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# Translational and rotational symmetries in third integral derivatives

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Abstract. Based on the invariance under translations and rotations of quantum chemical oneand two-electron integrals, a method for obtaining a complete set of independent relations among third integral derivatives is presented. It is shown that the number of dependent integral derivatives, which is equal to the number of independent relations, can be straightforwardly determined in terms of the remaining third derivatives which must be explicitly calculated. The set of such independent and dependent third integral derivatives can be chosen in a manner which imposes no restrictions on the nuclear positions. The special case of collinear nuclear centres is also separately analyzed.

Keywords. Translational symmetry; rotational symmetry.

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### 1. Introduction

The direct computation of analytical derivatives of the electronic energy with respect to nuclear coordinates has proved to be a powerful tool because it yields an immediate sense of the local topography of the energy surface. Recently, workers (Pulay 1983; Simons and Jørgensen 1984; Simons *et al* 1984) have extended techniques for calculating first and second derivatives to the calculation of anharmonicities of the energy surface.

A large number of third integral derivatives need to be calculated in order to implement a calculation of the third derivative of the energy surface. For example, consider the third derivatives of four-centre two-electron integrals in a calculation involving *n* primitive atomic basis functions. One can easily show that there are 364 third integral derivatives for each of the  $n^4$  such integrals. In the *N*-centre case there are (3N)(3N+1)(3N+2)/6 third derivatives for each of the  $n^4$  integrals.

Use of translational and rotational invariance (or symmetry) has proved to be a valuable tool in calculating derivatives of the energy surface by reducing the number of integral derivatives that need to be explicitly calculated (Komornicki *et al* 1977; Dupuis and King 1978; Kahn 1981; Takada *et al* 1981; Vincent and Schaefer 1983; Vincent *et al* 1983; Page *et al* 1984; Schlegel *et al* 1984; Banerjee *et al* 1985). The goal of this paper is to extend the formalism of an earlier paper (Banerjee *et al* 1985) to third integral derivatives. The present work provides a complete analysis of the invariance properties for third integral derivatives. We provide a method for treating the redundancy of invariance conditions. Such a treatment is absent from earlier work. Rotational

Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

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#### 128 James O Jensen, Ajit Banerjee and Jack Simons

invariance conditions are geometry dependent in the sense that poorly chosen conditions impose many geometrical constraints on the molecule. We present a systematic method for choosing the conditions in a manner which imposes no restrictions on the allowable geometries of the nuclear positions. In §2 we use translation and rotation operators to derive the essential invariance relations involving third integral derivatives. In §3 we derive a method for finding the independent integral derivatives and for explicitly calculating the remaining (dependent) integral derivatives using symmetry relations. Doe rest new Art A Market O 23MAL

# 2. Theoretical development

An integral I depends upon the gaussian basis functions appearing in I. Each of the gaussians is centred at one of the nuclear positions  $P_{K}$  (K = 1, N; N  $\leq 4$ ) engles r possions. The special case of collinear nuclear

$$I = I\{G_1(\mathbf{P}_1, \mathbf{r}_1), \quad G_2(\mathbf{P}_2, \mathbf{r}_2) \dots G_N(\mathbf{P}_N, \mathbf{r}_N)\}.$$
(1)

Abstract. Based on the invariance under tra

Each cartesian gaussian function is parameterized in terms of the centre  $P_{\kappa}$  and the internal coordinate  $\mathbf{r}_{\mathbf{k}}$  as

$$G_{K}(\mathbf{P}_{K},\mathbf{r}_{K}) = A(X-P_{Kx})^{n_{x}}(Y-P_{Ky})^{n_{y}}(Z-P_{Kz})^{n_{z}}\exp\left(-\xi r_{K}^{2}\right),$$
(2)

where A is the normalization constant and the vector R is the lab fixed coordinate with components X, Y, Z giving the location of the electron relative to the origin.

