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Some Unexpected Relationships Between First, Second and Third Derivative Electron Repulsion Integrals for Diatomic and Triatomic Molecules

Mark A. Vincent and Henry F. Schaefer III

Department of Chemistry, University of California, Berkeley, CA 94720, U.S.A.

It is demonstrated that for diatomic molecules, second and third derivative electron repulsion integrals need not be explicitly evaluated. Similarly for triatomic molecules an analogous simplification applies to all second derivative and 94% of all third derivative integrals. Such higher integral derivatives may be determined from intermediate quantities required in the evaluation of integral first derivatives, in conjunction with translational and rotational invariance properties. This result also has implications for theoretical studies of tetra-atomic and larger molecules. Specifically, the evaluation of most two- and three-center integral derivatives becomes very efficient.

Key words: Electron repulsion integrals.

1. Introduction

The impact of self-consistent-field (SCF) analytic first and second derivative methods in quantum chemistry has revolutionized the manner in which molecular structures and energetics are determined theoretically. However, the computation of two-electron integral derivatives remains a significant factor as far as time is concerned in such studies. Kahn [1] has shown how it is in principle possible to use the rotational invariance properties of integrals to reduce the amount of work that needs to be done in the determination of two-electron first derivatives. Taking his work [1] as a starting point, we have recently shown [2] how to exploit rotational invariance in the evaluation of second and third derivative electron repulsion integrals. Our work also showed how to implement the rotational invariance in an efficient way for first, second and third derivatives. In the course of programming these new developments for second derivatives, it became apparent that certain classes of second derivative integrals need never be explicitly evaluated. We present here a method for the determination of two-electron second derivative integrals, for diatomics and triatomics, using first derivative integrals only.

2. Method

Dupuis, Rys and King [3] have shown that it is possible to evaluate two-electron integrals in terms of three two-dimensional integrals, designated I_x, I_y, and I_z. An integral I is then formed from a product of these three, two dimensional integrals such that $I=\sum_{\alpha=1,N} I_x(\nu_\alpha).\ I_y(\nu_\alpha)\cdot I_z(\nu_\alpha)^*$, where N is the number of quadrature points. To evaluate a derivative of I with respect to a cartesian coordinate, one can directly differentiate the individual two-dimensional integrals and then form I' [e.g., $I'=\sum_{\alpha=1,M} I'_x(\nu_\alpha)\cdot I_y(\nu_\alpha)\cdot I_z(\nu_\alpha)^*$.] Thus a program for calculating first derivatives would have $I'_x(\nu_\alpha)$, $I'_y(\nu_\alpha)$ and $I'_z(\nu_\alpha)$ available for at least $(n-1)$ of the possible n values of x, y and z [n is the number of nuclei over which the integral I is centered]. From this we see that certain second derivatives are readily determined, e.g. $I''=\sum_{\alpha=1,N} I'_x(\nu_\alpha)I'_y(\nu_\alpha)I_z(\nu_\alpha)^*$. The main problem in the evaluation of I'' is to determine the I''_x (or I''_y or I''_z). It turns out, however, that rotational and translational invariance may be used to obtain the two-center and three-center terms I'', thus allowing all the second derivative integrals to be determined with a first derivative program. Although we have restricted our discussion to Rys quadrature methods here, the arguments presented apply to any integration scheme that forms the integral I from the product of three cartesians functions. In particular the method of McMurchie and Davidson, [4] in which singly- or multiply-differentiated charge distributions are computed and then used in the two-electron integral formulae, would benefit in a similar way from the ideas put forth here.

As an example let us consider a two-center two-electron integral, I, in detail. There are 21 second derivatives of I, of which fifteen can be found by translational invariance. Let us assume we have the derivatives

$$\frac{\partial^2 I}{\partial x_1\partial x_1},\quad \frac{\partial^2 I}{\partial x_1\partial y_1},\quad \frac{\partial^2 I}{\partial x_1\partial z_1},\quad \frac{\partial^2 I}{\partial y_1\partial y_1},\quad \frac{\partial^2 I}{\partial y_1\partial z_1},\quad \frac{\partial^2 I}{\partial z_1\partial z_1}$$

