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TRANSLATIONAL AND ROTATIONAL SYMMETRIES IN INTEGRAL DERIVATIVES OF ARBITRARY ORDER

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Based on the invariance under translations and rotations of quantum chemical one- and two-electron integrals, a method for obtaining a complete set of independent relations among integral derivatives of arbitrary order is presented. Explicit formulas for the dependent integral derivatives are derived in terms of the remaining (independent) ones. The formulas are derived in a manner which imposes no restrictions on the nuclear positions. The special case of collinear nuclear centers is also examined.

1. Introduction

The direct computation of analytical derivatives of the electronic energy with respect to nuclear coordinates has proven to be a powerful tool because it yields an immediate sense of the local topography of the energy surface. A large number of integral derivatives need to be calculated in order to implement a calculation of derivatives of the energy surface. For example, consider the derivatives of four-center two-electron integrals in a calculation involving n primitive atomic basis functions. One can easily show that for each of the n^4 integrals there are 12 first integral derivatives, 78 unique second integral derivatives, and 364 unique third integral derivatives. In the N-center case there are $\binom{3N+M-1}{M}$ Mth-order integral derivatives for each of the n^4 integrals.

The use of translational and rotational symmetry has proven 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 [1–11]. The goal of this paper is to extend the formalism of earlier papers [10,11] to integral derivatives of arbitrary order.

The present work provides a detailed analysis of invariance properties of integral derivatives. We provide a method for treating the redundancy of invariance conditions. Translational and rotational invariance conditions are geometry dependent in the sense that poorly chosen conditions impose geometrical constraints on the molecule. We present a systematic method to choose the conditions in a manner which imposes no restrictions on the allowable geometries of the nuclear positions.

For an integral over N non-collinear centers we will show that there exists, for a given order M, $\binom{3N+M-1}{M}$ total integral derivatives and $\binom{3N-6+M+1}{M}$ independent integral derivatives which must be explicitly calculated. Thus there are $[\binom{3N+M-1}{M}-\binom{3N-6+M-1}{M}]$ independent invariance relations. For the collinear case we will show that there are $[\binom{3N+M-1}{M}-\binom{3N-5+M-1}{M}]$ independent relations. We will demonstrate that there exists a set of $3N-6$ ($3N-5$ for the collinear case) coordinates whose derivatives must be explicitly calculated. Knowing this set of integral derivatives, all remaining integral derivatives can be calculated using the translational and rotational invariance conditions.

In section 2 we use translation and rotation operators to derive the essential invariance relations involving integral derivatives of arbitrary order. In section 3 we derive a method for finding the independent integral derivatives and for explicitly calculating the remaining (dependent) integral derivatives using symmetry relations. In section 4 we examine the independence and completeness of our working relations.

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2. Theoretical development

An integral I depends upon the gaussian basis functions appearing in I. Each of the gaussians is centered at one of the nuclear positions $\boldsymbol{P}_K$ ($K = 1, N$; $N \leqslant 4$)

$$I = I\{G_1(\boldsymbol{P}_1, \boldsymbol{r}_1), G_2(\boldsymbol{P}_2, \boldsymbol{r}_2), \ldots, G_N(\boldsymbol{P}_N, \boldsymbol{r}_N)\}. \tag{1}$$

Each cartesian gaussian function is parameterized in terms of the center $\boldsymbol{P}_K$ and the internal coordinate $\boldsymbol{r}_K$ as

$$G_K(\boldsymbol{P}_K, \boldsymbol{r}_K) = A(X - P_{Kx})^{n_x}(Y - P_{Ky})^{n_y}(Z - P_{Kz})^{n_z} \exp(-\xi r_K^2), \tag{2}$$

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

$$\boldsymbol{R} = \boldsymbol{P}_K + \boldsymbol{r}_K; \quad K = 1, N. \tag{3}$$

An operator $\hat{T}$ that involves a translation of all points in space by a vector $\boldsymbol{t} = (t_x, t_y, t_z)$ can be written as

$$\hat{T} = \exp(-\boldsymbol{t} \cdot \nabla_R), \tag{4}$$

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

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

where

$$\boldsymbol{L} = \boldsymbol{R} \times \nabla_R. \tag{6}$$

For two-electron integrals, which depend on two electronic coordinates $\boldsymbol{R}$ and $\boldsymbol{R}'$, the ∇_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

$$\partial G_K(\boldsymbol{P}_K, \boldsymbol{r}_K)/\partial X = -\partial G_K(\boldsymbol{P}_K, \boldsymbol{r}_K)/\partial P_{Kx} = \partial G_K(\boldsymbol{P}_K, \boldsymbol{r}_K)/\partial x_K. \tag{7}$$