$$\mathbf{R} = \mathbf{P}_K + \mathbf{r}_K; \quad K = 1, N.$$
(3)

An operator  $\hat{T}$  that involves a translation of all points in space by a vector  $\mathbf{t} = (t_x, t_y, t_z)$  can be written as an end of a system by broast bits that guidebrough

$$\hat{T} = \exp\{-\mathbf{t} \cdot \nabla_{\mathbf{R}}\}\tag{4}$$

where  $\nabla_{\mathbf{R}} = (\partial/\partial X, \partial/\partial Y, \partial/\partial Z)$  defines the gradient operator at all points **R** in space. An operator  $\hat{\mathbf{R}}$  that generates a rotation by the angle  $\boldsymbol{\phi} = (\phi_x, \phi_y, \phi_z)$  about an axis along the direction  $\phi$  through the lab fixed origin can be expressed as

$$\hat{R}(\boldsymbol{\phi}) = \exp\left\{-\boldsymbol{\phi}\cdot\mathbf{L}\right\},\tag{5}$$

Use of translational and rotational invariance (or symmetry) has proved terandw

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$$\nabla \times \mathbf{R} = \mathbf{L}$$
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For two-electron integrals, which depend on two electronic coordinates R and R', the  $\nabla_R$  operator will be implicitly assumed to operate on both variables (i.e., it is  $\nabla_R + \nabla_{R'}$ ). Also from the form of the gaussian function it is seen that derivatives. The present work provides a complete analysis of the invariance properties.

$$\frac{\partial}{\partial X}G_{K}(\mathbf{P}_{K},\mathbf{r}_{K}) = -\frac{\partial}{\partial P_{K_{X}}}G_{K}(\mathbf{P}_{K},\mathbf{r}_{K}) = \frac{\partial}{\partial x_{K}}G_{K}(\mathbf{P}_{K},\mathbf{r}_{K}).$$
(7)

The rotation operator  $\hat{R}$  is defined in terms of lab fixed coordinates. To generate rotations of both the centre and orientation of a gaussian function we must allow L to operate both on  $\mathbf{P}_{\kappa}$  and  $\mathbf{r}_{\kappa}$ . For example, the action of the L<sub>z</sub> component on a

# Third integral derivatives

powers of \$. Again there are three ways to generate rotational conditions asi naiszuag

$$L_{z}G_{K}(\mathbf{P}_{K},\mathbf{r}_{K}) = \left(X\frac{\partial}{\partial Y} - Y\frac{\partial}{\partial X}\right)G(\mathbf{P}_{K},\mathbf{r}_{K})$$
$$= \left\{-\left(P_{Kx}\frac{\partial}{\partial P_{Ky}} - P_{Ky}\frac{\partial}{\partial P_{Kx}}\right) + \left(x_{K}\frac{\partial}{\partial y_{K}} - y_{K}\frac{\partial}{\partial x_{K}}\right)\right\}G(\mathbf{P}_{K},\mathbf{r}_{K})$$
$$\equiv \left\{-L_{zK} + l_{zK}\right\}G_{K}(\mathbf{P}_{K},\mathbf{r}_{K}).$$
(8)

Thus  $L_z$  can be written as the sum of an operator  $L_{zK}$  which acts only on nuclear coordinates  $\mathbf{P}_K$  and an operator  $l_{zk}$  which acts only on the internal coordinate  $\mathbf{r}_K$ .