(where x_1, y_1 and z_1 are the cartesian coordinates of center one). Then the translational invariance equations to be solved are

$$\frac{\partial^2 I}{\partial x_1\partial x_2}=-\frac{\partial^2 I}{\partial x_1\partial x_1} \tag{1a}$$

$$\frac{\partial^2 I}{\partial y_1\partial y_2}=-\frac{\partial^2 I}{\partial y_1\partial y_1} \tag{1b}$$

$$\frac{\partial^2 I}{\partial z_1 \partial z_2} = -\frac{\partial^2 I}{\partial z_1 \partial z_1} \tag{1c}$$

$$\frac{\partial^2 I}{\partial x_1 \partial y_2} = -\frac{\partial^2 I}{\partial x_1 \partial y_1} \tag{1d}$$

$$\frac{\partial^2 I}{\partial x_1 \partial z_2} = -\frac{\partial^2 I}{\partial x_1 \partial z_1} \tag{1e}$$

$$\frac{\partial^2 I}{\partial y_1 \partial z_2} = -\frac{\partial^2 I}{\partial y_1 \partial z_1} \tag{1f}$$

$$\frac{\partial^2 I}{\partial x_2 \partial y_1} = -\frac{\partial^2 I}{\partial x_1 \partial y_1} \tag{1g}$$

$$\frac{\partial^2 I}{\partial x_2 \partial z_1} = -\frac{\partial^2 I}{\partial x_1 \partial z_1} \tag{1h}$$

$$\frac{\partial^2 I}{\partial y_2 \partial z_1} = -\frac{\partial^2 I}{\partial y_1 \partial z_1} \tag{1i}$$

$$\frac{\partial^2 I}{\partial x_2 \partial x_2} = -\frac{\partial^2 I}{\partial x_1 \partial x_2} \left(= \frac{\partial^2 I}{\partial x_1 \partial x_1} \right) \tag{1j}$$

$$\frac{\partial^2 I}{\partial y_2 \partial y_2} = -\frac{\partial^2 I}{\partial y_1 \partial y_2} \left(= \frac{\partial^2 I}{\partial y_1 \partial y_1} \right) \tag{1k}$$

$$\frac{\partial^2 I}{\partial z_2 \partial z_2} = -\frac{\partial^2 I}{\partial z_1 \partial z_2} \left(= \frac{\partial^2 I}{\partial z_1 \partial z_1} \right) \tag{1l}$$

$$\frac{\partial^2 I}{\partial x_2 \partial y_2} = -\frac{\partial^2 I}{\partial x_2 \partial y_1} \left(= \frac{\partial^2 I}{\partial x_1 \partial y_1} \right) \tag{1m}$$

$$\frac{\partial^2 I}{\partial x_2 \partial z_2} = -\frac{\partial^2 I}{\partial x_2 \partial z_1} \left(= \frac{\partial^2 I}{\partial x_1 \partial z_1} \right) \tag{1n}$$

$$\frac{\partial^2 I}{\partial y_2 \partial z_2} = -\frac{\partial^2 I}{\partial y_2 \partial z_1} \left(= \frac{\partial^2 I}{\partial y_1 \partial z_1} \right) \tag{1o}$$

where x_2, y_2 and z_2 are the coordinates of the second center in the integral.

These fifteen equations demonstrate the fact [5] that it is possible to avoid the explicit calculation of integral derivatives involving the differentiation with respect to the coordinates of one of the atomic centers. That is, for two-center integrals, by starting from the six second derivatives with respect to one nuclear center only we generate the remaining fifteen.

Of the six second derivative integrals discussed above, only one is unique. As we have stated already, this may be chosen as

$$\frac{\partial^2 I}{\partial x_1 \partial y_1}, \quad \frac{\partial^2 I}{\partial x_1 \partial z_1} \quad \text{or} \quad \frac{\partial^2 I}{\partial y_1 \partial z_1}$$

if only first derivatives are to be explicitly computed. Let us choose it to be $\partial^2 I/\partial x_1\,\partial y_1$. Now the expression for the rotational invariance equations for second derivatives are given in our previous paper [2] (Eq. (4)). A possible set of these equations is

$$\frac{\partial \delta I_{yx}}{\partial x_1}=\frac{\partial I}{\partial y_1}+(x_1-x_2)\frac{\partial^2 I}{\partial x_1\,\partial y_1}-(y_1-y_2)\frac{\partial^2 I}{\partial x_1\,\partial x_1} \tag{2a}$$

$$\frac{\partial \delta I_{zy}}{\partial x_1}=(y_1-y_2)\frac{\partial^2 I}{\partial x_1\,\partial z_1}-(z_1-z_2)\frac{\partial^2 I}{\partial x_1\,\partial y_1} \tag{2b}$$

$$\frac{\partial \delta I_{zx}}{\partial y_1}=(x_1-x_2)\frac{\partial^2 I}{\partial y_1\,\partial z_1}-(z_1-z_2)\frac{\partial^2 I}{\partial y_1\,\partial x_1} \tag{2c}$$

$$\frac{\partial \delta I_{yx}}{\partial y_1}=(x_1-x_2)\frac{\partial^2 I}{\partial y_1\,\partial y_1}-\frac{\partial I}{\partial x_1}-(y_1-y_2)\frac{\partial^2 I}{\partial y_1\,\partial x_1} \tag{2d}$$

$$\frac{\partial \delta I_{zx}}{\partial z_1}=(x_1-x_2)\frac{\partial^2 I}{\partial z_1\,\partial z_1}-\frac{\partial I}{\partial x_1}-(z_1-z_2)\frac{\partial^2 I}{\partial z_1\,\partial x_1}. \tag{2e}$$

By solving these Eqs. (2a–e) and then using Eqs. (1a–o) we can obtain all the second derivatives of I. For the sake of simplicity, relative to our earlier paper [2], we have not summed over the integrals that make up the shell block to which I belongs, in Eqs. (1a–o) and (2a–e).

