

# An efficient algorithm for calculating *ab initio* energy gradients using *s, p* Cartesian Gaussians

H. Bernhard Schlegel<sup>a)</sup>

Department of Chemistry, Wayne State University, Detroit, Michigan 48202  
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A method is presented for the calculation of analytical first derivatives of the two electron integrals over *s*- and *p*-type Cartesian Gaussian basis functions. Formulas are developed for derivatives with respect to the positions of the nuclei and basis functions (for use in geometry optimization) and with respect to the exponents of the primitive Gaussians (for use in basis set optimization). Full use is made of the *s = p* constraint on the Gaussian exponents. Contributions from an entire shell block are computed together and added to the total energy shell block and added to the total energy derivative directly, avoiding the computation and storage of the individual integral derivatives. This algorithm is currently being used in the *ab initio* molecular orbital program GAUSSIAN 80.

## INTRODUCTION

The utility of analytically calculated gradients of the Hartree-Fock energy has already been established beyond any doubt,<sup>1</sup> especially for tasks such as optimizing geometries, locating transition structures, and computing force constants. Energy derivatives have also been used to calculate properties such as polarizability and magnetic shielding as well as to optimize basis sets.<sup>2-5</sup> The success of these applications depends crucially on the efficiency of the energy gradient evaluation.

The simplest energy derivative to calculate is the gradient of the Hartree-Fock energy.<sup>6-9</sup> In the LCAO-MO approximation, the SCF energy gradient depends only on the derivatives of the one and two electron integrals over the basis functions, and does not require the explicit evaluation of the derivatives of the molecular orbital coefficients. Several programs are currently available for the calculation of SCF energy gradients.<sup>10-17</sup> Higher derivatives of the SCF energy, as well as gradients of Møller-Plesset and configuration interaction wave functions do require the MO coefficient derivatives in addition to the integral derivatives, and are therefore much more difficult to evaluate.<sup>18-23</sup>

This paper discusses an efficient algorithm for the computation of the derivatives of the two electron integrals with respect to the position and exponents of the primitive Gaussians that are used to construct the basis sets. The algorithm is especially suited for *s* and *p* type Cartesian Gaussians.<sup>24</sup> Furthermore, the individual integral derivatives are not constructed separately, but instead the components are summed directly to yield the overall derivative of the SCF energy. Another approach,<sup>25</sup> based on Rys polynomials,<sup>26,27</sup> is better suited for *d* and *f* type Gaussians and also for second derivatives of the integrals.<sup>18</sup>

## SCF ENERGY AND ENERGY GRADIENT

In the unrestricted Hartree-Fock approximation, the SCF energy can be expressed as

$$E = \sum_{\mu\nu} P_{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \mathbf{P}_{\mu\nu\lambda\sigma} (\mu\nu | \lambda\sigma) + V_{\text{nuc}}, \quad (1)$$

in terms of the one and two electron integrals

$$h_{\mu\nu} = \int \phi_{\mu}^* \hat{H}^{\text{core}} \phi_{\nu} d\tau, \quad (2)$$

$$(\mu\nu | \lambda\sigma) = \iint \phi_{\mu}^*(1) \phi_{\nu}(1) \frac{1}{r_{12}} \phi_{\lambda}^*(2) \phi_{\sigma}(2) d\tau_1 d\tau_2. \quad (3)$$

In the preceding equations,  $V_{\text{nuc}}$  is the nuclear-nuclear repulsion energy and  $\hat{H}^{\text{core}}$  is the electron Hamiltonian (kinetic energy + potential energy in the electrostatic field of the nuclei). The one and two particle density matrices are defined as

$$P_{\mu\nu} = P_{\mu\nu}^{\alpha} + P_{\mu\nu}^{\beta}, \quad P_{\mu\nu}^{\alpha} = \sum_i^{\text{occ}} C_{\mu i}^{\alpha*} C_{\nu i}^{\alpha}, \quad (4)$$

$$\mathbf{P}_{\mu\nu\lambda\sigma} = P_{\mu\nu} P_{\lambda\sigma} - P_{\mu\sigma} P_{\lambda\nu} - P_{\mu\sigma}^{\beta} P_{\lambda\nu}^{\beta}. \quad (5)$$

For closed shell restricted Hartree-Fock wave functions, the formulas for the density matrices are somewhat simpler since  $P_{\mu\nu}^{\alpha} = P_{\mu\nu}^{\beta}$ .

