

First and second derivatives of two electron integrals over Cartesian Gaussians using Rys polynomials

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Formulas are developed for the first and second derivatives of two electron integrals over Cartesian Gaussians. Integrals and integral derivatives are evaluated by the Rys polynomial method. Higher angular momentum functions are not used to calculate the integral derivatives; instead the integral formulas are differentiated directly to produce compact and efficient expressions for the integral derivatives. The use of this algorithm in the *ab initio* molecular orbital programs GAUSSIAN 80 and GAUSSIAN 82 is discussed. Representative timings for some small molecules with several basis sets are presented. This method is compared with previously published algorithms and its computational merits are discussed.

INTRODUCTION

The importance of analytical calculated energy derivatives is well established.¹ Analytical gradients or first derivatives have improved the speed of geometry optimizations by an order of magnitude. Analytically differentiating the energy twice yields vibrational force constants and harmonic frequencies more efficiently than numerical differentiation of the gradients which, in turn, is much more efficient than double numerical differentiation of the energy. Analytical second derivatives are also very useful in searching for transition structures. Expressions are available for first and second derivatives of Hartree-Fock,²⁻⁷ second order Møller-Plesset perturbation,⁶ multiconfiguration SCF⁷⁻¹¹ and configuration interaction¹¹⁻¹⁴ energies. To a large extent, the efficiency of the energy derivative calculations depends on the speed of the two-electron integral derivatives.

In a previous paper,¹⁵ we outlined an algorithm for first derivatives of two-electron integrals over *s* and *p* type Cartesian Gaussians. Although very efficient, this method is difficult to extend to higher angular momenta and higher derivatives. Integral evaluation algorithms have recently been reviewed by Hegarty and van der Velde.¹⁶ Compared to conventional methods, the speed of calculating two-electron integrals involving *d* and *f* functions can be improved by a factor of two or more, if the Rys polynomial method is used.¹⁷⁻¹⁹ In this paper, we present an efficient algorithm for the first and second derivatives of Cartesian Gaussians using Rys polynomials. As far as possible, we will follow the notation of Refs. 6 and 15. These methods have been implemented in the GAUSSIAN system²⁰ of *ab initio* molecular orbital programs since 1978.

INTEGRAL DERIVATIVE ALGORITHM

The Hartree-Fock energy, first derivatives, and second derivatives can be expressed as¹⁻⁷:

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

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

$$\begin{aligned} \frac{\partial^2 E}{\partial x \partial y} = & \sum_{\mu\nu} P_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial x \partial y} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu\lambda\sigma} \frac{\partial^2 (\mu\nu|\lambda\sigma)}{\partial x \partial y} \\ & + \frac{\partial^2 V_{\text{nuc}}}{\partial x \partial y} - \sum_{\mu\nu} P'_{\mu\nu} \frac{\partial^2 S_{\mu\nu}}{\partial x \partial y} + \sum_{\mu\nu} \frac{\partial P_{\mu\nu}}{\partial y} \frac{\partial h_{\mu\nu}}{\partial x} \\ & + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \frac{\partial P_{\mu\nu\lambda\sigma}}{\partial y} \frac{\partial (\mu\nu|\lambda\sigma)}{\partial x} - \sum_{\mu\nu} \frac{\partial P'_{\mu\nu}}{\partial y} \frac{\partial S_{\mu\nu}}{\partial x} \end{aligned} \quad (3)$$

in terms of the one and two particle density matrices $P_{\mu\nu}$ and $P_{\mu\nu\lambda\sigma}$, the overlap and one electron integrals $S_{\mu\nu}$ and $h_{\mu\nu}$, the two-electron integrals $(\mu\nu|\lambda\sigma)$, the nuclear-nuclear repulsion V_{nuc} , and the energy weighted density matrix $P'_{\mu\nu}$. Energy derivatives for other calculational levels can be found elsewhere.^{1,2,6-14} The integral derivatives can be obtained by differentiating the integrals analytically; derivatives of the density matrices and the molecular orbital coefficients must be found by a coupled-perturbed Hartree-Fock (CPHF) or MCSCF (CPMCSCF) procedure.

