computed with GAUSSIAN 82¹⁷ using a cutoff in the two electron integrals evaluation of 10^{-10} and an SCF convergence criterion of 10^{-10} . Typical timing results on a VAX 11/780 for H₂SO with the 6-31G(*d*) basis set are 118 min for the derivatives of the two electron integrals with respect to the exponents compared to 44 min for the derivatives with respect to the atom positions and 21 min for the two electron integrals (no symmetry, all integrals, and derivatives computed using Rys polynomials).¹⁸ A modest improvement in speed can be obtained if the exponent derivatives are calculated for the valence shell only (97 vs 118 min).

The exponent gradients for sulfur atom at the UHF/6-31G(*d*) level are small (Table I), consistent with the fact that the basis set was obtained by minimizing the energy of the atom. Since the exponents of the *s*- and *p*-type primitive Gaussians are constrained to be equal during the basis set optimization, the sum of the *s* and *p* gradients for each exponent is significantly smaller than either the *s* or the *p* gradient individually. The gradients for sulfur atom serve as a reference for the remainder of the calculations on sulfur containing molecules.

Net charge has the largest effect on the exponent derivatives. In HS⁻ and H₃S⁺, the gradients for the outer Gaus-

TABLE I. Exponent derivatives (a.u.) for sulfur using the 6-31G basis set.

Exponent	Exponent derivatives				
	S(triplet)	HS ⁻	H ₂ S	H ₃ S ⁺	
1s	21917.1	-0.000 000 01	-0.000 000 01	-0.000 000 01	-0.000 000 01
	3301.49	-0.000 000 06	-0.000 000 06	-0.000 000 06	-0.000 000 06
	754.146	0.000 006 54	0.000 005 98	0.000 006 36	0.000 006 69
	212.711	0.000 082 58	0.000 075 88	0.000 082 22	0.000 086 51
	67.989 6	0.000 132 77	0.000 147 86	0.000 166 47	0.000 166 64
	23.051 5	-0.000 269 83	-0.000 219 25	-0.000 247 08	-0.000 301 41
2s	423.735	0.000 004 14	0.000 003 96	0.000 004 12	0.000 004 25
	100.710	0.000 106 10	0.000 103 22	0.000 108 24	0.000 111 98
	32.159 9	-0.000 621 39	-0.000 558 04	-0.000 573 20	-0.000 590 51
	11.807 9	0.000 285 98	0.000 285 19	0.000 298 61	0.000 311 27
	4.631 10	0.000 197 29	0.001 686 23	0.002 107 62	0.002 175 94
	1.870 25	0.006 939 81	0.006 475 81	0.008 222 44	0.008 880 03
2p	423.735	-0.000 000 29	-0.000 000 27	-0.000 000 37	-0.000 000 41
	100.710	-0.000 006 52	-0.000 005 26	-0.000 008 70	-0.000 010 80
	32.159 9	-0.000 094 98	-0.000 067 63	-0.000 055 92	-0.000 057 73
	11.807 9	-0.001 308 16	-0.001 355 10	-0.000 615 37	-0.000 213 76
	4.631 10	0.000 906 45	-0.001 997 82	0.002 071 27	0.004 783 92
	1.870 25	0.015 302 49	0.012 176 49	0.014 108 85	0.015 401 41
3s(inner)	2.615 84	0.000 146 08	0.000 359 37	0.001 501 97	0.002 248 57
	0.922 167	0.000 246 00	0.000 556 08	0.000 637 95	0.000 664 50
	0.341 287	0.001 399 43	-0.010 830 11	0.020 311 18	0.038 636 87
3s(outer)	0.117 167	-0.022 956 91	0.045 616 65	-0.008 896 53	-0.047 426 32
3p(inner)	2.615 84	-0.000 196 09	-0.000 509 37	-0.000 111 79	0.000 207 80
	0.922 167	0.000 005 92	-0.013 429 93	0.007 737 38	0.027 077 13
	0.341 287	-0.001 459 33	-0.152 869 48	-0.003 802 20	0.083 642 83
3p(outer)	0.117 167	0.022 390 07	0.687 663 19	0.026 424 97	-0.142 226 17

TABLE II. Exponent derivatives (a.u.) for sulfur using the 6-31G(*d*) basis set.