The derivative of the SCF energy can be written correspondingly

$$\frac{dE}{dx} = \sum_{\mu\nu} P_{\mu\nu} \frac{dh_{\mu\nu}}{dx} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \mathbf{P}_{\mu\nu\lambda\sigma} \frac{d(\mu\nu | \lambda\sigma)}{dx} + \frac{dV_{\text{nuc}}}{dx} - \sum_{\mu\nu} P'_{\mu\nu} \frac{dS_{\mu\nu}}{dx}, \quad (6)$$

with the overlap integral

$$S_{\mu\nu} = \int \phi_{\mu}^* \phi_{\nu} d\tau \quad (7)$$

and the energy weighted density matrix

$$P'_{\mu\nu} = \sum_i^{\text{occ}} \epsilon_i^{\alpha} C_{\mu i}^{\alpha*} C_{\nu i}^{\alpha} + \sum_i^{\text{occ}} \epsilon_i^{\beta} C_{\mu i}^{\beta*} C_{\nu i}^{\beta}, \quad (8)$$

where  $\epsilon_i$  is the energy of the *i*th molecular orbital.

Of the integral derivatives required in Eq. (6), those involving the one electron integrals  $h_{\mu\nu}$  and  $S_{\mu\nu}$  as well as the nuclear-nuclear repulsion  $V_{\text{nuc}}$  are relatively straightforward. Since they are neither numerous nor time consuming, computational speed is a secondary

<sup>a)</sup>Fellow of the Alfred P. Sloan Foundation, 1981-83.

consideration. In contrast, the efficiency of the two electron integral derivatives is of the utmost importance because of their large numbers ( $10^5$ – $10^6$  integrals typically) and the many different derivatives required (up to 16 derivatives for a four center integral).

## TWO ELECTRON INTEGRALS

The two electron integrals in Eq. (3) involve up to four different basis functions. The basis function is constructed from linear combinations of Gaussian-type primitives

$$\phi_\mu = \sum_a \xi_{a\mu} N_a g_a, \quad (9)$$

where  $\xi_{a\mu}$  are the contraction coefficients and  $N_a$  are the normalization factors. Each primitive function is written as a polynomial times a spherical Gaussian

$$g_a(\mathbf{l}_A \mathbf{r}_A \alpha) = x_A^{l_{Ax}} y_A^{l_{Ay}} z_A^{l_{Az}} \exp(-\alpha |\mathbf{r}_A|^2), \quad (10)$$

where  $\mathbf{l}_A = (l_{Ax}, l_{Ay}, l_{Az})$ ,  $\mathbf{r}_A = \mathbf{r} - \mathbf{A} = (x_A, y_A, z_A)$ ;  $\mathbf{r}$  is the electron coordinate and  $\mathbf{A} = (A_x, A_y, A_z)$  is the Gaussian center. The Gaussians are chosen to follow the nuclei rigidly. Thus, the derivatives of the energy with respect to the nuclear positions require the derivatives of the integrals with respect to the position of the Gaussian primitives.

Higher angular momentum Gaussians (i.e.,  $p$ ,  $d$ , and  $f$  etc.) can be obtained by differentiation of spherical Gaussians

$$g_a(\mathbf{l}_A \mathbf{r}_A \alpha) = \hat{M}^{l_{Ax}} \hat{M}^{l_{Ay}} \hat{M}^{l_{Az}} g_a(\mathbf{0} \mathbf{r}_A \alpha), \quad (11)$$

where

$$\begin{aligned} \hat{M}^{l_{Ax}} &= 0, \quad \text{for } l_{Ax} < 0, \\ &= 1, \quad \text{for } l_{Ax} = 0, \end{aligned} \quad (12)$$

and

$$\hat{M}^{l_{Ax}+1} = \frac{1}{2\alpha} \left( \hat{M}^{l_{Ax}} \frac{\partial}{\partial A_x} + l_{Ax} \hat{M}^{l_{Ax}-1} \right);$$

$\hat{M}^{l_{Ay}}$  and  $\hat{M}^{l_{Az}}$  are defined similarly.