Since an integral is unchanged when all of its coordinates are translated or rotated, we can write

$$I\{G_1, G_2 \dots\} = I\{\hat{T}(G_1, G_2 \dots)\}$$
(9)  
$$I(G_1, G_2 \dots) = I\{\hat{F}(G_1, G_2 \dots)\}$$
(10)

and

$$I\{G_1, G_2 \dots\} = I\{R(G_1, G_2 \dots)\}.$$
 (10)

Equations (9) and (10) also hold when I is replaced by a first derivative  $\partial I/\partial P_K$  or by a second derivative  $\partial^2 I/\partial P_K \partial P_J$ . The RHS of (9) is then expanded in a power series in t. The terms of each order in t are separately set to zero yielding through third-order the relations

$$T^{(1)}I = \sum_{J=1}^{N} I_{J\alpha} = 0,$$

$$T^{(2)}I = \sum_{JK}^{N} I_{J\alpha K\beta} = 0,$$

$$N$$
(11)

(der)

$$T^{(3)}I = \sum_{JKL} I_{J\alpha K\beta L\gamma} = 0, \quad \alpha, \beta, \gamma = x, y, z,$$

where the shorthand notation

$$I_{J_{\alpha}} = \frac{\partial I}{\partial P_{J_{\alpha}}}, \quad I_{J_{\alpha}K\beta} = \frac{\partial^2 I}{\partial P_{J_{\alpha}}\partial P_{K\beta}}, \quad \text{etc.}$$

has been introduced.

There are three ways to generate relations involving third integral derivatives from the above conditions:

$$T^{(3)}I = \sum_{JKL}^{N} I_{J\alpha K\beta L\gamma} = 0, \qquad (12)$$

$$\partial/\partial P_{L\gamma}(T^{(2)}I) = \sum_{JK}^{N} I_{J\alpha K\beta L\gamma} = 0, \qquad (13)$$

$$\partial^2/\partial P_{\kappa\beta}\partial P_{L\gamma}(T^{(1)}I) = \sum_{J=1}^N I_{J\alpha\kappa\beta L\gamma} = 0.$$
(14)

It is easy to show that the relations in (14) can be used to generate all the relations in (13) and (12). Thus we exclude these from further consideration and look only at (14).

Likewise the rotation operator  $\hat{R}$  is substituted into (10) and the RHS expanded in

129

powers of  $\phi$ . Again there are three ways to generate rotational conditions among third derivatives:

$$R^{(3)}I = \mathbf{L}\mathbf{L}\mathbf{L}I = 0, \tag{15}$$

$$\partial^2 / \partial P_{J\mu} \partial P_{K\nu}(R^{(1)}I) = \partial^2 / P_{J\mu} \partial P_{K\mu}(\mathbf{L}I) = 0$$
<sup>(16)</sup>

$$\partial/\partial P_{I_{n}}(R^{(2)}I) = \partial/\partial P_{I_{n}}(\mathbf{L}\mathbf{L}I) = 0$$
(17)

It can be shown that the relations in (17) can be used to generate all of the relations in (15) and (16). Thus we need only look at Eq. (17).

Equation (8) is substituted into (17) to yield

$$\sum_{J=1}^{N} L_{\gamma J} I_{K\mu M\nu} = \sum_{J=1}^{N} l_{\gamma J} I_{K\mu M\nu} \quad K, M = 1, N; \quad \gamma, \mu, \nu = x, y, z.$$
(18)

The operator  $L_{\gamma J}$  has been pulled outside of the integral  $I_{K\mu M\nu}$  since the  $\mathbf{P}_{J}$ , which  $L_{\gamma J}$  involves, are not integration variables. In addition, the notation  $l_{\gamma J}I_{K\mu M\nu}$  has been introduced to denote that the  $l_{\gamma J}$  operator is applied to the vector  $\mathbf{r}$  in the gaussian  $G_{J}$  appearing in  $I_{K\mu M\nu}$ . That is,  $l_{\gamma J}I_{K\mu M\nu}$  represents  $I_{K\mu M\nu}(l_{\gamma J}G_{J})$ .

