Analytical second derivatives of two electron integrals over *s* and *p* Cartesian Gaussians

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An efficient algorithm for computing second derivatives of two electron integrals is outlined and has been coded for *s*- and *p*-type Cartesian Gaussians. This method is an extension of a previous algorithm for two electron integral first derivatives [H. B. Schlegel, J. Chem. Phys. 77, 3676 (1982)] and is suitable for scalar machines with modest memories. Timing data indicates that the present algorithm is 3–6 times faster than a scalar version of the Rys polynomial method. Furthermore, the computational time for the two electron integral second derivatives is only 2–3 times longer than for the integral first derivatives by the same approach. The code has been incorporated in the recently released version of GAUSSIAN 88.

INTRODUCTION

The development of the Rys polynomial method[1-3] was an important advance in the calculation of two electron integrals and their derivatives, particularly for higher angular momentum basis functions. Recently, it has been shown that the Obara–Saika[4] algorithm, and modifications of this algorithm by Head-Gordon and Pople,[5] are superior to the Rys polynomial method, particularly when the calculations are carried out on vector machines with large memories. However, for *s* and *p* basis functions, older methods for computing integrals[6,7] and integral first derivatives[8] still offer some advantages in terms of speed and memory requirements.

The present note outlines an efficient algorithm for calculating second derivatives of two electron integrals. This is an extension of our previous algorithm for first derivatives of two electron integrals[8] and is most suitable for *s* and *p* Cartesian Gaussians. In GAUSSIAN 86 [Ref. 9(a)] and earlier versions, the integral second derivatives are computed by a Rys polynomial method.[10] This has been shown to be a significant bottleneck in larger vibrational frequency calculations.[11] The current method overcomes these problems and improves the speed of computing the two electron integral second derivatives by a factor of 3–6 relative to the Rys polynomial approach.[10]

THEORY

An unnormalized primitive Cartesian Gaussian can be written as

$$g_a(\mathbf{l}_A,\mathbf{r},\mathbf{A},\alpha) = (x-A_x)^{l_{Ax}}(y-A_y)^{l_{Ay}} \times (z-A_z)^{l_{Az}}\exp(-\alpha|\mathbf{r}-\mathbf{A}|^2), \quad (1)$$

where $\mathbf{l}_A = (l_{Ax},l_{Ay},l_{Az})$ describes the angular momentum of the Gaussian, $\mathbf{r}$ is the coordinate of the electron, and $\mathbf{A}$ is the center of the Gaussian. A shell of primitive Gaussians refers to the set of Gaussians sharing the same center and exponent but differing in angular momentum. A higher angular momentum Gaussian ($\mathbf{l}>\mathbf{0}$) can be obtained by differentiating a spherical Gaussian ($\mathbf{l}=\mathbf{0}$).[12] In terms of raising operators,[8]

$$g_a(\mathbf{l}_A,\mathbf{r},\mathbf{A},\alpha) = \hat{M}^{l_{Ax}}\hat{M}^{l_{Ay}}\hat{M}^{l_{Az}}g_a(\mathbf{0},\mathbf{r},\mathbf{A},\alpha), \quad (2)$$

where

$$\hat{M}^{l_{Ax}+1} = \frac{1}{2\alpha}\left(\hat{M}^{l_{Ax}}\frac{\partial}{\partial A_x} + l_{Ax}\hat{M}^{l_{Ax}-1}\right),$$
$$\hat{M}^n = 0 \text{ for } n<0 \text{ and } \hat{M}^0 = 1. \quad (3)$$

Alternatively, the raising operator can also be expressed as a series of partial derivatives:

$$\hat{M}^n = \sum_{m=0}^{[n/2]} \frac{n!}{2^n\alpha^{n-m}m!(n-2m)!}\frac{\partial^{n-2m}}{\partial A_x^{n-2m}}, \quad n\geqslant 0. \quad (4)$$

The effect of a raising operator on a linear function of the coordinates is needed for the derivation of the integral derivative expressions. It can be shown by induction from Eq. (3) or by direct substitution of Eq. (4) that

$$\hat{M}^n\Lambda = \Lambda\hat{M}^n + \frac{n}{2\alpha}\frac{\partial\Lambda}{\partial A_x}\hat{M}^{n-1}, \quad (5)$$

where Λ is a linear function of A_x.