The overlap, one-electron, and two-electron integrals over the basis functions ϕ are given by

$$S_{\mu\nu} = \int \phi_{\mu}^* \phi_{\nu} d\tau, \quad (4)$$

$$h_{\mu\nu} = \int \phi_{\mu}^* \hat{h} \phi_{\nu} d\tau, \quad (5)$$

$$(\mu\nu|\lambda\sigma) = \iint \phi_\mu^*(1) \phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda^*(2) \phi_\sigma(2) d\tau_1 d\tau_2, \quad (6)$$

where \hat{h} is the core or one-electron Hamiltonian. The basis functions are constructed from linear combinations of Gaussian-type primitives

$$\phi_\mu = \sum_a \xi_{a\mu} N_a g_a, \quad (7)$$

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

$$g_a(\mathbf{l}_A, \mathbf{r}_A, \alpha) = x_A^{l_{Ax}} y_A^{l_{Ay}} z_A^{l_{Az}} \exp(-\alpha|\mathbf{r}_A|^2), \quad (8)$$

where

$$\mathbf{l}_A = (l_{Ax}, l_{Ay}, l_{Az}), \quad \mathbf{r}_A = \mathbf{r} - \mathbf{A} = (x_A, y_A, z_A);$$

\mathbf{r} is the electron coordinate and $\mathbf{A} = (A_x, A_y, A_z)$ the Gaussian center. The higher Cartesian Gaussians can also be obtained by differentiating a spherical Gaussian

$$g_a(\mathbf{l}_A, \mathbf{r}_A, \alpha) = \hat{M}^{l_{Ax}} \hat{M}^{l_{Ay}} \hat{M}^{l_{Az}} g_a(\mathbf{0}, \mathbf{r}_A, \alpha), \quad (9)$$

where

$$\hat{M}^{l_{Ax}+1} = \frac{1}{2\alpha} \left[\hat{M}^{l_{Ax}} \frac{\partial}{\partial A_x} + l_{Ax} \hat{M}^{l_{Ax}-1} \right]; \quad \hat{M}^0 = 1. \quad (10)$$

If A is a linear function of A_x , then the following useful relation can be obtained from Eq. (10) by induction:

$$\hat{M}^{l_{Ax}A} = A \hat{M}^{l_{Ax}} + \frac{l_{Ax}}{2\alpha} \frac{\partial A}{\partial A_x} \hat{M}^{l_{Ax}-1}. \quad (11)$$

The general two-electron integral over contracted functions, Eq. (6), can be reduced to a linear combination of two-electron integrals over Gaussian primitives:

$$\begin{aligned} & (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) \\ &= \iint g_a(\mathbf{l}_A, \mathbf{r}_A(1), \alpha) g_b(\mathbf{l}_B, \mathbf{r}_B(1), \beta) \frac{1}{r_{12}} \\ & \quad \times g_c(\mathbf{l}_C, \mathbf{r}_C(2), \gamma) g_d(\mathbf{l}_D, \mathbf{r}_D(2), \delta) d\tau_1 d\tau_2. \end{aligned} \quad (12)$$

If the Coulomb operator is expressed as a Gaussian transform

$$\frac{1}{r_{12}} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp(-u^2 r_{12}^2) du, \quad (13)$$

the two electron integral can be written as

$$\begin{aligned} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) &= \frac{2}{\sqrt{\pi}} \int_0^\infty I'_x(l_{Ax} l_{Bx} l_{Cx} l_{Dx} u) \\ & \quad \times I'_y(l_{Ay} l_{By} l_{Cy} l_{Dy} u) I'_z(l_{Az} l_{Bz} l_{Cz} l_{Dz} u) du \end{aligned} \quad (14)$$

in terms of three two-dimensional integrals I'_x , I'_y and I'_z where

$$\begin{aligned} & I'_x(l_{Ax} l_{Bx} l_{Cx} l_{Dx} u) \\ &= \iint x_A(1)^{l_{Ax}} x_B(1)^{l_{Bx}} x_C(2)^{l_{Cx}} x_D(2)^{l_{Dx}} \\ & \quad \times \exp(-\alpha x_A(1)^2 - \beta x_B(1)^2 - \gamma x_C(2)^2 - \delta x_D(2)^2 \\ & \quad - u^2(x_1 - x_2)^2) dx_1 dx_2, \end{aligned} \quad (15)$$