The rotation operator $\hat{R}$ is defined in terms of lab fixed coordinates. To generate rotations of both the center and orientation of a gaussian function we must allow $\boldsymbol{L}$ to operate both on $\boldsymbol{P}_K$ and $\boldsymbol{r}_K$. For example, the action of the L_z component on a gaussian is

$$\begin{aligned} L_z G_K(\boldsymbol{P}_K, \boldsymbol{r}_K) &= (X\partial/\partial Y - Y\partial/\partial X) G_K(\boldsymbol{P}_K, \boldsymbol{r}_K) \\ &= \left[-(P_{Kx}\partial/\partial P_{Ky} - P_{Ky}\partial/\partial P_{Kx}) + (x_K\partial/\partial y_K - y_K\partial/\partial x_K)\right] G_K(\boldsymbol{P}_K, \boldsymbol{r}_K) \\ &\equiv (-L_{zK} + l_{zK}) G_K(\boldsymbol{P}_K, \boldsymbol{r}_K). \end{aligned} \tag{8}$$

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

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

$$I\{G_1, G_2, \ldots\} = I\{\hat{T}(G_1, G_2, \ldots)\} \tag{9}$$

and

$$I\{G_1, G_2, \ldots\} = I\{\hat{R}(G_1, G_2, \ldots)\}. \tag{10}$$

Eqs. (9) and (10) also hold when I is replaced by a first derivative $\partial I/\partial P_K$ or a second derivative $\partial^2 I/\partial P_{K_1}\partial P_{K_2}$ or a derivative of any order; that is, all integral derivatives are also translationally and rotationally invariant.

Substituting the translation operator $\hat{T}$ into eq. (9), the right-hand side can then be expanded in a power series in $\boldsymbol{t}$. The terms of each order in $\boldsymbol{t}$ are separately set to zero yielding the relations

$$T^{(1)}I = \sum_{K_1=1}^{N} I_{K_1\alpha_1} = 0, \tag{11a}$$

$$T^{(2)}I = \sum_{K_1K_2}^{N} I_{K_1\alpha_1K_2\alpha_2} = 0, \tag{11b}$$

$$T^{(3)}I = \sum_{K_1K_2K_3}^{N} I_{K_1\alpha_1K_2\alpha_2K_3\alpha_3} = 0, \quad \alpha_1, \alpha_2, \alpha_3, \ldots = x, y, z, \tag{11c}$$

$$\vdots$$

where the short-hand notation

$$I_{K_1\alpha_1} = \partial I/\partial P_{K_1\alpha_1}, \quad I_{K_1\alpha_1K_2\alpha_2} = \partial^2 I/\partial P_{K_1\alpha_1}\partial P_{K_2\alpha_2}, \quad \text{etc.}$$

has been introduced.

For integral derivatives of a given order M, there are M ways to generate relations from eqs. (11):

$$T^{(1)}I_{K_2\alpha_2\ldots K_M\alpha_M} = \sum_{K_1=1}^{N} I_{K_1\alpha_1K_2\alpha_2\ldots K_M\alpha_M} = 0, \tag{12}$$

$$T^{(2)}I_{K_3\alpha_3\ldots K_M\alpha_M} = \sum_{K_1K_2}^{N} I_{K_1\alpha_1K_2\alpha_2\ldots K_M\alpha_M} = 0, \tag{13a}$$

$$\vdots$$

$$T^{(M)}I = \sum_{K_1K_2\ldots K_M}^{N} I_{K_1\alpha_1K_2\alpha_2\ldots K_M\alpha_M} = 0. \tag{13b}$$

It is easy to see that the relations of eq. (12) can be used to generate all of the relations in eqs. (13). Thus, in the analysis of translational invariance that follows, we look only at eq. (12).

The analysis of the rotational invariance is similar to that of translation. The rotation operator $\hat{R}$ is substituted into eq. (10), and the right-hand side of eq. (10) expanded in powers of $\boldsymbol{\phi}$. It is straightforward to show that, for integral derivatives of a given order M, the relations

$$R^{(1)}I_{K_2\alpha_2\ldots K_M\alpha_M} = \boldsymbol{L}I_{K_2\alpha_2\ldots K_M\alpha_M} = -Q_{K_2\alpha_2K_3\alpha_3\ldots K_n\alpha_n}, \tag{14}$$

can be used to generate all of the rotational invariance relations for an Mth-order integral derivative. Here, $Q_{K_2\alpha_2\ldots K_n\alpha_n}$ represents the first-order change in the tensor quantity $I_{K_2\alpha_2\ldots K_n\alpha_n}$ due to the change in coordinate system. Eqs. (12) and (14) are generalizations of earlier results [10,11].