Exponent	Exponent derivatives										
	HS ⁻	H ₂ S	H ₃ S ⁺	H ₂ S ₂	H ₃ CSH	H ₂ CS	CS	H ₂ SO	SO ₂	SO ₃	
1s	219 17.1	-0.000 000 01	-0.000 000 01	-0.000 000 01	-0.000 000 01	-0.000 000 01	-0.000 000 01	-0.000 000 01	-0.000 000 01	-0.000 000 01	-0.000 000 01
	3301.49	0.000 000 04	0.000 000 04	0.000 000 04	0.000 000 04	0.000 000 04	0.000 000 04	0.000 000 05	0.000 000 05	0.000 000 06	
	754.146	0.000 008 73	0.000 009 10	0.000 009 45	0.000 009 07	0.000 009 07	0.000 009 10	0.000 009 20	0.000 009 52	0.000 010 09	
	212.711	0.000 064 48	0.000 070 53	0.000 075 14	0.000 069 38	0.000 069 46	0.000 069 61	0.000 072 04	0.000 072 72	0.000 075 09	
	67.989 6	-0.000 688 16	-0.000 670 87	-0.000 666 69	-0.000 683 44	-0.000 679 79	-0.000 685 96	-0.000 673 06	-0.000 707 34	-0.000 754 92	
	23.051 5	-0.002 944 07	-0.002 966 62	-0.002 966 15	-0.002 982 74	-0.002 976 96	-0.002 979 68	-0.002 980 97	-0.003 027 26	-0.003 082 86	
2s	423.735	0.000 003 96	0.000 004 11	0.000 004 24	0.000 004 10	0.000 004 09	0.000 004 09	0.000 004 13	0.000 004 22	0.000 004 25	
	100.710	0.000 102 02	0.000 106 29	0.000 109 53	0.000 105 46	0.000 105 61	0.000 105 31	0.000 106 90	0.000 107 52	0.000 106 40	
	32.159 9	-0.000 572 59	-0.000 600 30	-0.000 627 94	-0.000 604 63	-0.000 598 71	-0.000 600 25	-0.000 604 12	-0.000 634 90	-0.000 665 97	
	11.807 9	0.000 292 46	0.000 312 14	0.000 327 27	0.000 306 69	0.000 308 58	0.000 302 19	0.000 309 81	0.000 310 31	0.000 289 42	
	4.631 10	0.000 627 69	0.000 203 65	-0.000 313 33	0.000 003 58	0.000 206 26	0.000 282 80	0.000 336 62	-0.000 507 18	-0.001 165 39	
	1.870 25	0.005 009 55	0.005 575 54	0.005 590 97	0.005 238 78	0.005 277 74	0.005 428 04	0.005 693 71	0.005 302 19	0.005 070 98	
2p	423.735	-0.000 000 22	-0.000 000 29	-0.000 000 32	-0.000 000 28	-0.000 000 27	-0.000 000 25	-0.000 000 30	-0.000 000 17	-0.000 000 02	
	100.710	-0.000 004 39	-0.000 007 30	-0.000 008 90	-0.000 007 12	-0.000 006 31	-0.000 005 74	-0.000 007 65	-0.000 003 97	0.000 000 03	
	32.159 9	-0.000 096 65	-0.000 091 36	-0.000 101 87	-0.000 101 55	-0.000 092 16	-0.000 093 70	-0.000 080 73	-0.000 142 07	-0.000 198 58	
	11.807 9	-0.001 684 13	-0.001 082 04	-0.000 834 26	-0.001 188 20	-0.001 270 31	-0.001 408 32	-0.000 962 14	-0.002 044 40	-0.003 221 72	
	4.631 10	-0.002 594 55	0.001 197 51	0.003 635 97	0.001 334 75	0.000 047 50	-0.001 043 21	0.000 585 95	-0.001 640 99	-0.006 335 81	
	1.870 25	0.012 601 99	0.014 810 60	0.016 418 26	0.015 172 14	0.013 726 91	0.013 124 75	0.013 431 53	0.014 250 20	0.012 475 70	
3s(<i>i</i>)	2.615 84	-0.000 253 29	-0.000 272 40	-0.000 411 81	-0.000 265 23	-0.000 228 23	-0.000 111 92	-0.000 019 82	-0.000 330 97	-0.000 152 83	
	0.922 167	0.000 360 08	0.000 034 82	-0.000 258 99	0.000 055 11	0.000 087 96	0.000 227 63	0.000 160 60	-0.000 022 03	0.000 211 92	
	0.341 287	-0.016 828 95	0.004 058 54	0.015 696 68	0.002 460 23	0.002 224 24	-0.004 111 75	0.003 378 48	0.002 201 74	-0.010 986 81	
3s(<i>o</i>)	0.117 167	0.041 220 42	-0.010 797 04	-0.040 697 55	-0.003 677 03	-0.003 644 92	-0.006 908 06	-0.000 190 33	0.010 810 68	-0.013 362 49	
3p(<i>i</i>)	2.615 84	-0.000 500 82	-0.000 079 15	0.000 266 79	0.000 018 55	-0.000 134 56	-0.000 311 33	-0.000 258 23	-0.000 058 94	-0.000 450 37	
	0.922 167	-0.013 076 63	0.009 216 49	0.029 663 81	0.013 524 87	0.006 316 88	-0.004 471 59	-0.001 918 56	0.010 769 77	-0.012 915 70	
	0.341 287	-0.152 696 19	0.002 296 23	0.096 852 79	0.038 762 68	-0.012 834 25	-0.050 098 11	-0.009 409 50	0.006 283 17	-0.084 685 96	
3p(<i>o</i>)	0.117 167	0.708 794 34	0.025 165 87	-0.159 117 77	-0.065 634 91	0.032 236 63	0.090 828 10	-0.021 406 51	-0.033 694 96	0.001 423 03	
3d	0.65	0.007 985 51	0.021 316 36	0.036 970 43	0.030 053 59	0.012 028 41	0.001 700 79	0.005 309 85	0.027 762 15	-0.033 490 69	