The general two electron integral over Gaussian primitives is given by

$$(\mathbf{l}_A\mathbf{l}_B|\mathbf{l}_C\mathbf{l}_D) = \int\int g_a(\mathbf{l}_A,\mathbf{r}_1,\mathbf{A},\alpha)g_b(\mathbf{l}_B,\mathbf{r}_1,\mathbf{B},\beta) \times\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}g_c(\mathbf{l}_C,\mathbf{r}_2,\mathbf{C},\gamma)g_d(\mathbf{l}_D,\mathbf{r}_2,\mathbf{D},\delta)d\mathbf{r}_1\,d\mathbf{r}_2. \quad (6)$$

For spherical Gaussians, the explicit form of the two electron integral is

$$(\mathbf{0},\mathbf{0}|\mathbf{0},\mathbf{0}) = (ss|ss) = \theta F_0(-U)\exp(T), \quad (7)$$

where

$$\theta = 2\pi^{5/2}/(pq\sqrt{p+q}),$$
$$p=\alpha+\beta,\quad q=\gamma+\delta,\rho=pq/(p+q),$$
$$U=-\rho|\mathbf{P}-\mathbf{Q}|^2,\quad \mathbf{P}=(\alpha\mathbf{A}+\beta\mathbf{B})/p,$$
$$\mathbf{Q}=(\gamma\mathbf{C}+\delta\mathbf{D})/q,$$
$$T=-u|\mathbf{A}-\mathbf{B}|^2-v|\mathbf{C}-\mathbf{D}|^2,$$
$$u=\alpha\beta/(\alpha+\beta),\quad v=\gamma\delta/(\gamma+\delta).$$

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The auxiliary function, $F_m(t)$, has the following properties[12]:

$$F_m(t) = \int_0^1 u^{2m} \exp(-tu^2) du, \tag{8}$$

$$\frac{dF_m(t)}{dt} = -F_{m+1}(t). \tag{9}$$

The first derivative of $(ss|ss)$ with respect to R_m ($R = A,B,C,D$; $m = x,y,z$) is

$$\frac{d(ss|ss)}{dR_m} = \theta F_0(-U)\exp(T)\frac{dT}{dR_m} + \theta F_1(-U)\exp(T)\frac{dU}{dR_m} = (ss|ss)\frac{dT}{dR_m} + (ss|ss)'\frac{dU}{dR_m}. \tag{10}$$

A single prime [e.g., $(ss|ss)'$] is used to denote an integral with $F_m(t)$ replaced by $F_{m+1}(t)$. The first derivatives of T and U are simple linear functions of the coordinates and are independent of the angular momentum:

$$\frac{dT}{dE_m} = -2u(A_m - B_m)(\delta_{AE} - \delta_{BE}) - 2v(C_m - D_m)(\delta_{CE} - \delta_{DE}),$$

$$\frac{dU}{dE_m} = -2\rho(P_m - Q_m)[(\alpha\ \delta_{AE} + \beta\ \delta_{BE})/p - (\gamma\ \delta_{CE} + \delta\ \delta_{DE})/q]. \tag{11}$$

The second derivative of $(ss|ss)$ is

$$\frac{d^2(ss|ss)}{dR_m\,dS_n} = \theta F_0(-U)\exp(T)\left(\frac{dT}{dR_m}\frac{dT}{dS_n} + \frac{d^2T}{dR_m\,dS_n}\right) + \theta F_1(-U)\exp(T)\left(\frac{dU}{dR_m}\frac{dT}{dS_n} + \frac{dT}{dR_m}\frac{dU}{dS_n} + \frac{d^2U}{dR_m dS_n}\right) + \theta F_2(-U)\exp(T)\left(\frac{dU}{dR_m}\frac{dU}{dS_n}\right)$$
$$= (ss|ss)\left(\frac{dT}{dR_m}\frac{dT}{dS_n} + \frac{d^2T}{dR_m\,dS_n}\right) + (ss|ss)'\left(\frac{dU}{dR_m}\frac{dT}{dS_n} + \frac{dT}{dR_m}\frac{dU}{dS_n} + \frac{d^2U}{dR_m\,dS_n}\right) + (ss|ss)''\left(\frac{dU}{dR_m}\frac{dU}{dS_n}\right). \tag{12}$$