A set of Gaussian primitives with the same exponent  $\alpha$  and on the same center but differing in angular momentum constitute a primitive shell (i.e., a set  $s p_x p_y$  and  $p_z$  type Gaussians make up an  $sp$  shell). It has already been demonstrated that the  $s = p$  constraint on the Gaussian exponents leads to a substantial savings in the integral evaluation time.<sup>28</sup> The STO-3G, 4-31G, 6-31G, and 3-21G basis sets are all of this type.<sup>29-31</sup>

The two electron integrals over contracted basis functions (3) reduce to linear combinations of two electron integrals over Gaussian primitives. The general two electron integral involving four Gaussians with different exponents on different centers is

$$\begin{aligned} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) &= \int \int g_a(\mathbf{l}_A \mathbf{r}_A(1)\alpha) g_b(\mathbf{l}_B \mathbf{r}_B(1)\beta) \frac{1}{|\mathbf{r}(1) - \mathbf{r}(2)|} \\ &\times g_c(\mathbf{l}_C \mathbf{r}_C(2)\gamma) g_d(\mathbf{l}_D \mathbf{r}_D(2)\delta) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (13)$$

For spherical Gaussians, the general four center two electron integral is<sup>32</sup>:

$$\begin{aligned} (\mathbf{0}, \mathbf{0} | \mathbf{0}, \mathbf{0}) &= (ss | ss) \\ &= \theta F_0(\rho \overline{PQ}^2) \exp(-u \overline{AB}^2) \exp(-v \overline{CD}^2), \end{aligned} \quad (14)$$

where  $p = \alpha + \beta$ ,  $q = \gamma + \delta$ ,  $\rho = pq/(p+q)$ ,

$$\theta = 2\pi^{5/2}/pq(\sqrt{p+q}), \quad u = \alpha\beta/(\alpha+\beta),$$

$$v = \gamma\delta/(\gamma+\delta), \quad \overline{AB}^2 = |\mathbf{A} - \mathbf{B}|^2,$$

$$\overline{CD}^2 = |\mathbf{C} - \mathbf{D}|^2, \quad \overline{PQ}^2 = |P - Q|^2,$$

$$P = (\alpha \mathbf{A} + \beta \mathbf{B})/p, \quad Q = (\gamma \mathbf{C} + \delta \mathbf{D})/q.$$

The function  $F_m(t)$  has the property

$$\begin{aligned} F_m(t) &= \int_0^1 u^{2m} \exp(-tu^2) du, \\ \frac{dF_m(t)}{dt} &= -F_{m+1}(t). \end{aligned} \quad (15)$$

The two electron integrals over other types of Gaussians can be derived by integrating Eq. (13) directly.

Alternatively, the derivative operators used in Eq. (12) can be used to obtain these integrals from Eq. (14),

$$(\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) = \left( \prod_{\substack{U=ABCD \\ i=x,y,z}} \hat{M}^{l_U i} \right) (ss | ss) = \hat{M}(\omega)(ss | ss). \quad (16)$$

## INTEGRAL DERIVATIVES IN TERMS OF HIGHER ANGULAR MOMENTUM FUNCTIONS

The simplest method for calculating integral derivatives is to differentiate the Gaussians first and then to integrate. Differentiating with respect to the centers yields

$$\frac{d}{dA_x} g_a(\mathbf{l}_A \mathbf{r}_A \alpha) = 2\alpha g_a(\mathbf{l}_A^{1x} \mathbf{r}_A \alpha) - l_{Ax} g_a(\mathbf{l}_A^{-1x} \mathbf{r}_A \alpha), \quad (17)$$

where

$$\mathbf{l}_A^{1x} = (l_{Ax} \pm 1, l_{Ay}, l_{Az}).$$

Thus, the two electron integral derivative can be expressed in terms of integrals over Gaussians with higher and lower angular momenta,

$$\frac{\partial}{\partial A_x} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) = 2\alpha (\mathbf{l}_A^{1x} \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) - l_{Ax} (\mathbf{l}_A^{-1x} \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D). \quad (18)$$