For three-center two-electron integrals there are 45 second derivatives, 24 of which may be found by translational invariance and 15 by rotational invariance. The six integrals to be evaluated may be chosen such that they involve the product of first derivatives only. A possible set being

$$\frac{\partial^2 I}{\partial x_1\,\partial y_1}\quad \frac{\partial^2 I}{\partial x_1\,\partial y_2}\quad \frac{\partial^2 I}{\partial x_1\,\partial z_1}\quad \frac{\partial^2 I}{\partial y_2\,\partial x_2}\quad \frac{\partial^2 I}{\partial y_2\,\partial z_1}\quad \frac{\partial^2 I}{\partial z_1\,\partial x_2}.$$

These may then be substituted into the three equations represented by Eq. (4) of our earlier paper [2], with $\gamma_r = x_1, y_2, z_1, x_2, y_1$ and z_2. Thus it is unnecessary to explicitly determine any of the three-center, second derivative, two-dimensional integrals. For four center two-electron integrals, however, at least three true second derivatives have to be calculated, one for each of the two dimensional integrals, I_α.

3. Third Derivatives

Kahn [1] has noted in his paper that for the first derivatives of a two-center two-electron integral one only needs to determine one derivative. We have noted a similar thing for second derivatives, and as one might expect the same carries over to third derivatives. Thus for diatomic molecules both second and third derivative integrals are obtained from only the first derivatives of the two dimensional integrals I_x, I_y, I_z. From what we have said $\partial^2 I/\partial x_1\,\partial y_1\,\partial z_1$ would be an obvious choice.

Table 1. Breakdown of types of electron repulsion integrals and derivatives for model molecular systems having no elements of point group symmetry. Each atom has ten basis functions centered thereon

	Number of Atoms						
Number of Integrals	4	5	6	7	8	9	10
One-Center	6 160	7 700	9 240	10 780	12 320	13 860	15 400
Two-Center	114 450	190 750	286 125	400 575	534 100	686, 700	858 375
Three-Center	186 000	465 000	930 000	1 627 500	2 604 000	3 906 000	5 580 000
Four-Center	30 000	150 000	450 000	1 050 000	2 100 000	3 780 000	6 300 000
Two-Center Derivatives	686 700	1 144 500	1 716 750	2 403 450	3 204 600	4 120 200	5 150 250
Three-Center Derivatives	1 674 000	4 185 000	8 370 000	14 647 500	23 436 000	35 154 000	50 220 000
Four-Center Derivatives	360 000	1 800 000	5 400 000	12 600 000	25 200 000	45 360 000	75 600 000
Two-Center Second Derivatives	2 403 450	4 005 750	6 008 625	8 412 075	11 216 100	14 420 700	18 025 875
Three-Center Second Derivatives	8 370 000	20 925 000	41 850 000	73 237 500	117 180 000	175 770 000	251 100 000
Four-Center Second Derivatives	2 340 000	11 700 000	35 100 000	81 900 000	163 800 000	294 840 000	491 400 000

In the case of a three-center two-electron integral there are a total of 165 third derivatives, of which 109 may be found by translational invariance [2]. Of the remaining 56 third derivative integrals, 46 may be obtained via the rotational invariance equations. The remaining 10 third derivatives may be found by using both the first and second derivatives of the two-dimensional integrals. However, the third derivatives of the two-dimensional integrals need never be evaluated.

4. Concluding Remarks

The above analysis is also of considerable value for tetra-atomic and larger molecules. This is because the fraction of three-center integrals is substantial for such molecules. Consider, for example, a molecule composed of first row atoms (B, C, N, O, and F), each described by a double zeta basis set, ten functions per atom. Table 1 then gives the number of electron repulsion integrals of each type as a function of the number of atoms comprising the molecule.

Table 1 shows that for the specimen tetra-atomic molecule, only 8.9% of the two-electron integrals are four-center in nature. In fact, one must go to an eleven atom molecule (110 basis functions) before the four-center integrals form a majority. For the first derivative integrals, the molecule must include nine atoms before 50% of the integrals are four-center in nature. And even for the second derivative integrals, seven centers are required before the four-center terms predominate. Thus the relationships described here should be of considerable value for molecules larger than triatomic. Nevertheless the great simplification of the computation of all second and most third derivative integrals for triatomic molecules is the primary result of the present investigation.

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