Substituting the definitions of  $L_{y}$  and  $l_{y}$  into (18) we then obtain

$$\sum_{J=1}^{N} (P_{J\alpha}I_{J\beta K\mu M\nu} - P_{J\beta}I_{J\alpha K\mu M\nu}) = I_{\alpha\beta K\mu M\nu},$$

$$\alpha\beta = xy, yz, zx; K, M = 1, N; \mu, \nu = x, \nu, z; (K\mu) \ge (M\nu),$$
(19a)

where

$$I_{\alpha\beta\kappa\mu M\nu} = \sum_{J=1}^{N} l_{\gamma J} I_{\kappa\mu M\nu} - \delta_{\alpha\mu} I_{\kappa\beta M\nu} + \delta_{\beta\mu} I_{\kappa\alpha M\mu} - \delta_{\alpha\nu} I_{\kappa\mu M\beta} + \delta_{\beta\nu} I_{\kappa\mu M\alpha}$$
  
$$\alpha\beta\gamma = xyz, yzx, zxy.$$
(19b)

The  $l_{\alpha J}$  operator transforms a gaussian into two gaussians in the same shell. Using  $l_{\alpha J}$  as an example we see that

$$l_{zJ}G_{J}(n_{x}, n_{y}, n_{z}) = \left(x_{J}\frac{\partial}{\partial y_{J}} - y_{J}\frac{\partial}{\partial x_{J}}\right)G_{J}(n_{x}, n_{y}, n_{z})$$
  
$$= n_{y}\left(\frac{2n_{x}+1}{2n_{y}-1}\right)^{1/2}G_{J}(n_{x}+1, n_{y}-1, n_{z})$$
  
$$-n_{x}\left(\frac{2n_{y}+1}{2n_{x}-1}\right)^{1/2}G_{J}(n_{x}-1, n_{y}+1, n_{z}).$$
 (20)

 $\partial^2/\partial \mathbf{h}_{gg}\partial P_{gg}(\overline{U}^{(k)}I) \approx \sum_{i}^{R} I_{math,i} = 0$ 

Thus we see that the RHS of (19a) is a linear combination of second derivatives of integrals.

#### 3. Implementation

The relations in (14) and (19) are not independent. A systematic method must be developed to eliminate the redundant relations and to best utilize the remaining (independent) ones.

130

As a first step we rewrite (14) as

$$I_{NaK\betaL\gamma} = \sum_{J=1}^{N-1} I_{JaK\betaL\gamma},$$
(21a)  
 $\alpha, \beta, \gamma = x, y, z; K, L = 1, N-1; (K\beta) \ge (L\gamma),$   
 $I_{NaN\betaL\gamma} = \sum_{K=1}^{N-1} I_{NaK\betaL\gamma},$ 
(21b)  
 $\alpha\beta = xy, yz, zx, xx, yy, zz; \gamma = x, y, z; L = 1, N-1,$   
 $I_{NaN\betaN\gamma} = \sum_{L=1}^{N-1} I_{NaN\betaL\gamma},$ 
(21c)

#### $\alpha\beta\gamma = xxx, xxy, xxz, xyy, xyz, xzz, yyy, yyz, yzz, zzz,$

where we have given the centres some arbitrary numbering from 1 to N. A straightforward calculation shows that (21) contain  $\{3(3N-3)(3N-2)/2 + 18(N-1) + 10\}$  conditions which relate certain third integrals derivatives to others.

The next step is to substitute (21) into the rotational-invariance relations of (19). This allows all reference to atom N to be removed from the rotational conditions. The result is

$$\sum_{I=1}^{N-1} (\tilde{P}_{J\alpha} I_{J\beta K\mu M\nu} - \tilde{P}_{J\beta} I_{J\alpha K\mu M\nu}) = I_{\alpha\beta K\mu M\nu}$$
(22)

$$\alpha\beta = xy, yz, zx; K, M = 1, N - 1; \mu, v = x, y, z; (K\mu) \ge (Mv),$$

where  $\tilde{P}_{J\alpha} = P_{J\alpha} - P_{N\alpha}$ . There are  $\{3(3N-3)(3N-2)/2\}$  conditions in (22). Equations (21) and (22) thus yield a total of  $\{27N^2 - 27N + 10\}$  relations among third integral derivatives.