In a similar manner, the derivative with respect to the exponent is given by

$$\frac{d}{d\alpha} g_a(\mathbf{l}_A \mathbf{r}_A \alpha) = -g_a(\mathbf{l}_A^{2x} \mathbf{r}_A \alpha) - g_a(\mathbf{l}_A^{2y} \mathbf{r}_A \alpha) - g_a(\mathbf{l}_A^{2z} \mathbf{r}_A \alpha), \quad (19)$$

where  $\mathbf{l}_A^{2x} = (l_{Ax} + 2, l_{Ay}, l_{Az})$  and yield two electron integral derivatives

$$\begin{aligned} \frac{\partial}{\partial \alpha} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) &= -(\mathbf{l}_A^{2x} \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) \\ &\quad - (\mathbf{l}_A^{2y} \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) - (\mathbf{l}_A^{2z} \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D). \end{aligned} \quad (20)$$

This approach leads to relatively simple expressions for the integral derivatives, that can be evaluated readily provided integrals over higher angular momentum Gaussians are available. Analogous formulas are practical for the one electron integral derivatives over  $s$  and  $p$  functions, since the formulas for  $d$  and  $f$  function integrals are not difficult to program.<sup>33</sup> For two electron

integrals, the additional calculations involving the higher angular momentum functions are prohibitive. Gradient calculations using this method are several times slower than the energy calculation alone, even when special steps are taken to optimize the derivative evaluation.

### DIRECT DIFFERENTIATION OF THE TWO ELECTRON INTEGRALS WITH RESPECT TO POSITION

An alternative approach to the calculation of two electron integral derivatives is to differentiate Eq. (14) directly

$$\begin{aligned} \frac{d(ss|ss)}{dR_i} &= - \left( u \frac{d\overline{AB^2}}{dR_i} + v \frac{d\overline{CD^2}}{dR_i} \right) \theta F_0(\rho\overline{PQ^2}) \exp(-u\overline{AB^2}) \\ &\times \exp(-v\overline{CD^2}) - \rho \frac{d\overline{PQ^2}}{dR_i} \theta F_1(\rho\overline{PQ^2}) \exp(-u\overline{AB^2}) \exp(-v\overline{CD^2}) \\ &= \Lambda(R_i)(ss|ss) + \Lambda(R_i)'(ss|ss)' . \end{aligned} \quad (21)$$

$R_i$  is an arbitrary Cartesian coordinate of a Gaussian center. The integral  $(ss|ss)'$  is the same as  $(ss|ss)$  except that  $F_0(t)$  is replaced by  $F_1(t)$ . Note that  $\Lambda$  and  $\Lambda'$  are linear functions of  $A$ ,  $B$ ,  $C$ , and  $D$ .

Direct differentiation of the integrals for higher angular momentum Gaussians would be quite cumbersome.

Instead, the operators  $\hat{M}$  can be used to generate the integral derivatives over higher angular momentum Gaussians from Eq. (21),

$$\begin{aligned} \frac{d}{dR_i} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) &= \frac{d}{dR_i} \hat{M}(\omega)(ss|ss) \\ &= \hat{M}(\omega) \frac{d}{dR_i} (ss|ss) \\ &= \hat{M}(\omega) \Lambda(R_i)(ss|ss) + \hat{M}(\omega) \Lambda(R_i)'(ss|ss)' . \end{aligned} \quad (22)$$

Since  $\Lambda$  and  $\Lambda'$  are linear functions of  $A$ ,  $B$ ,  $C$ , and  $D$ , only the first derivatives are nonzero. If we define the auxiliary operators  $\hat{M}_{U_i}$ ,

$$M_{Ax}(\omega) = \hat{M}^{Ax}{}^{-1} \left( \prod_{\substack{U=ABCD \\ i=xy\neq \\ U_i \neq Ax}} \hat{M}^i U_i \right) , \quad (23)$$

it can be shown that

$$\hat{M}(\omega) \Lambda(Ax) = \Lambda \hat{M}(\omega) + \sum_{U=ABCD} l_{Ux} \Lambda_A \hat{M}_{Ax}(\omega) , \quad (24)$$

where

$$\Lambda = \Lambda(Ax), \quad \Lambda_A = \frac{1}{2\alpha} \frac{d\Lambda(Ax)}{dAx} , \quad \text{etc.}$$