A double prime is used to denote an integral with $F_m(t)$ replaced by $F_{m+2}(t)$. The second derivatives of T and U are independent of the coordinates and the angular momentum:

$$\frac{d^2T}{dE_m\,dF_n} = -2[u(\delta_{AE} - \delta_{BE})(\delta_{AF} - \delta_{BF}) + v(\delta_{CE} - \delta_{DE})(\delta_{CF} - \delta_{DF})]\delta_{mn}, \tag{13}$$

$$\frac{d^2U}{dE_m\,dF_n} = -2\rho\{[(\alpha\ \delta_{AE} + \beta\ \delta_{BE})/p - (\gamma\ \delta_{CE} + \delta\ \delta_{DE})/q] \times [(\alpha\ \delta_{AF} + \beta\ \delta_{BF})/p - (\gamma\ \delta_{CF} + \delta\ \delta_{DF})/q]\}\delta_{mn}.$$

The general two electron integral can be obtained by applying the raising operators to the integral over spherical Gaussians. To simplify the notation, a number of products of the raising operators are defined:

$$\hat{M}(\omega) = \left(\prod_{\substack{E=ABCD\\ i=xyz}} \hat{M}^{l_{Ei}}\right), \tag{14}$$

$$\hat{M}_{Ax}(\omega) = \left(\prod_{\substack{E=ABCD\\ i=xyz\\ Ei\neq Ax}} \hat{M}^{l_{Ei}}\right)\frac{l_{Ax}}{2\alpha}\hat{M}^{l_{Ax}-1}, \tag{15}$$

$$\hat{M}_{AxBy}(\omega) = \left(\prod_{\substack{E=ABCD\\ i=xyz\\ Ei\neq Ax,By}} \hat{M}^{l_{Ei}}\right)\frac{l_{Ax}l_{By}}{4\alpha^2}\hat{M}^{l_{Ax}-1}\hat{M}^{l_{By}-1} \tag{16}$$

and similarly for $\hat{M}_{By}(\omega)$, etc., and $\hat{M}_{BzCx}(\omega)$, etc. These differ slightly from the earlier definition[8] by the inclusion of the $l_{Ax}/2\alpha$ factor in $\hat{M}_{Ax}(\omega)$ to make subsequent equations less cluttered. With these definitions, the generalization of Eq. (5) becomes

$$\hat{M}(\omega)\Lambda_1(m) = \Lambda_1(m)\hat{M}(\omega) + \sum_E^{ABCD}\frac{d\Lambda_1(m)}{dE_m}\hat{M}_{Em}(\omega),$$

$$\hat{M}(\omega)\Lambda_1(m)\Lambda_2(n) = \Lambda_1(m)\Lambda_2(n)\hat{M}(\omega) + \sum_E^{ABCD}\left[\frac{d\Lambda_1(m)}{dE_m}\Lambda_2(n)\hat{M}_{Em}(\omega) + \Lambda_1(m)\frac{d\Lambda_2(n)}{dE_n}\hat{M}_{En}(\omega)\right] + \sum_{EF}^{ABCD}\frac{d\Lambda_1(m)}{dE_m}\frac{d\Lambda_2(n)}{dE_n}\hat{M}_{EmFn}(\omega), \tag{17}$$

where $\Lambda_1(m)$ is a linear function of A_m, B_m, C_m, D_m, and $\Lambda_2(n)$ is a linear function of A_n, B_n, C_n, D_n (e.g., the first derivatives of T and U with respect to R_m and S_n).