Eq. (8) is substituted into eq. (14) to yield

$$\sum_{K_1=1}^{N} L_{\alpha_1K_1}I_{K_2\alpha_2\ldots K_M\alpha_M} = \sum_{K_1=1}^{N} l_{\alpha_1K_1}I_{K_2\alpha_2\ldots K_M\alpha_M} + Q_{\beta_1\sigma_1K_2\alpha_2K_3\alpha_3\ldots K_n\alpha_n}$$

$$\alpha_1, \alpha_2, \ldots, \alpha_M = x, y, z; \quad K_2, K_3, \ldots, K_M = 1, N; \quad \alpha_1\beta_1\sigma_1 = xyz, yzx, zxy, \tag{15a}$$

where

$$Q_{\beta_1\sigma_1K_2\alpha_2K_3\alpha_3\dots K_n\alpha_n} = \delta_{\sigma_1\alpha_2} I_{K_2\beta_1,K_3\alpha_3\dots K_n\alpha_n} - \delta_{\beta_1\alpha_2} I_{K_2\delta_1K_3\alpha_3\dots K_n\alpha_n}$$
$$+ \delta_{\sigma_1\alpha_3} I_{K_2\alpha_2K_3\beta_1\dots K_n\alpha_n} - \delta_{\beta_1\alpha_3} I_{K_2\alpha_2K_3\sigma_1\dots K_n\alpha_n} + \dots$$
$$+ \delta_{\sigma_1\alpha_n} I_{K_2\alpha_2K_3\alpha_3\dots K_n\beta_1} - \delta_{\beta_1\alpha_n} I_{K_2\alpha_2K_3\alpha_3\dots K_n\sigma_1}. \tag{15b}$$

The operator $L_{\alpha_1K_1}$ has been pulled outside of the integral $I_{K_2\alpha_2\dots K_M\alpha_M}$ since the $\boldsymbol{P}_{K_1}$, which $L_{\alpha_1K_1}$ involves, are not integration variables. In addition, the notation $l_{\alpha_1K_1} I_{K_2\alpha_2\dots K_M\alpha_M}$ has been introduced to denote that the $l_{\alpha_1K_1}$ operator is applied to the vector $\boldsymbol{r}$ in the gaussian G_{K_1} appearing in $I_{K_2\alpha_2\dots K_M\alpha_M}$. That is, $l_{\alpha_1K_1} I_{K_2\alpha_2\dots K_M\alpha_M}$ represents $I_{K_2\alpha_2\dots K_M\alpha_M}(l_{\alpha_1K_1}G_{K_1})$.

Substituting the definitions of $L_{\alpha_1K_1}$ and $l_{\alpha_1K_1}$ into eq. (15) we obtain

$$\sum_{K_1=1}^{N} \left(P_{K_1\beta_1} I_{K_1\sigma_1\dots K_M\alpha_M} - P_{K_1\sigma_1} I_{K_1\beta_1\dots K_M\alpha_M} \right) = I_{\beta_1\sigma_1K_2\alpha_2\dots K_M\alpha_M},$$
$$\alpha_1\beta_1\sigma_1 = xyz,\ yzx,\ zxy; \quad K_2, K_3, \dots, K_M = 1, N; \quad \alpha_2, \alpha_3, \dots, \alpha_M = x, y, z;$$
$$(K_2\alpha_2) \geqslant (K_3\alpha_3) \geqslant \dots \geqslant (K_M\alpha_M), \tag{16a}$$

where

$$I_{\beta_1\sigma_1K_2\alpha_2\dots K_M\alpha_M} = \sum_{K_1=1}^{N} l_{\alpha_1K_1} I_{K_2\alpha_2\dots K_M\alpha_M} + Q_{\beta_1\sigma_1K_2\alpha_2\dots K_n\alpha_n}. \tag{16b}$$

The $l_{\alpha_1K_1}$ operator transforms a gaussian into two gaussians in the same shell as the original gaussian. Using l_{zK_1} as an example, we see that

$$l_{zK_1}G_{K_1}(n_x, n_y, n_z) = \left(x_{K_1}\partial/\partial y_{K_1} - y_{K_1}\partial/\partial x_{K_1}\right)G_{K_1}(n_x, n_y, n_z)$$
$$= n_y\left[(2n_x+1)/(2n_y-1)\right]^{1/2} G_{K_1}(n_x+1, n_y-1, n_z)$$
$$- n_x\left[(2n_y+1)/(2n_x-1)\right]^{1/2} G_{K_1}(n_x-1, n_y+1, n_z). \tag{17}$$

Thus we see that the right-hand side of eq. (16) is a linear combination of $(M-1)$th derivatives of integrals. Specific cases ($M = 1, 2, 3$) of eqs. (16) appeared in earlier papers [10,11].