We can expand Eq. (22):

$$\begin{aligned} \frac{d}{dAx} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) &= \Lambda \hat{M}(\omega)(ss|ss) + \sum_{U=ABCD} l_{Ux} \Lambda_U \hat{M}_{Ux}(\omega)(ss|ss) + \Lambda' \hat{M}(\omega)(ss|ss)' + \sum_{U=ABCD} l_{Ux} \Lambda'_U \hat{M}_{Ux}(\omega)(ss|ss)' \\ &= \Lambda(\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) + \Lambda_A l_{Ax} (\mathbf{l}_A^{-1x} \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) + \Lambda_B l_{Bx} (\mathbf{l}_A \mathbf{l}_B^{-1x} | \mathbf{l}_C \mathbf{l}_D) + \Lambda'_A (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D)' + \Lambda'_A l_{Ax} (\mathbf{l}_A^{-1x} \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) \\ &+ \Lambda'_B l_{Bx} (\mathbf{l}_A \mathbf{l}_B^{-1x} | \mathbf{l}_C \mathbf{l}_D)' + \Lambda'_C l_{Cx} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C^{-1x} \mathbf{l}_D) + \Lambda'_D l_{Dx} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D^{-1x})' . \end{aligned} \quad (25)$$

At first inspection, Eq. (25) appears to require more effort to evaluate than Eq. (18). However, two features of Eq. (25) make the direct differentiation approach more manageable and efficient. The integral derivatives in Eq. (25) do not require integrals over higher angular momentum Gaussians. For  $p$  type Gaussians, only integrals of  $s$  and  $p$  Gaussians are needed to compute the integral derivatives. Since the integrals and integral derivatives are computed over entire shell blocks, the additional integrals over lower angular momentum functions are readily available. Furthermore, the code used to compute  $(\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D)$  can be used to compute  $(\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D)'$  with the simple replacement of  $F_m(t) \rightarrow F_{m+1}(t)$ . Secondly, since there is no need to store the integral derivatives explicitly, they can be combined with the appropriate density matrix elements and summed as the individual terms are generated.

The contribution to the energy from a given primitive shell block can be written as

$$\tilde{V} = \sum_{\omega}^{\text{block}} \mathbf{P}(\omega) (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) , \quad (26)$$

where

$$\mathbf{P}(\omega) = \mathbf{P}_{\mu\nu\lambda\sigma} \xi_{a\mu} \xi_{b\nu} \xi_{c\lambda} \xi_{d\sigma} N_a N_b N_c N_d .$$

The two electron density matrix is defined in Eq. (5); the contraction coefficients and normalization factors are given in Eq. (9). The sum on  $\omega$  extends over all the members of the primitive shell block. In the case of four different  $sp$  shells, this involves a total of 256 integrals.

The contribution from a shell block to the derivative is given by

$$\begin{aligned} \frac{d\tilde{V}}{dAx} &= \sum_{\omega}^{\text{block}} \mathbf{P}(\omega) d(\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) / dAx = \Lambda \left[ \sum_{\omega} \mathbf{P}(\omega) (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) \right] + \Lambda_A \left[ \sum_{\omega} \mathbf{P}(\omega) l_{Ax} (\mathbf{l}_A^{-1x} \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) \right] \\ &+ \Lambda_B \left[ \sum_{\omega} \mathbf{P}(\omega) l_{Bx} (\mathbf{l}_A \mathbf{l}_B^{-1x} | \mathbf{l}_C \mathbf{l}_D) \right] + \Lambda'_A \left[ \sum_{\omega} \mathbf{P}(\omega) (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D)' \right] + \Lambda'_A \left[ \sum_{\omega} \mathbf{P}(\omega) l_{Ax} (\mathbf{l}_A^{-1x} \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D)' \right] \\ &+ \Lambda'_B \left[ \sum_{\omega} \mathbf{P}(\omega) l_{Bx} (\mathbf{l}_A \mathbf{l}_B^{-1x} | \mathbf{l}_C \mathbf{l}_D)' \right] + \Lambda'_C \left[ \sum_{\omega} \mathbf{P}(\omega) l_{Cx} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C^{-1x} \mathbf{l}_D)' \right] + \Lambda'_D \left[ \sum_{\omega} \mathbf{P}(\omega) l_{Dx} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D^{-1x})' \right] \\ &= \Lambda \tilde{V} + \Lambda_A \tilde{V}_{Ax} + \Lambda_B \tilde{V}_{Bx} + \Lambda'_A \tilde{V}' + \Lambda'_A \tilde{V}'_{Ax} + \Lambda'_B \tilde{V}'_{Bx} + \Lambda'_C \tilde{V}'_{Cx} + \Lambda'_D \tilde{V}'_{Dx} , \end{aligned} \quad (27)$$

where  $\tilde{V}'$  is defined similar to  $\tilde{V}$  in Eq. (25) with  $(\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D)$  replaced by  $(\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D)'$ .

