

Efficient Computation of Two-Electron-Repulsion Integrals and Their n th-Order Derivatives Using Contracted Gaussian Basis Sets

Peter M. W. Gill,* Martin Head-Gordon, and John A. Pople

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213
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We present a general algorithm for the evaluation of the n th derivatives (with respect to the nuclear Cartesian coordinates) of two-electron-repulsion integrals (ERIs) over Gaussian basis functions. The algorithm is a generalization of our recent synthesis of the McMurchie/Davidson and Head-Gordon/Pople methodologies for ERI generation. Any ERI n th derivative may be viewed as an inner product between a function (which we term a *bra*) of electron 1 and a function (which we term a *ket*) of electron 2. After defining bras and kets appropriately, we derive five recurrence relations that enable any bra to be constructed recursively from very simple bras which we call p -bras. We show how these recurrence relations (and their analogues for kets) may be used to compute ERI n th derivatives from easily calculated one-center Hermite integrals. The five recurrence relations are overcomplete in the sense that there is generally more than one path through them by which a given bra can be constructed. We have written a computer program that selects an efficient path to any necessary bra or ket. We present comparative FLOP counts and timings which demonstrate that, for calculations using contracted basis sets, the new methodology (the BRAKET algorithm) is very competitive, both theoretically and practically, with all previous approaches.

Introduction

Ever since Boys' introduction of Gaussian basis sets to quantum chemistry in 1950,¹ the calculation and handling of the notorious two-electron-repulsion integrals (ERIs) over Gaussian functions has been an important avenue of research for practicing computational chemists. Indeed, the emergence of practically useful quantum chemistry computer programs such as the GAUSSIAN suites² has been fueled in no small part by the development of sophisticated algorithms³⁻⁸ to compute the very large number of ERIs that are involved in calculations on molecular systems of even modest size.

In recent times, dramatic improvements in computer speed have paved the way for the introduction of the so-called "direct" methods.⁹⁻¹⁵ Within this framework, rather than being computed once and then stored for subsequent use, ERIs (and, if necessary, their derivatives) are computed *as often as they are needed* and are then discarded. Although these approaches are obviously more expensive computationally than their conventional analogues, they permit much larger systems to be treated and do not require prohibitive amounts of disk space. Their practical usefulness is, however, predicated on the availability of highly efficient algorithms for ERI generation.

An *unnormalized primitive Cartesian Gaussian function*

$\varphi_{\mathbf{a}k}(\mathbf{r}) = (x - A_x)^{\alpha_x}(y - A_y)^{\alpha_y}(z - A_z)^{\alpha_z} \exp[-\alpha_k(\mathbf{r} - \mathbf{A})^2]$ (1)
centered at \mathbf{A} and with exponent α_k is uniquely defined by its

angular momentum vector $\mathbf{a} = (a_x, a_y, a_z)$, by its position vector \mathbf{A} and by its exponent α_k . Its angular momentum is defined as $a = (a_x + a_y + a_z)$. For example, if $\mathbf{a} = (0, 1, 1)$, then $\varphi_{\mathbf{a}k}$ represents a d_{yz} function. It is convenient to group such functions by their exponents. Thus, we will refer to a set of primitive functions with a given exponent and on a given center as a *primitive shell*.

Primitive functions are often linearly combined to form a *contracted Cartesian Gaussian function*

$$\phi_{\mathbf{a}}(\mathbf{r}) = \sum_{k=1}^K D_{\mathbf{a}k} \varphi_{\mathbf{a}k} \quad (2)$$

where the $D_{\mathbf{a}k}$ are known as contraction coefficients and K is known as the degree of contraction of the contracted function.

A *primitive ERI* over four primitive Gaussians is the integral

$$[\mathbf{a}_k \mathbf{b}_l | \mathbf{c}_m \mathbf{d}_n] = \int \int \varphi_{\mathbf{a}k}(\mathbf{r}_1) \varphi_{\mathbf{b}l}(\mathbf{r}_1) r_{12}^{-1} \varphi_{\mathbf{c}m}(\mathbf{r}_2) \varphi_{\mathbf{d}n}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (3)$$

The left-hand subscripts are rarely of particular interest and it is common to denote the integral (3) by $[\mathbf{a} \mathbf{b} | \mathbf{c} \mathbf{d}]$.