where $x_A(1) = x_1 - A_x$, etc. If a change of variables is made from u to t ,

$$\begin{aligned} t^2 &= u^2/(\rho + u^2); \quad I'_x = 1/\sqrt{1-t^2} I'_x; \\ \rho &= (\alpha + \beta)(\gamma + \delta)/(\alpha + \beta + \gamma + \delta), \end{aligned} \quad (16)$$

then the two-electron integral has the form

$$\begin{aligned} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) &= 2 \sqrt{\frac{\rho}{\pi}} \int_0^1 I_x(t) I_y(t) I_z(t) dt \\ &= \int_0^1 P_L(t) e^{-\rho P Q^2 t^2} dt, \end{aligned} \quad (17)$$

where $P_L(t)$ is a L th degree polynomial in t^2 ,

$$L = |\mathbf{l}_A| + |\mathbf{l}_B| + |\mathbf{l}_C| + |\mathbf{l}_D|.$$

Dupuis, Rys, and King¹⁷⁻¹⁹ have developed a numerical quadrature to compute this integral exactly, based on Rys polynomials:

$$\begin{aligned} (\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D) &= \sum_{a=1}^n P_L(t_a) W_a; \quad n > L/2 \\ &= \sum_{a=1}^n I_x(t_a) I_y(t_a) I_z(t_a) W_a^*, \end{aligned} \quad (18)$$

where

$$W_a^* = 2\sqrt{\rho/\pi} \exp(\rho P Q^2 t_a^2) W_a. \quad (19)$$

The appropriate roots and weights of the Rys polynomials are t_a and W_a , respectively. Thus the problem of calculating the six-dimensional two-electron integral has been reduced to the evaluation of three two-dimensional integrals $I_x(t)$, $I_y(t)$, and $I_z(t)$ at n different roots t_a and taking the weighted sum. In the original implementation by Dupuis, Rys, and King, these integrals were also done by numerical quadrature¹⁷; current implementations use more efficient and compact recurrence relations to evaluate the two-dimensional integrals.^{19,20} Note also that the exponential term in W_a^* cancels a corresponding term in $I_x(t_a) I_y(t_a) I_z(t_a)$ and is not calculated explicitly.

Derivatives of the two-electron integrals can be written in terms of derivatives of the basic two-dimensional integrals. Equation (17) is differentiated with respect to the position of a Gaussian and the derivative is taken under the integral. The integrand has the form of an $L + 1$ degree polynomial in t^2 multiplied by the same exponential as in Eq. (17) and can also be integrated using the Rys quadrature:

$$\begin{aligned} & \frac{\partial(\mathbf{l}_A \mathbf{l}_B | \mathbf{l}_C \mathbf{l}_D)}{\partial A_x} \\ &= 2 \sqrt{\frac{\rho}{\pi}} \int_0^1 \frac{\partial I_x(t)}{\partial A_x} I_y(t) I_z(t) dt \\ &= \int_0^1 P'_{L+1}(t) e^{-\rho P Q^2 t^2} dt \\ &= \sum_{a=1}^{n'} \frac{\partial I_x(t_a)}{\partial A_x} I_y(t_a) I_z(t_a) W_a^*; \quad n' > (L+1)/2. \end{aligned}$$