For an N-centre integral there are  $\{(3N)(3N+1)(3N+2)/6\}$  third derivatives of the integral. We will show that the number of *independent* third derivatives is  $\{N'(N'+1)(N'+2)/6\}$  where N' = 3N - 6 (3N - 5 for collinear geometries).

#### Non-collinear case:

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The total number of dependent third integral derivatives that we expect is

$$\frac{1}{6}\left\{(3N)\left(3N+1\right)\left(3N+2\right)-(3N-6)\left(3N-5\right)\left(3N-4\right)\right\}=27N^2-36N+20.$$

Since there are  $\{27N^2 - 27N + 10\}$  relations among the integral derivatives and only  $\{27N^2 - 36N + 20\}$  dependent integral derivatives, there must be  $\{9N - 10\}$  too many relations. These excess relations can be removed via what we called in an earlier paper (Banerjee *et al* 1985) relations among the relations (RAR). It is easily seen that the relations given in (21) are in fact independent. The dependent relations are therefore contained in (22).

We discovered a class of RAR of (22) for third derivatives given by

$$\sum_{j=1}^{n-1} \{ \tilde{P}_{J\gamma} E_{\alpha\beta J\beta K\mu} + \tilde{P}_{J\alpha} E_{\beta\gamma J\beta K\mu} - \tilde{P}_{J\beta} (E_{\alpha\beta J\gamma K\mu} + E_{\beta\gamma J\alpha K\mu}) \} = 0,$$
(23)

$$\alpha\beta\gamma = xyz, yzx, zxy; K = 1, N - 1; \mu = x, y, z,$$

where  $E_{aBKuMv}$  represents the left- or right-hand side of a relation in (22) for the given

values of  $\alpha$ ,  $\beta$ , K,  $\mu$ , M, and  $\nu$ . These  $\{9N - 9\}$  RAR can be verified by simple substitution. In fact, only  $\{9N - 10\}$  of the above RAR are independent.

Since atom 1 and atom N are on different centres,  $\tilde{P}_{1x}$ ,  $\tilde{P}_{1y}$ , or  $\tilde{P}_{1z}$  has to be nonzero. For ease of notation we will assume that  $\tilde{P}_{1y} \neq 0$ . The cases where  $\tilde{P}_{1y} = 0$  but  $P_{1x}$  or  $P_{1z}$  is nonzero can be recovered by cyclic permutation of x, y, and z.

If  $\tilde{P}_{1y} \neq 0$  then the  $\{9N - 10\}$  relations that need to be discarded from (22) are of the form  $\{E_{xy1zK\mu}, E_{zx1zK\mu}, E_{zx1xK\mu}, (K = 1, N - 1; \mu = x, y, z)\}$ . The relation  $E_{zx1x1z}$  appears twice in this list, and therefore there are  $\{9N - 10\}$  unique relations. This list of relations can be obtained by writing (23) in matrix form and then using row operations to transform the matrix into a lower-echelon form using care to use only  $\tilde{P}_{1y}$  as pivot elements.

Equation (22) then transforms into

$$\sum_{J=1}^{N-1} (\tilde{P}_{J\alpha} I_{J\beta K\mu M\nu} - \tilde{P}_{J\beta} I_{J\alpha K\mu M\nu}) = I_{\alpha\beta K\mu M\nu},$$

$$K, M = 1, N-1; \alpha\beta = xy, yz, zx; \mu, \nu = x, y, z; (K\mu) \ge (M\nu);$$

$$(E_{x\nu 1zM\nu}, E_{zx1zM\nu}, E_{zx1xM\nu}).$$
(24)

The discarded conditions  $E_{xy1zMv}$ ,  $E_{zx1zMv}$ ,  $E_{zx1xMv}$  are enclosed in parentheses above. Equation (24) can be thought of as a system of linear equations with  $\{(27N^2 - 63N + 38)/2\}$  independent equations in  $\{(9N^3 - 18N^2 + 11N - 2)/2\}$  variables (third derivatives).