Combining (2) and (3) leads to a *contracted ERI*

$$(\mathbf{a} \mathbf{b} | \mathbf{c} \mathbf{d}) = \sum_{k_A}^{K_A} \sum_{k_B}^{K_B} \sum_{k_C}^{K_C} \sum_{k_D}^{K_D} D_{\mathbf{a}k_A} D_{\mathbf{b}k_B} D_{\mathbf{c}k_C} D_{\mathbf{d}k_D} [\mathbf{a}_{k_A} \mathbf{b}_{k_B} | \mathbf{c}_{k_C} \mathbf{d}_{k_D}] \quad (4)$$

which we distinguish from a primitive ERI by the use of parentheses instead of square brackets.

A *class* of ERIs is defined as the set of all $(\mathbf{a} \mathbf{b} | \mathbf{c} \mathbf{d})$ associated with a given shell quartet. For example, if each of the four shells were a p shell (which, of course, is composed of three functions: p_x , p_y , and p_z), the associated class would contain 81 ($=3^4$) ERIs.

It is useful to express, as a quadratic in K^2 , the total number of FLOPs (Floating-point OPERations, viz., adds, subtracts, multiplies, and divides) N required by a given algorithm to compute a class of ERIs of a given type

$$N = xK^4 + yK^2 + zK^0 \quad (5)$$

where, for simplicity, each of the four shells involved is assumed to have the same degree of contraction K and neither the centers \mathbf{A} and \mathbf{B} nor the centers \mathbf{C} and \mathbf{D} are assumed to be coincident. The coefficients x , y , and z vary greatly from one algorithm to another and may be used to rationalize the relative performances of different approaches.

In a recent paper,¹⁶ we presented a preliminary discussion of a new methodology in which the best features of the McMurchie/Davidson and Head-Gordon/Pople methodologies for ERI generation are combined.

(16) Gill, P. M. W.; Head-Gordon, M.; Pople, J. A. *Int. J. Quantum Chem., Symp.* 1989, 23, 269.

- (1) Boys, S. F. *Proc. R. Soc. London* 1950, A200, 542.
(2) For example: Frisch, M. J.; et al. GAUSSIAN 88; Carnegie Mellon Quantum Chemistry Publishing Unit; Carnegie Mellon University, Pittsburgh, PA 15213.
(3) Pople, J. A.; Hehre, W. J. *J. Comput. Phys.* 1978, 27, 161.
(4) (a) Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* 1976, 65, 111. (b) King, H. F.; Dupuis, M. *J. Comput. Phys.* 1976, 21, 44. (c) Rys, J.; Dupuis, M.; King, H. F. *J. Comput. Chem.* 1983, 4, 154.
(5) McMurchie, L. E.; Davidson, E. R. *J. Comput. Phys.* 1978, 26, 218.
(6) (a) Schlegel, H. B. *J. Chem. Phys.* 1982, 77, 3676. (b) Schlegel, H. B. *J. Chem. Phys.* 1989, 90, 5630.
(7) Obara, S.; Saika, A. *J. Chem. Phys.* 1986, 84, 3963.
(8) Head-Gordon, M.; Pople, J. A. *J. Chem. Phys.* 1988, 89, 5777.
(9) Almlöf, J.; Faegri, K.; Korsell, K. *J. Comput. Chem.* 1982, 3, 385.
(10) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem., Symp.* 1979, 13, 225.
(11) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* 1988, 153, 503.
(12) Saebø, S.; Almlöf, J. *Chem. Phys. Lett.* 1989, 154, 83.
(13) Head-Gordon, M.; Pople, J. A. *J. Phys. Chem.* 1988, 92, 3063.
(14) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Int. J. Quantum Chem., Symp.* 1989, 23, 291.
(15) (a) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* 1990, 166, 275. (b) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* 1990, 166, 281.