Similarly, for the second derivatives

$$\frac{\partial^2(l_A l_B | l_C l_D)}{\partial A_x \partial B_y} = \sum_{a=1}^{n'} \frac{\partial I_x(t_a)}{\partial A_x} \frac{\partial I_y(t_a)}{\partial B_y} I_z(t_a) W_a^*,$$

$$n' > (L+2)/2, \quad (21)$$

$$\frac{\partial^2(l_A l_B | l_C l_D)}{\partial A_x \partial B_x} = \sum_{a=1}^{n''} \frac{\partial^2 I_x(t_a)}{\partial A_x \partial B_x} I_y(t_a) I_z(t_a) W_a^*,$$

$$n'' > (L+2)/2. \quad (22)$$

For spherical Gaussians, the two-dimensional integral is given by

$$I_x(0000t) = \pi/\sqrt{\mu q} \exp(-\rho t^2 PQ_x^2 - u AB_x^2 - v CD_x^2), \quad (23)$$

where $\mu = \alpha + \beta$, $q = \gamma + \delta$, $u = \alpha\beta/\mu$, $v = \gamma\delta/q$, $\rho = \mu q/(\mu + q)$, $AB_x = A_x - B_x$, $CD_x = C_x - D_x$, $PQ_x = P_x - Q_x$, $P_x = (\alpha A_x + \beta B_x)/\mu$, and $Q_x = (\gamma C_x + \delta D_x)/q$. The first and second derivatives of $I_x(0000t)$ are

$$\frac{\partial I_x(0000t)}{\partial A_x} = [(-2\rho t^2 \alpha/\mu) PQ_x - 2u AB_x] \times [\pi/\sqrt{\mu q} \exp(-\rho t^2 PQ_x^2 - u AB_x^2 - v CD_x^2)]$$

$$= \Lambda(A_x) I_x(0000t) = DI_{Ax}(0000t), \quad (24)$$

$$\frac{\partial^2 I_x(0000t)}{\partial A_x \partial B_x} = [(-2\rho t^2 \alpha/\mu) PQ_x - 2u AB_x] \times [(-2\rho t^2 \beta/\mu) PQ_x + 2u AB_x] - 2\rho t^2 u/\mu + 2u \times [\pi/\sqrt{\mu q} \exp(-\rho t^2 PQ_x^2 - u AB_x^2 - v CD_x^2)]$$

$$= [\Lambda(A_x) \Lambda(B_x) + \Lambda_{AB}] I_x(0000t) = DDI_{ABx}(0000t), \quad (25)$$

where

$$\Lambda_{AB} = \partial \Lambda(A_x)/\partial B_x = \partial \Lambda(B_x)/\partial A_x.$$

Note that $\Lambda(A_x)$ and $\Lambda(B_x)$ are linear functions of the coordinates and that Λ_{AB} is independent of the coordinates.

Although the two-dimensional integrals for higher order Cartesian Gaussians are calculated using recurrence relations, they can also be obtained formally by applying the operators \hat{M} to $I_x(0000t)$,

$$I_x(l_{Ax} l_{Bx} l_{Cx} l_{Dx} t) = \hat{M}^{l_{Ax}} \hat{M}^{l_{Bx}} \hat{M}^{l_{Cx}} \hat{M}^{l_{Dx}} I_x(0000t). \quad (26)$$

Similarly, derivatives of the two-dimensional integrals for higher order Cartesian Gaussians can be obtained by applying the operators \hat{M} to $DI_x(0000t)$ and $DDI_x(0000t)$, using Eq. (11) for \hat{M} operating on Λ .

$$\frac{\partial I_x(l_{Ax} l_{Bx} l_{Cx} l_{Dx} t)}{\partial A_x} = \hat{M}^{l_{Ax}} \hat{M}^{l_{Bx}} \hat{M}^{l_{Cx}} \hat{M}^{l_{Dx}} \frac{\partial I_x(0000t)}{\partial A_x} = \hat{M}^{l_{Ax}} \hat{M}^{l_{Bx}} \hat{M}^{l_{Cx}} \hat{M}^{l_{Dx}} \Lambda(A_x) I_x(0000t)$$

$$= \Lambda(A_x) I_x(l_{Ax} l_{Bx} l_{Cx} l_{Dx} t) + (l_{Ax}/2\alpha) \Lambda_{AA} I_x(l_{Ax} - 1 l_{Bx} l_{Cx} l_{Dx} t) + (l_{Bx}/2\beta) \Lambda_{AB} I_x(l_{Ax} l_{Bx} - 1 l_{Cx} l_{Dx} t) + (l_{Cx}/2\gamma) \Lambda_{AC} I_x(l_{Ax} l_{Bx} l_{Cx} - 1 l_{Dx} t) + (l_{Dx}/2\delta) \Lambda_{AD} I_x(l_{Ax} l_{Bx} l_{Cx} l_{Dx} - 1 t) = DI_{Ax}(l_{Ax} l_{Bx} l_{Cx} l_{Dx} t), \quad (27)$$