We divide the variables into two groups, the dependent variables equal to the number of relations above and the independent variables that must be known from some other source. It is *not* possible to arbitrarily choose the dependent and independent variables in (24). Since the  $\tilde{P}_{J\alpha}$  are arbitrary (possible zero), a bad choice of dependent variables will result in (24) being insoluble.

A non-collinear integral contains at least three centres. If  $\tilde{P}_{1y} \neq 0$  then there is a centre K such that either  $(\tilde{P}_{Kx}\tilde{P}_{1y} - \tilde{P}_{Ky}\tilde{P}_{1x}) \neq 0$  or  $(\tilde{P}_{Kz}\tilde{P}_{1y} - \tilde{P}_{Ky}\tilde{P}_{1z}) \neq 0$ . If a centre K does not exist such that one of these is nonzero then the centres are collinear contrary to assumption. For the sake of simplicity we rename centre K as centre 2; this is simply a convention and has no consequences.

Let us assume for example that  $(\tilde{P}_{2z}\tilde{P}_{1y} - P_{2y}\tilde{P}_{1z}) \neq 0$ . Equation (24) can then be written as a matrix equation with the third derivatives as variables. For the three- and four-centre cases we have algebraically (Hearn 1984) reduced this matrix equation to echelon form using only  $\tilde{P}_{1y}$  as pivot elements. For three-centre integrals the 10 independent third derivatives are all the unique third derivatives constructed from the differential elements  $\partial P_{1y}$ ,  $\partial P_{2y}$ , and  $\partial P_{2z}$ , which are to be explicitly calculated. Similarly, the 56 independent derivatives for the four-centre case can be constructed uniquely from the differential elements  $\partial P_{1y}$ ,  $\partial P_{2y}$ ,  $\partial P_{2z}$ ,  $\partial P_{3x}$ ,  $\partial P_{3y}$ , and  $\partial P_{3z}$ . For the above choice of the independent and dependent third derivatives the additional assumption  $(\tilde{P}_{2z}\tilde{P}_{1y} - \tilde{P}_{2y}P_{1z}) \neq 0$  is required since (in addition to  $\tilde{P}_{1y}$ ) they appear as the corresponding coefficients of the dependent derivatives in the echelon form.

If instead  $(\tilde{P}_{2x}\tilde{P}_{1y} - \tilde{P}_{2y}\tilde{P}_{1x}) \neq 0$  then the analysis is similar. For the three-centre case the independent variables are constructed from the differential elements  $\partial P_{1y}$ ,  $\partial P_{2x}$ ,  $\partial P_{2y}$ , and for the four-centre case  $\partial P_{1y}$ ,  $\partial P_{2x}$ ,  $\partial P_{2y}$ ,  $\partial P_{3x}$ ,  $\partial P_{3y}$ , and  $\partial P_{3z}$ .

For a given choice of independent integral derivatives  $I_{r+1}, \ldots I_n$ , the remaining

derivatives  $I_1, \ldots, I_r$  are calculated straightforwardly from (24) as a solution of the simultaneous linear equation

$$\mathbf{A}_{(rxr)}\begin{bmatrix}I_{1}\\ \vdots\\ \vdots\\ I_{r}\end{bmatrix} = -\mathbf{B}_{rx(n-r)}\begin{bmatrix}I_{r+1}\\ \vdots\\ \vdots\\ I_{n}\end{bmatrix} + \begin{bmatrix}b_{1}\\ \vdots\\ \vdots\\ b_{r}\end{bmatrix}$$
(25)

where A contains the r columns of the coefficient matrix of (24) corresponding to be the dependent derivatives  $I_1 \ldots I_r$ , while **B** contains the corresponding columns for the n-r independent integrals. The elements of the **b** vectors correspond to the righthand side of (24).