Since the  $\Lambda$  factors are the same for each combination of primitives within the shell block, the expressions for the sums can be factored into a set of partial sums  $\tilde{V}$ ,  $\tilde{V}_{U_i}$ , etc. Although there are 12  $\tilde{V}_{U_i}$ 's, the sums for each contain fewer terms than  $\tilde{V}$ . The additional effort needed to compute the set of  $\tilde{V}_{U_i}$ 's is comparable to that required for  $\tilde{V}$ . Furthermore, these sums are computed only once for a shell block, and then multiplied by the appropriate  $\Lambda$  terms to yield *all* 12 derivatives. The fact that this method produces one derivative or all the derivatives with essentially the same effort is the key to the efficacy of the approach.

### DIRECT DIFFERENTIATION OF THE TWO ELECTRON INTEGRALS WITH RESPECT TO EXPONENT

The derivative of the  $(ss|ss)$  integral with respect to the exponent  $\epsilon$  is

$$\begin{aligned} \frac{d(ss|ss)}{d\epsilon} &= -\left(\overline{AB^2} \frac{du}{d\epsilon} + \overline{CD^2} \frac{dv}{d\epsilon} + \frac{1}{\theta} \frac{d\theta}{d\epsilon}\right) \theta F_0(\rho \overline{PQ^2}) \\ &\times \exp(-u \overline{AB^2}) \exp(-v \overline{CD^2}) - \left(\overline{PQ^2} \frac{d\rho}{d\epsilon} + \rho \frac{d\overline{PQ^2}}{d\epsilon}\right) \\ &\times \theta F_1(\rho \overline{PQ^2}) \exp(-u \overline{AB^2}) \exp(-v \overline{CD^2}) \\ &= \Gamma(ss|ss) + \Gamma'(ss|ss)', \end{aligned} \tag{28}$$

where  $\Gamma$  and  $\Gamma'$  are quadratic functions of A, B, C, and D. The integral  $(ss|ss)'$  is as defined above. The derivatives for higher angular momentum functions are given by

$$\begin{aligned} \frac{\partial(\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D)}{\partial\alpha} &= \frac{\partial}{\partial\alpha} \hat{M}(\omega) (ss|ss) \\ &= \frac{-(l_{Ax} + l_{Ay} + l_{Az})}{\alpha} \hat{M}(\omega) (ss|ss) + \hat{M}(\omega) \frac{\partial(ss|ss)}{\partial\alpha} \\ &= \frac{-(l_{Ax} + l_{Ay} + l_{Az})}{\alpha} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) \\ &+ \hat{M}(\omega) \Gamma(ss|ss) + \hat{M}(\omega) \Gamma'(ss|ss)'. \end{aligned} \tag{29}$$

Since  $\Gamma$  and  $\Gamma'$  are quadratic functions of A, B, C, and D, only the first and second derivatives are nonzero. If we define the auxiliary operators  $\hat{M}_{U_i V_j}$ ,

$$\begin{aligned} \hat{M}_{AxAx}(\omega) &= \hat{M}^{l_{Ax}-2} \prod_{\substack{U=ABCD \\ i=xy\epsilon \\ U \neq Ax}} \hat{M}^{l_{U_i}}; \\ \hat{M}_{AxBx}(\omega) &= \hat{M}^{l_{Ax}-1} \hat{M}^{l_{Bx}-1} \prod_{\substack{U=ABCD \\ i=xy\epsilon \\ U \neq Ax, Bx}} \hat{M}^{l_{U_i}}, \end{aligned} \tag{30}$$

it can be shown that

$$\hat{M}(\omega) \Gamma = \Gamma \hat{M}(\omega) + \sum_{\substack{U=ABCD \\ i=xy\epsilon}} l_{U_i} \Gamma_{U_i} \hat{M}_{U_i}(\omega) + \sum_{\substack{U, V=ABCD \\ i=xy\epsilon}} l_{U_i} (l_{V_i} - \delta_{UV}) \Gamma_{UV} \hat{M}_{U_i V_i}(\omega). \tag{31}$$