$$\frac{\partial^2 I_x(l_{Ax} l_{Bx} l_{Cx} l_{Dx} t)}{\partial A_x \partial B_x} = \hat{M}^{l_{Ax}} \hat{M}^{l_{Bx}} \hat{M}^{l_{Cx}} \hat{M}^{l_{Dx}} \frac{\partial^2 I_x(0000t)}{\partial A_x \partial B_x} = \hat{M}^{l_{Ax}} \hat{M}^{l_{Bx}} \hat{M}^{l_{Cx}} \hat{M}^{l_{Dx}} [\Lambda(A_x) \Lambda(B_x) + \Lambda_{AB}] I_x(0000t)$$

$$= \hat{M}^{l_{Ax}} \hat{M}^{l_{Bx}} \hat{M}^{l_{Cx}} \hat{M}^{l_{Dx}} \Lambda(A_x) \frac{\partial I_x(0000t)}{\partial B_x} + \Lambda_{AB} I_x(l_{Ax} l_{Bx} l_{Cx} l_{Dx} t)$$

$$= \Lambda(A_x) DI_{Bx}(l_{Ax} l_{Bx} l_{Cx} l_{Dx} t) + \Lambda_{AB} I_x(l_{Ax} l_{Bx} l_{Cx} l_{Dx} t) + (l_{Ax}/2\alpha) \Lambda_{AA} DI_{Bx}(l_{Ax} - 1 l_{Bx} l_{Cx} l_{Dx} t) + (l_{Bx}/2\beta) \Lambda_{AB} DI_{Bx}(l_{Ax} l_{Bx} - 1 l_{Cx} l_{Dx} t) + (l_{Cx}/2\gamma) \Lambda_{AC} DI_{Bx}(l_{Ax} l_{Bx} l_{Cx} - 1 l_{Dx} t) + (l_{Dx}/2\delta) \Lambda_{AD} DI_{Bx}(l_{Ax} l_{Bx} l_{Cx} l_{Dx} - 1 t)$$

$$= DDI_{ABx}(l_{Ax} l_{Bx} l_{Cx} l_{Dx} t).$$

Note that these formulas do not require the two-dimensional integrals for higher order Cartesian Gaussians. Furthermore, they are independent of the actual method used to compute the original two-dimensional integrals I .

DISCUSSION

The algorithm outlined above has been implemented in the GAUSSIAN system of programs. For the integral and integral derivative evaluations, the basis functions are grouped into shells. A set of Gaussians with the same exponent on the same center but differing in angular momenta constitute a

primitive shell (i.e., s, p_x, p_y, p_z and/or $d_{x^2}, d_{xy}, d_{y^2}, d_{xz}, d_{yz}, d_{z^2}$). A shell block refers to the set of two-electron integrals over functions in a particular combination of four shells. For a given primitive shell block, all of the necessary two-dimensional integrals I , first derivatives DI and, when required, second derivatives DDI , are computed for each of the roots. The appropriate quantities are then combined and summed over the n roots to form the desired derivatives. The shell blocks are classified as either one center, two center, three center or four center; translational invariance is taken

TABLE I. Two electron integral and integral derivative programs used in the GAUSSIAN system.