The general two electron integral can be written as

$$(l_A l_B|l_C l_D) = \hat{M}(\omega)(ss|ss). \tag{18}$$

The contribution of the entire shell block to the two electron repulsion energy is

$$V_0 = \sum_\omega^{\text{block}} P(\omega)(l_A l_B|l_C l_D) = \sum_\omega^{\text{block}} P(\omega)\hat{M}(\omega)(ss|ss), \tag{19}$$

where $P(\omega)$ is the two electron density matrix over unnormalized Gaussian primitives.

The first derivative of a general two electron integral is given by

$$\frac{d(\mathbf{l}_A\mathbf{l}_B|\mathbf{l}_C\mathbf{l}_D)}{dR_m} = \hat{M}(\omega)\left[(ss|ss)\frac{dT}{dR_m} + (ss|ss)'\frac{dU}{dR_m}\right]$$
$$= \frac{dT}{dR_m}\hat{M}(\omega)(ss|ss) + \frac{dU}{dR_m}\hat{M}(\omega)(ss|ss)'$$
$$+ \sum_E^{ABCD}\left[\frac{d^2T}{dR_m dE_m}\hat{M}_{Em}(\omega)(ss|ss) + \frac{d^2U}{dR_m dE_m}\hat{M}_{Em}(\omega)(ss|ss)'\right]. \quad (20)$$

This equation has been published previously.[8] Note that $\hat{M}_{Em}(\omega)(ss|ss)$ is simply a constant times an integral over lower angular momentum functions [e.g., $\hat{M}_{Ax}(\omega)(ss|ss) = (l_{Ax}/2)(\mathbf{l}_A^{-1x}\mathbf{l}_B|\mathbf{l}_C\mathbf{l}_D)$, where $\mathbf{l}_A^{\pm 1x} = (l_{Ax}\pm 1, l_{Ay}, l_{Az})$].

Since the derivative of an integral is directly related to an integral over higher angular momentum functions,[8,12]

$$(\mathbf{l}_A^{+1x}\mathbf{l}_B|\mathbf{l}_C\mathbf{l}_D) = \frac{1}{2\alpha}\left[\frac{d(\mathbf{l}_A\mathbf{l}_B|\mathbf{l}_C\mathbf{l}_D)}{dR_m} + l_{Ax}(\mathbf{l}_A^{-1x}\mathbf{l}_B|\mathbf{l}_C\mathbf{l}_D)\right], \quad (21)$$

Eq. (20) [or Eq. (32) in Ref. 8] also constitutes a recurrence relation for the generation of integrals over higher angular momentum functions. This relation is identical to the one used independently by Obara and Saika [Eq. (A24) in Ref. 4].

The contribution of the entire shell block of integral derivatives can be obtained by multiplying by $P(\omega)$ and summing. Because $d^2T/dR_m\,dE_m$ and $d^2U/dR_m\,dE_m$ are constant for the shell block, they can be factored out of the summation:

$$\frac{dV_0}{dR_m} = \frac{dT}{dR_m}\sum_\omega^{\text{block}} P(\omega)\hat{M}(\omega)(ss|ss) + \frac{dU}{dR_m}\sum_\omega^{\text{block}} P(\omega)\hat{M}(\omega)(ss|ss)'$$
$$+ \sum_E^{ABCD}\left[\frac{d^2T}{dR_m\,dE_m}\sum_\omega^{\text{block}} P(\omega)\hat{M}_{Em}(\omega)(ss|ss) + \frac{d^2U}{dR_m\,dE_m}\sum_\omega^{\text{block}} P(\omega)\hat{M}_{Em}(\omega)(ss|ss)'\right]$$
$$= \frac{dT}{dR_m}V_0 + \frac{dU}{dR_m}V_0' + \sum_E^{ABCD}\left(\frac{d^2T}{dR_m\,dE_m}V_{Em} + \frac{d^2U}{dR_m\,dE_m}V_{Em}'\right), \quad (22)$$

where

$$V_{Ax} = \sum_\omega^{\text{block}} P(\omega)\hat{M}_{Ax}(\omega)(ss|ss) = \sum_\omega^{\text{block}} P(\omega)(\mathbf{l}_A^{-1x}\mathbf{l}_B|\mathbf{l}_C\mathbf{l}_D) \quad (23)$$

and similarly for the other V_{Em}. The prime indicates that the $F_m(t)$ in the integrals in the expression are replaced by $F_{m+1}(t)$. As elaborated in a previous paper,[8] Eq. (22) is used to calculate integral derivatives over s- and p-type primitives in the GAUSSIAN series of programs.[9]