We can expand Eq. (29):

$$\begin{aligned} \frac{\partial(\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D)}{\partial\alpha} &= \frac{\partial \hat{M}(\omega) (ss|ss)}{\partial\alpha} = -\left(\frac{l_{Ax} + l_{Ay} + l_{Az}}{\alpha} + \Gamma\right) \hat{M}(\omega) (ss|ss) + \hat{M}(\omega) \frac{\partial(ss|ss)}{\partial\alpha} \\ &= \left(\frac{-l_{Ax} + l_{Ay} + l_{Az}}{\alpha} + \Gamma\right) \hat{M}(\omega) (ss|ss) \\ &+ \sum_{\substack{U=ABCD \\ i=xy\epsilon}} l_{U_i} \Gamma_{U_i} \hat{M}_{U_i}(ss|ss) + \sum_{\substack{U, V=ABCD \\ i=xy\epsilon}} l_{U_i} (l_{V_i} - \delta_{UV}) \Gamma_{UV} \hat{M}_{U_i V_i}(\omega) (ss|ss) \\ &+ \Gamma' \hat{M}(\omega) (ss|ss)' + \sum_{\substack{U=ABCD \\ i=xy\epsilon}} l_{U_i} \Gamma_{U_i} \hat{M}_{U_i}(ss|ss)' + \sum_{\substack{U, V=ABCD \\ i=xy\epsilon}} l_{U_i} (l_{V_i} - \delta_{UV}) \Gamma'_{UV} \hat{M}_{U_i V_i}(\omega) (ss|ss)'. \end{aligned} \tag{32}$$

Summation of the integral derivatives over the shell block yields

$$\begin{aligned} \frac{\partial \tilde{V}}{\partial\alpha} &= \sum_{\omega}^{\text{block}} \left[ \frac{\partial \mathbf{P}(\omega)}{\partial\alpha} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) + \mathbf{P}(\omega) \frac{\partial(\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D)}{\partial\alpha} \right] = \tilde{V} + \Gamma \tilde{V} + \sum_{\substack{U=ABCD \\ i=xy\epsilon}} \Gamma_{U_i} \tilde{V}_{U_i} + \sum_{U, V=ABCD} \Gamma_{UV} \tilde{V}_{UV} \\ &+ \Gamma' \tilde{V}' + \sum_{\substack{U=ABCD \\ i=xy\epsilon}} \Gamma'_{U_i} \tilde{V}'_{U_i} + \sum_{U, V=ABCD} \Gamma'_{UV} \tilde{V}'_{UV}. \end{aligned} \tag{33}$$

The additional terms in Eq. (33) are defined by

$$\tilde{V} = \sum_{\omega}^{\text{block}} \mathbf{P}(\omega) \left[ \frac{3}{4\alpha} - \frac{(l_{Ax} + l_{Ay} + l_{Az})}{2\alpha} \right] (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D), \tag{34}$$

$$\tilde{V}_{UV} = \sum_{i=xy\epsilon}^{\text{block}} \sum_{\omega} \mathbf{P}(\omega) l_{U_i} (l_{V_i} - \delta_{UV}) \hat{M}_{U_i V_i}(\omega) (ss|ss). \tag{35}$$

TABLE I. Comparison of energy gradient calculation times.

Molecule	Basis set <sup>b</sup>	Timing data <sup>a</sup>				Timing Ratios	
		Two electron integrals	Total energy	Two electron integral derivatives	Total gradient	Integral derivatives	Gradient
						Integrals	Energy
BH <sub>4</sub>	3-21G	1.3	4.6	1.4	2.4	1.08	0.52
BH <sub>4</sub> -H <sub>2</sub> O	3-21G	13.7	30.2	13.2	16.2	1.18	0.54
BH <sub>4</sub> -CH <sub>2</sub> O	3-21G	27.3	72.7	30.4	35.5	1.11	0.49
BH <sub>4</sub> -CH <sub>2</sub> O+H <sub>2</sub> O	3-21G	83.6	202.8	75.2	83.8	0.90	0.41
C <sub>2</sub> H <sub>3</sub> F	STO-3G	7.9	13.2	22.6	25.1	2.86	1.90
	3-21G	18.7	38.0	25.8	27.5	1.38	0.72
	4-31G	29.2	53.4	55.2	59.0	1.89	1.10
	6-31G	37.8	62.2	72.8	77.2	1.93	1.24
4-hydroxypyridine <sup>c</sup>	STO-3G	475	951	1272	1341	2.67	1.41
	3-21G	2202	7529	1773	1839	0.81	0.24
	6-31G	3012	10322	3932	4064	1.31	0.39

<sup>a</sup>cpu times in seconds on an Amdahl 470/V6 under MTS, unless otherwise indicated; total energy=integral+SCF times; total gradient=one and two electron integral derivative times+conversion to internal coordinates.