3. Implementation

In this section we look more closely at the relations in eqs. (12) and (16). These relations are *not* independent. We wish to choose an independent subset of these relations. We also wish for this subset to be complete in the sense that all translational and rotational invariance conditions can be generated from it.

As a first step we note that for an integral with N' degree of freedom, there are N' first integral derivatives, $N'(N'+1)/2$ unique second integral derivatives, and $N'(N'+1)(N'+2)/3!$ unique third integral derivatives. For Mth order there are $\binom{N'+M-1}{M}$ integral derivatives where we have used the notation for the binominal coefficient. Thus for an integral over N non-collinear centers we will show that there exists, for a given order M, $\binom{3N+M-1}{M}$ total integral derivatives and $\binom{3N-6+M-1}{M}$ independent integral derivatives which must be explicitly calculated. Thus we have $[\binom{3N+M-1}{M} - \binom{3N-6+M-1}{M}]$ independent relations in eqs. (12) and (16). For the collinear case we will show that there are $[\binom{3N+M-1}{M} - \binom{3N-5+M-1}{M}]$ independent relations.

Our goal is to demonstrate that there exists a set of $3N-6$ ($3N-5$ for the collinear case) coordinates such that all integral derivatives with respect to these coordinates must be explicitly calculated. We denote these coordinates as independent coordinates. Knowing this set of $\binom{3N-6+M-1}{M}$ $[\binom{3N-5+M-1}{M}$ for the collinear case] integral derivatives, all remaining integral derivatives can be calculated using the translational and rotational invariance conditions which are the subjects of this paper. The remaining six (five for the collinear case) coordinates we denote as dependent coordinates.

In the following we examine the non-collinear case. We present our working equations in a very detailed form in order to make them easy to implement. We assign the atomic centers some arbitrary numbers from 1 to N requiring only that centers 1, 2 and 3 be non-collinear.

Using eq. (12), it is easy to show that $1x$ can be chosen as a dependent coordinate. That is, all integral derivatives with respect to $1x$ can be calculated from the invariance conditions

$$I_{1xK_1\alpha_2\dots K_M\alpha_M} = -\sum_{K_1=2}^{N} I_{K_1xK_2\alpha_2K_3\alpha_3\dots K_M\alpha_M},$$

$$(K_2\alpha_2) \geqslant (K_3\alpha_3) \geqslant \dots \geqslant (K_M\alpha_M); \quad K_2\alpha_2,\ K_3\alpha_3,\dots,K_M\alpha_M \neq 1x, \tag{18a}$$

$$I_{1x1xK_3\alpha_3\dots K_M\alpha_M} = -\sum_{K_2=2}^{N} I_{1xK_2xK_3\alpha_3\dots K_M\alpha_M},$$

$$(K_3\alpha_3) \geqslant (K_4\alpha_4) \geqslant \dots \geqslant (K_M\alpha_M); \quad K_3\alpha_3,\dots,K_M\alpha_M \neq 1x, \tag{18b}$$

$$\vdots$$

$$I_{1x1x\dots 1x} = -\sum_{K_M=2}^{N} I_{1x1x\dots K_Mx}. \tag{18c}$$

There are $\binom{3N+M-2}{M-1}$ integrals that can be evaluated on the left-hand side of eqs. (18). This is easy to see since the first index of every integral is $1x$. Therefore we are permuting $M-1$ indices through $3N$ degrees of freedom.

Likewise $1y$ and $1z$ can be chosen as dependent coordinates; as a result of which we can write equations analogous to eqs. (18):

$$I_{1yK_2\alpha_2\dots K_M\alpha_M} = -\sum_{K_1=2}^{N} I_{K_1yK_2\alpha_2\dots K_M\alpha_M},$$

$$(K_2\alpha_2) \geqslant (K_3\alpha_3) \geqslant \dots \geqslant (K_M\alpha_M); \quad K_2\alpha_2,\dots,K_M\alpha_M \neq 1x,\ 1y, \tag{19a}$$

$$I_{1y1yK_3\alpha_3\dots K_M\alpha_M} = -\sum_{K_2=2}^{N} I_{1yK_2yK_3\alpha_3\dots K_M\alpha_M},$$