The second derivative of a general two electron integral is given by

$$\frac{d^2(\mathbf{l}_A\mathbf{l}_B|\mathbf{l}_C\mathbf{l}_D)}{dR_m\,dS_n} = \hat{M}(\omega)\left[(ss|ss)\left(\frac{dT}{dR_m}\frac{dT}{dS_n} + \frac{d^2T}{dR_m\,dS_n}\right)\right.$$
$$\left. + (ss|ss)'\left(\frac{dU}{dR_m}\frac{dT}{dS_n} + \frac{dT}{dR_m}\frac{dU}{dS_n} + \frac{d^2U}{dR_m\,dS_n}\right) + (ss|ss)''\frac{dU}{dR_m}\frac{dU}{dS_n}\right]$$
$$= \left(\frac{dT}{dR_m}\frac{dT}{dS_n} + \frac{d^2T}{dR_m\,dS_n}\right)\hat{M}(\omega)(ss|ss)$$
$$+ \left(\frac{dU}{dR_m}\frac{dT}{dS_n} + \frac{dT}{dR_m}\frac{dU}{dS_n} + \frac{d^2U}{dR_m\,dS_n}\right)\hat{M}(\omega)(ss|ss)' + \left(\frac{dU}{dR_m}\frac{dU}{dS_n}\right)\hat{M}(\omega)(ss|ss)''$$
$$+ \sum_E^{ABCD}\left[\frac{d^2T}{dR_m\,dE_m}\frac{dT}{dS_n}\hat{M}_{Em}(\omega)(ss|ss) + \frac{dT}{dR_m}\frac{d^2T}{dS_n\,dE_n}\hat{M}_{En}(\omega)(ss|ss)\right]$$
$$+ \sum_{EF}^{ABCD}\frac{d^2T}{dR_m\,dE_m}\frac{d^2T}{dS_n\,dF_n}\hat{M}_{EmFn}(\omega)(ss|ss)$$
$$+ \sum_E^{ABCD}\left[\left(\frac{d^2U}{dR_m\,dE_m}\frac{dT}{dS_n} + \frac{d^2T}{dR_m\,dE_m}\frac{dU}{dS_n}\right)\hat{M}_{Em}(\omega)(ss|ss)'\right.$$
$$\left. + \left(\frac{dU}{dR_m}\frac{d^2T}{dS_n\,dE_n} + \frac{dT}{dR_m}\frac{d^2U}{dS_n\,dE_n}\right)\hat{M}_{En}(\omega)(ss|ss)'\right]$$
$$+ \sum_{EF}^{ABCD}\left[\left(\frac{d^2U}{dR_m\,dE_m}\frac{d^2T}{dS_n\,dF_n} + \frac{d^2T}{dR_m\,dE_m}\frac{d^2U}{dS_n\,dF_n}\right)\hat{M}_{EmFn}(\omega)(ss|ss)'\right]$$

$$+\sum_{E}^{ABCD}\left[\frac{d^2U}{dR_m\,dE_m}\frac{dU}{dS_n}\hat{M}_{Em}(\omega)(ss|ss)''+\frac{dU}{dR_m}\frac{d^2U}{dS_n\,dE_n}\hat{M}_{En}(\omega)(ss|ss)''\right]$$

$$+\sum_{EF}^{ABCD}\frac{d^2U}{dR_m\,dE_m}\frac{d^2U}{dS_n\,dF_n}\hat{M}_{EmFn}(\omega)(ss|ss)''. \tag{24}$$