Program name	Program type	Algorithm	Basis function range	Comments
L311	integrals	axis switching ^a	<i>sp</i>	efficient with contracted functions
L314	integrals	Rys polynomial ^b	<i>spdf</i>	efficient with uncontracted functions
L316	first derivatives	this paper	<i>spd</i>	derivatives written to disk
L702	first derivatives	previous paper ^c	<i>sp</i>	efficient for <i>s</i> and <i>p</i> functions
L703	first derivatives	this paper	<i>spd</i>	derivatives combined with density matrices
L708	second derivatives	this paper	<i>spd</i>	derivatives combined with density matrices

^a Reference 22.^b References 17–19.^c Reference 15.

into account so that only 0, 3, 6, or 9 first derivatives and 0, 6, 21, or 45 second derivatives are calculated. The use of rotational invariance can further diminish the number of integral derivatives that must be calculated.^{7,21} Symmetry also reduces the computational effort, since integral derivatives are calculated only once for an entire set of symmetry equivalent shell blocks. Additional savings are possible when the integral derivatives are combined directly with the density matrices; an entire shell block is eliminated if its contribution to the total derivative is below a threshold.

The two-electron integral and integral derivative codes used in the current versions of GAUSSIAN 80 and GAUSSIAN 82²⁰ are summarized in Table I. The Rys polynomial method discussed above is used whenever *d*- or *f*-type basis functions occur in the integrals (program L314) or integral derivatives

(L703). If only *s* and *p* orbitals are involved in a particular shell block, previously published algorithms for integrals²² (program L311) and integral derivatives¹⁵ (L702) are more efficient. All second derivatives of the two-electron integrals are calculated with the Rys polynomial method (program L708).

In frequency calculations, all integral first derivatives are computed by program L316 and integral second derivatives by program L708. The use of L316 instead of L702 and L703 (as employed for the gradients) leads to some loss in efficiency; however, the integral first derivatives are required in a different form for the CPHF step in the frequency calculations. Since the frequency calculations are dominated by the integral second derivative evaluations, this is not a serious disadvantage (see Table II and discussion below). As

TABLE II. Comparison of calculation times (in seconds).

Machine	Molecule	Basis	Total times			Two electron times ^a					
			Energy	Energy + gradients	Energy + gradients + frequencies	Integrals 1st derivatives				2nd derivatives	
						L311	L314	L702	L703	L316	L708
Vax	C ₂ H ₄	STO-3G	47	85	582	10		26		114	287
		3-21G	77	124	1041	24		36		132	276
		4-31G	89	182	1758	36		73		305	736
		6-31G*	274	771	5015	43	153	93	375	827	1736
	CH ₃ OH	STO-3G	62	126	1035	21		51		220	627
		3-21G	128	208	1570	47		68		238	572
		4-31G	157	321	2875	98		144		554	1507
		6-31G*	665	1572	8421	94	360	176	701	1527	3842
Amdahl	C ₂ H ₄	STO-3G	5.5	9.7	59.7	1.0		2.5		14.2	25.4
		3-21G	8.8	14.0	106.4	2.3		3.5		15.7	25.7
		4-31G	10.4	19.8	176.0	3.6		7.1		37.2	65.5
		6-31G*	38.7	88.2	528.8	4.7	16.7	8.9	37.4	104.9	162.0
	CH ₃ OH	STO-3G	7.3	14.3	110.2	2.2		5.2		28.9	59.6
		3-21G	14.2	23.0	163.3	4.9		7.0		29.8	55.2
		4-31G	18.2	35.1	308.8	8.1		14.6		72.9	148.5
		6-31G*	86.3	189.2	904.9	10.3	39.4	17.8	82.1	201.7	376.8
Cray	C ₂ H ₄	STO-3G	1.51	2.58	21.61	0.27		0.58		2.93	12.03
		3-21G	3.11	4.60	39.31	1.80		0.74		4.20	12.53
		4-31G	3.41	6.08	64.09	1.06		1.83		8.43	30.41
		6-31G*	9.40	22.02	176.04	1.40	4.14	2.24	9.05	24.01	72.87
	CH ₃ OH	STO-3G	1.93	3.53	40.90	0.55		1.11		5.80	28.01
		3-21G	4.60	6.88	58.65	1.48		1.80		6.93	25.94
		4-31G	5.47	9.70	111.18	2.22		3.38		15.36	67.00
		6-31G*	23.18	45.59	301.61	2.85	9.51	4.13	16.95	40.94	164.52

^a See Table I and the text for descriptions and utilization of the individual integral and integral derivative programs.

noted by Pulay,⁷ it is possible to circumvent the storage of the integral first derivatives by contracting them with the density matrix elements to form pseudo-Fock operators. This technique has also been used for some time in one version of GAUSSIAN 80.²³ The direct approach has the advantage of eliminating a large disk file and reducing the amount of computation in the CPHF step. However, it becomes unwieldy when all $3N-6$ (N = number of atoms) pseudo-Fock operators plus the density matrices do not fit into high speed memory.