#### Collinear case:

The total number of dependent third integral derivatives in this case is

$$\frac{1}{6} \{ (3N)(3N+1)(3N+2) - (3N-5)(3N-4)(3N-3) \} \\ = (45N^2 - 45N + 20)/2$$

Thus we have  $\{(9N^2 - 9N)/2\}$  excess relations that need to be removed via RAR.

There exists another class of RAR given by the formula

$$\tilde{P}_{1z} E_{xyJ\mu Kv} + \tilde{P}_{1x} E_{yzJ\mu Kv} + \tilde{P}_{1y} E_{zxJ\mu Kv} = 0$$

$$J, K = 1, N - 1; \mu, v = x, y, z; (J\mu) \ge (Kv).$$
(26)

Equation (26) holds only in the collinear case. There are  $\{(9N^2 - 15N + 6)/2\}$  RAR in (26). With (23) there are a total of  $\{(9N^2 + 3N - 12)/2\}$  RAR. Again there is an excess of RAR. A detailed analysis shows that as expected there are only  $\{9N^2 - 9N)/2\}$  independent RAR in (23) and (26); one particular choice is to discard all of the relations of the form  $\{E_{xxJ\mu Ky}$  and  $E_{xyJzJ\mu}(J, K = 1, N - 1; \mu, v = x, y, z)\}$ .

The analysis to find the dependent and independent variables is similar to that in the non-collinear case although no assumptions other than  $\tilde{P}_{1y} \neq 0$  have to be made. If the above conditions are discarded, the independent variables are all the unique third derivatives that can be constructed from the differential element  $\partial P_{1y}$ ,  $\partial P_{2x}$ ,  $\partial P_{2y}$ , and  $\partial P_{2z}$  for the three-centre case and  $\partial P_{1y}$ ,  $\partial P_{2x}$ ,  $\partial P_{2y}$ ,  $\partial P_{2z}$ ,  $\partial P_{3y}$ , and  $\partial P_{3z}$  for the four-centre case. For the two-centre case the only third derivative that need be calculated is  $I_{1y1y1y}$ .

#### 4. Discussion and conclusions

Making a minimum number of choices of the geometry, we have shown how to choose a set of independent third integral derivatives, which needs to be explicitly calculated, and a set of dependent third integral derivatives that can be expressed in terms of the independent ones. Knowing the values of the independent third derivative integrals, it is possible to solve for the dependent integral derivatives by using (24) or (23) followed by (21).

After a detailed examination of the translational and rotational invariance of third integral derivatives, we have found that the results are quite analogous to the results for the second derivatives obtained by Banerjee et al (1985). Analogous to (22) we have for the second derivatives

$$\sum_{J=1}^{N-1} (\tilde{P}_{J\alpha} I_{J\beta K\mu} - \tilde{P}_{J\beta} I_{J\alpha K\mu}) = I_{\alpha\beta K\mu}$$

$$\alpha\beta = xy, yz, zx; K = 1, N-1; \mu = x, y, z.$$

$$(27)$$

From (22) we discard relations of the form  $\{E_{xy1zK\mu}, E_{zx1zK\mu}, E_{zx1zK\mu}, (K = 1, N - 1; \mu = x, y, z)\}$ . For the second derivative case we discard the relations  $\{E_{xy1z}, E_{zx1x}, E_{zx1x}\}$ . For the three-centre case the independent variables are those third derivatives that can be constructed from the differentials  $\partial P_{1y}$ ,  $\partial P_{2y}$ ,  $\partial P_{2z}$ . In the second derivative case the dependent variables are those second derivatives that can be constructed from the differentials  $\partial P_{1y}$ ,  $\partial P_{2y}$ ,  $\partial P_{2z}$ . In the second derivative case the dependent variables are those second derivatives that can be constructed from the differentials  $\partial P_{1y}$ ,  $\partial P_{2y}$ ,  $\partial P_{2z}$ . We feel that the results for fourth derivatives can be possibly written by inspection.

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134

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