sians are about an order of magnitude larger than for H₂S, and the *p*-type Gaussians are affected much more than the *s*-type Gaussians (Tables I and II). In the anion, the outermost 3*p* Gaussian would expand if allowed to relax, but the inner 3*p* Gaussians would contract, resulting in a larger split of the 3*p* shell. The reverse would happen in the cation. In all three molecules, the effects are largest for the outer 3*p* function and smaller for the outer 3*s* and inner 3*s* and inner 3*p* functions. Much smaller systematic changes can also be seen in the gradients of the core exponents. The addition of *d* functions (Table II vs Table I) causes only small changes in the exponent derivatives.

Changes in bonding have about an order of magnitude smaller effect on the exponent derivatives than changes in net charge. Three series can be constructed from the neutral molecules in Table II: (a) sulfur with single bonds to different atoms (XSH, X = H, HS, H₃C), (b) sulfur with single, double, and triple bonds to carbon (H₃CSH, H₂CS, CS), and (c) sulfur with hypervalent bonding (H₂SO, SO₂, SO₃). The changes in the gradients are larger for the outer valence shell than the inner valence shell, and larger for the 3*p* than the 3*s*. Changes in the *d* exponent gradients are relatively small, despite the wide range of bonding environments. None of the three series offers any clear trends. Single bonds of sulfur to H, S, and C have different effects, even though the electronegativities are very similar. The change in going from a double bond to a triple bond is different than the change in going from a single bond to a double bond. The exponent gradients for hypervalent systems do not show any distinct, systematic differences when compared to normal valent species. Perhaps the lack of clear discrepancies suggests that the 6-31G(*d*) basis set for sulfur may be reasona-

bly well balanced for neutral molecules. However, the fact that the exponent gradients are not negligibly small indicates that the atomic basis set is not optimal for any of the molecular environments considered. Although not included in the tables, the derivatives with respect to the basis set contraction coefficients are also not zero; for the valence functions, they are of the same order of magnitude as the exponent derivatives. Because of the strong coupling among the exponents and between the contraction coefficients and the exponents, an approximate Hessian matrix is needed in order to estimate the changes in the basis set parameters and in the total energy. Recent studies indicate that a fairly accurate estimate of the Hessian may be needed to predict these changes.⁵

ACKNOWLEDGMENT

This work was supported by a grant from the National Science Foundation (CHE 83-12505).

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