Representative total cpu times for energy, gradient (energy + first derivative), and frequency (energy + first and second derivatives) calculations are listed in Table II. In addition, the timings have been broken down to the individual programs that deal with the two-electron integrals and integral derivatives. Two molecules, C_2H_4 and CH_3OH , have been examined at four different basis sets: Minimal (STO-3G²⁴), extended (3-21G²⁵ and 4-31G²⁶), and polarization (6-31H*²⁷), containing 42, 42, 56, and 72 primitive Gaussians and 14, 26, 26, and 38 contracted basis functions, respectively. Computations were run on three classes of machines: A minicomputer (VAX 11/780), a mainframe (AMDAHL 470V/8, approximately the same speed as the IBM 3033), and a supercomputer (CRAY-1S). In the CRAY calculations, scalar versions were used throughout except for the Hartree-Fock SCF step.

From comparisons of the total times for the energy, gradients, and frequencies, several trends are clear. Averaged over the two molecules and the three machines, energy + gradient calculations require 1.8 (sp only) to 2.3 (spd) times longer than calculations of the energy alone. Analogously, frequency evaluation takes 8.6 (sp only) and 6.2 (spd) times longer than the energy + gradients. The 3-21G timings are noticeably shorter than those for the 4-31G basis set. For energy + gradients, the 3-21 G times are ~70% of the 4-31G times; at the second derivative level, 3-21G calculations require only half the time needed for the 4-31G basis set. To the extent that the 3-21G basis set provides results comparable to 4-31G, it is clearly more economical to use. Comparison of the STO-3G, 3-21G, and 4-31G execution times for L708 (rightmost column in Table II) illustrates the point that although 3-21G has more basis functions than STO-3G, the number of primitives is the same and the execution times in L708 are very similar. The 4-31G times for L708 are considerably longer because of an increase in the number of primitives from 42 to 56, even though the number of contracted functions is the same.

It is instructive to compare the present method with other algorithms. The HONDO program²⁸ produces integral derivatives using the fact that the derivative of a Cartesian Gaussian can be expressed in terms of higher and lower order Gaussians. Calculations of the gradient contributions arising from a DDDD shell block require the corresponding FDDD, DFDD, DDFD, DDDF and PDDD, DPDD, DDDP, DDDP blocks. For the particular case of a fully uncontracted DDDD shell block, the HONDO algorithm requires ~101 000 floating point multiples; the algorithm presented here requires 98 000 floating multiplies. For second derivative evaluation, the approach in HONDO may require fewer

floating point operations than the algorithm outlined in this paper; however, many more shell blocks must be held in core, leading to serious data handling problems that can degrade the overall efficiency. In a recent paper, Saxe *et al.*²⁹ discuss a method of evaluating integral second derivatives that is similar to the one presented here. They also evaluate the quantities *DDI*, but by a completely different and more complicated method. The present approach requires fewer floating point operations and is much easier to code for higher order Gaussians. However, in both cases, the rate determining computational step is the formation of the integral derivatives by combining the two-dimensional integrals and their derivatives.

SUMMARY

An efficient algorithm has been presented for the analytical computation of first and second derivatives of the two-electron integrals using the method of Rys polynomials.¹⁷⁻¹⁹ The formulas are compact and can be used for basis functions with arbitrary angular momentum. Furthermore, the method is independent of the details of evaluation of the two-dimensional integrals that occur in the Rys polynomial method. By suitably combining programs incorporating the method given here with previously published^{15,22} highly efficient methods for evaluating integrals and their derivatives over basis functions involving only *s* and *p* functions, it is possible to construct a procedure that calculates gradients in about $\frac{1}{2}$ the time that would be required if only the Rys integrals method were used. The present method offers certain computational advantages over previously published algorithms.

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