<sup>b</sup>See Refs. 29-31 for basis set definitions.

<sup>c</sup>Calculated on a CDC Cyber 172 under NOS.

Equation (34) arises from the difference in the normalization factors, as  $l_A$  or  $\alpha$  are changed.

## SUMMARY OF DIRECT DIFFERENTIATION ALGORITHM

The computational implementation of the above approach to two electron integral derivatives can be outlined as follows:

- For the primitive shell block, test that  $\sum_{\omega} \mathbf{P}(\omega)(ss|ss)$  is larger than a given threshold and that the Gaussians are not all on the same center. Omit the shell block if either test fails.
- Compute all the  $(l_A l_B | l_C l_D)$  integrals in the primitive shell block.
- Compute the sums  $\bar{V}$ ,  $\bar{V}_{U_i}$  (and  $\bar{V}_{U_V}$  if needed for exponent derivatives) by combining the necessary integrals in the shell block with the density matrix and contraction coefficients.
- Form the contributions to the 12 derivatives with respect to position (and/or four derivatives with respect to the exponents) by combining the terms from (c) with  $\Lambda$  and  $\Lambda_U$  (and/or  $\Gamma$ ,  $\Gamma_{U_i}$ , and  $\Gamma_{U_V}$ ).
- Substitute  $F_{m+1}(t)$  for  $F_m(t)$  and repeat (b), (c), and (d) for the primed quantities (e.g.,  $\bar{V}'$ ,  $\Lambda'$ , etc.).
- Repeat (a) to (e) for all the primitive shell blocks.

The accuracy of the integral derivatives depends on the approximation to  $F_m(t)$  and the convergence on the density matrix.  $F_m(t)$  should be computed to an accuracy of at least  $10^{-8}$  and the SCF convergence must be  $10^{-7}$  to ensure gradients correct to  $10^{-6}$ .

## EXAMPLES AND COMPUTATION TIMES

The method outlined above for computing energy derivatives with respect to position has been incorporated into FORCE<sup>12</sup> and LINK 702 of GAUSSIAN 80.<sup>11</sup> Table I contains a

representative sample of energy gradient calculations using GAUSSIAN 80. On average, the gradient calculation time is considerably less than the total energy time. The relative performance is considerably better for extended basis sets. The poorer relative speed on minimal basis sets is not an indication of inefficiency in the derivative calculations but is more a reflection of the special adaptation of the *sp* integral section (SHELL) of GAUSSIAN 80 to highly contracted basis sets and planar molecules as well as the lower number of integrals processed by the SCF section. That this is the case can be seen from the timing data for the STO-3G and 3-21G calculations on vinyl fluoride and hydroxypyridine. Both basis sets have the same number of primitive Gaussians. The time for the gradient calculations is only 10%-50% larger with the extended basis set, but the integral calculation time has increased by a factor of 2 to 4. Since extended basis sets are often needed to compute satisfactory optimized geometries, the 3-21G basis set offers a good compromise between basis set flexibility and efficiency in the gradient calculations. Note that the timing ratios remain nearly constant as the number of atoms is increased. Although it is difficult to compare the absolute speed of the gradient programs, the present algorithm and associated computer code appear to be significantly faster than other currently available gradient programs. To date, ~10 000 structures have been optimized<sup>34</sup> using the energy gradient methods in GAUSSIAN 80. An efficient algorithm for using gradients to optimize geometries and locate transition structures is discussed elsewhere.<sup>35</sup>

Energy derivatives with respect to Gaussian exponents and contraction coefficients, as well as basis function and nuclear positions can be carried out with the program DRVEXP.<sup>12</sup> For the same size molecule, calculations with DRVEXP take roughly twice as long as with GAUSSIAN 80 or FORCE. In part this is due to the additional work required for the exponent derivatives. Experience with FORCE indicates that further optimization of

the computer code could improve the speed of DRVEXP by ~30%.

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