Similar to the first derivatives, the contribution of the entire shell block can be obtained by multiplying by $P(\omega)$ and summing over all combinations within the shell block. With the definition

$$V_{AxBy}=\sum_{\omega}^{\text{block}}P(\omega)\hat{M}_{AxBy}(\omega)(ss|ss)=\sum_{\omega}^{\text{block}}P(\omega)(\mathbf{l}_A^{-1x}\mathbf{l}_B^{-1y}|\mathbf{l}_C\mathbf{l}_D) \tag{25}$$

and similarly for the other V_{EmFn}, the final expression for the contribution of the shell block to the second derivative can be written as

$$\frac{d^2V_0}{dR_m\,dS_n}=\left(\frac{dT}{dR_m}\frac{dT}{dS_n}+\frac{d^2T}{dR_m\,dS_n}\right)V_0+\left(\frac{dU}{dR_m}\frac{dT}{dS_n}+\frac{dT}{dR_m}\frac{dU}{dS_n}+\frac{d^2U}{dR_m\,dS_n}\right)V_0'+\left(\frac{dU}{dR_m}\frac{dU}{dS_n}\right)V_0''$$
$$+\sum_{E}^{ABCD}\left(\frac{d^2T}{dR_m\,dE_m}\frac{dT}{dS_n}V_{Em}+\frac{dT}{dR_m}\frac{d^2T}{dS_n\,dE_n}V_{En}\right)+\sum_{EF}^{ABCD}\frac{d^2T}{dR_m\,dE_m}\frac{d^2T}{dS_n\,dF_n}V_{EmFn}$$
$$+\sum_{E}^{ABCD}\left[\left(\frac{d^2U}{dR_m\,dE_m}\frac{dT}{dS_n}+\frac{d^2T}{dR_m\,dE_m}\frac{dU}{dS_n}\right)V'_{Em}+\left(\frac{dU}{dR_m}\frac{d^2T}{dS_n\,dE_n}+\frac{dT}{dR_m}\frac{d^2U}{dS_n\,dE_n}\right)V'_{En}\right]$$
$$+\sum_{EF}^{ABCD}\left(\frac{d^2U}{dR_m\,dE_m}\frac{d^2T}{dS_n\,dF_n}+\frac{d^2T}{dR_m\,dE_m}\frac{d^2U}{dS_n\,dF_n}\right)V'_{EmFn}$$
$$+\sum_{E}^{ABCD}\left(\frac{d^2U}{dR_m\,dE_m}\frac{dU}{dS_n}V''_{Em}+\frac{dU}{dR_m}\frac{d^2U}{dS_n\,dE_n}V''_{En}\right)+\sum_{EF}^{ABCD}\frac{d^2U}{dR_m\,dE_m}\frac{d^2U}{dS_n\,dF_n}V''_{EmFn}. \tag{26}$$

IMPLEMENTATION

The calculation of the second derivatives of the two electron integrals over *s*- and *p*-type Gaussians is carried out similar to the computation of the integral first derivatives.[8] The main code to compute the integrals is traversed three times, first time with the original $F_m(t)$ to produce the $(\mathbf{l}_A\mathbf{l}_B|\mathbf{l}_C\mathbf{l}_D)$, the second time with the $F_m(t)$ replaced by $F_{m+1}(t)$ to produce the $(\mathbf{l}_A\mathbf{l}_B|\mathbf{l}_C\mathbf{l}_D)'$ and the third time with the original $F_m(t)$ replaced by $F_{m+2}(t)$ to produce the $(\mathbf{l}_A\mathbf{l}_B|\mathbf{l}_C\mathbf{l}_D)''$. During each pass, V_0, up to 12 V_{Em} and up to 54 V_{EmFn} are accumulated (if *d* orbitals were included, there would be a maximum of 78 V_{EmFn}). At the end of each pass, the V's are multiplied by the appropriate factors and the contributions added to the second derivatives. Translational invariance is used to reduce the total number of second derivatives per shell block to 45. With the use of a small number of intermediate sums, a considerable amount of work can be moved out of the innermost loop over the Gaussians. Further savings in computational work is attained by using explicit code for the $(ss|ss)$ and $(ps|ss)$ cases. Memory requirements are not substantially different than for the gradient calculation.

A count of the number of floating point operations in the innermost loops suggests that the integral second derivatives should take only 2–3 times longer than the integral first derivatives. For the case of four contracted *sp* shells on different centers (e.g., 256 integrals), in which each contracted function is composed of k Gaussians primitives (e.g., the STO-kG basis), approximately $9581k^4+192k^2+9$ multiplies, $8623k^4+188k^2+204$ adds/subtracts, $2k^4+2k^2$ divides, $2k^2$ exponentials and $1k^4$ square roots are required for the first and second derivatives compared to approximately $4177k^4+62k^2$ multiplies, $3824k^4+48k^2+18$ adds/subtracts, $2k^4+2k^2$ divides, $2k^2$ exponentials and $1k^4$ square roots for the first derivatives alone [both require the same number of additional floating point operations to form $P(\omega)$]. In the loops over the Gaussian primitives, there is no dependence on the total number of atoms.

Table I compares timing data for the present algorithm and the Rys polynomial method for some sample calcula-

TABLE I. Comparison of calculational times for first and second derivatives of two electron integrals over atomic orbitals.[a]

	First derivatives			Second derivatives		
Molecule	Present method and Ref. 8	Rys poly. method[b]	Ratio	Present method	Rys poly. method[b]	Ratio
3-21 G basis, VAX 3600						
C_2H_6	34	89	1:2.6	91	251	1:2.7
C_2H_5F	103	289	1:2.8	251	857	1:3.4
$C_2H_4F_2$	144	434	1:3.0	342	1483	1:4.3
$C_2H_3F_3$	229	729	1:3.2	522	2501	1:4.8
6-31G basis, VAX 3600						
C_2H_6	86	293	1:3.4	215	825	1:3.8
C_2H_5F	288	1055	1:3.6	691	3060	1:4.4
$C_2H_4F_2$	408	1560	1:3.8	965	5360	1:5.5
$C_2H_3F_3$	671	2612	1:3.9	1534	8848	1:5.8
6-31G basis, Cray-XMP						
C_2H_6	3.8	7.6	1:2.0	9.5	37.8	1:4.0
C_2H_5F	11.2	15.2	1:1.4	24.1	89.5	1:3.7
$C_2H_4F_2$	15.3	23.2	1:1.5	32.9	135.1	1:4.1
$C_2H_3F_3$	23.9	39.2	1:1.6	49.4	252.9	1:5.1

[a] cpu time in seconds.
[b] Using the approach of Ref. 10.

tions using s,p basis sets. The last entry in the table ($C_2H_3F_3$ with the 6-31G basis set run on a Cray-XMP) has been used previously in timing tests for frequency calculations.[11] For both the first and second derivatives, the present algorithm is 3–6 times faster than the scalar version of the Rys polynomial method implemented in the GAUSSIAN series of programs[9,12] (e.g., the VAX 3600 timings). On the Cray, the present algorithm is 1.5–2 times faster than the vectorized Rys method for first derivatives, and 4–5 times faster than the vectorized Rys method for second derivatives. The vectorized Rys code for second derivatives in GAUSSIAN 86 is, in turn 3–4 times faster than the nonvectorized Rys code in GAUSSIAN 82. For the present method, the computation of the second derivatives of the two electron integrals is only 2–3 times longer than the first derivatives, whereas it is 3–6 times longer for the Rys polynomial method. For $C_2H_3F_3$ on the Cray, the two electron integral second derivative calculation with Rys polynomials requires for 253 using GAUSSIAN 86 down from 736 s (Ref. 11) using GAUSSIAN 82. The present method reduces in time for the integral second derivatives only 50 s. The GRADSCF timing for the first and second derivatives of the one and two electron integrals is 163 s.[11]

SUMMARY

An efficient algorithm has been outlined for computing two electron integral second derivatives for s and p Gaussians.[13] Timing data indicate that the present algorithm is 3–6 times faster than the Rys polynomial method. Sample calculations also show that the computation of the integral second derivatives is only 2–3 times longer than the integral first derivatives. This removes a major bottleneck in the computation of force constants and frequencies at the Hartree–Fock level. The code has been incorporated in the recently released version of GAUSSIAN 88.[9]

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[13] The present program could be extended to include d functions, but the code would become awkwardly large.