$$(K_3\alpha_3) \geqslant (K_4\alpha_4) \geqslant \dots \geqslant (K_M\alpha_M); \quad K_3\alpha_3,\dots,K_M\alpha_M \neq 1x,\ 1y, \tag{19b}$$

$$\vdots$$

$$I_{1y1y\dots 1y} = -\sum_{K_M=2}^{N} I_{1y1y\dots K_My}, \tag{19c}$$

$$I_{1zK_2\alpha_2K_3\alpha_3\dots K_M\alpha_M} = -\sum_{K_1=2}^{N} I_{K_1zK_2\alpha_2\dots K_M\alpha_M},$$

$$(K_2\alpha_2) \geqslant (K_3\alpha_3) \geqslant \dots \geqslant (K_M\alpha_M); \quad K_2\alpha_2,\dots,K_M\alpha_M \neq 1x,\ 1y,\ 1z, \tag{20a}$$

$$I_{1z1zK_3\alpha_3\ldots K_M\alpha_M} = -\sum_{K_2=2}^{N} I_{1zK_2zK_3\alpha_3\ldots K_M\alpha_M},$$

$$(K_3\alpha_3) \geqslant \ldots \geqslant (K_M\alpha_M); \quad K_3\alpha_3, \ldots, K_M\alpha_M \neq 1x, 1y, 1z, \tag{20b}$$

$$\vdots$$

$$I_{1z1z\ldots1z} = -\sum_{K_M=2}^{N} I_{1z1z\ldots K_Mz}. \tag{20c}$$

In eqs. (19) we are permuting $M-1$ indices through $3N-1$ degrees of freedom therefore there are only $\binom{3N-1+M-2}{M-1}$ conditions. Likewise, eqs. (20) with $3N-2$ degrees of freedom have $\binom{3N-2+M-2}{M-1}$ conditions. Using the identity

$$\binom{W-1}{M-1} = \binom{W}{M} - \binom{W-1}{M}, \tag{21}$$

for an arbitrary W, it is straighforward to show that the total number of conditions in eqs. (18)–(20) is $[\binom{3N+M-1}{M} - \binom{3N-3+M-1}{M}]$ as expected. Eqs. (18)–(20) are generalizations of earlier results [10,11].

The next step is to substitute eqs. (18)–(20) into the rotational invariance relations of eq. (16). This allows all reference to atom 1 to be removed from the rotational conditions. The result is

$$\sum_{K_1=2}^{N} \left(\tilde{P}_{K_1\beta_1} I_{K_1\gamma_1K_2\alpha_2\ldots K_M\alpha_M} - \tilde{P}_{K_1\gamma_1} I_{K_1\beta_1K_2\alpha_2\ldots K_M\alpha_M} \right) = I_{\beta_1\gamma_1K_2\alpha_2\ldots K_M\alpha_M},$$

$$\beta_1\gamma_1 = xy,\ yz,\ zx; \quad K_2, K_3, \ldots, K_M = 2, N; \quad \alpha_2, \alpha_3, \ldots, \alpha_M = x, y, z;$$

$$(K_2\alpha_2) \geqslant (K_3\alpha_3) \geqslant \ldots \geqslant (K_M\alpha_M), \tag{22}$$

where $\tilde{P}_{K_1\beta_1} = P_{K_1\beta_1} - \mathrm{P}_{1\beta_1}$ gives the position of atom K_1 relative to atom 1. Eq. (22) for the specific cases $M = 1, 2, 3$ appeared in earlier work [10,11].

Since atom 1 and atom 2 do not have the same center by assumption, $\tilde{P}_{2x}$, $\tilde{P}_{2y}$, or $\tilde{P}_{2z}$ has to be non-zero. For ease of notation the rest of this paper will be concerned with the special case of $\tilde{P}_{2z} \neq 0$. The other cases can be recovered by cyclic permutation of all x, y, and z.

We now show that $2x$ can be chosen as a dependent coordinate. Solving eq. (22) for integral derivatives involving $2x$, we obtain

$$I_{2xK_2\alpha_2\ldots K_M\alpha_M} = \frac{1}{\tilde{P}_{2z}} \left[I_{zxK_2\alpha_2\ldots K_M\alpha_M} + \tilde{P}_{2x} I_{2zK_2\alpha_2\ldots K_M\alpha_M} - \sum_{K_1=3}^{N} \left(\tilde{P}_{K_1z} I_{K_1xK_2\alpha_2\ldots K_M\alpha_M} - \tilde{P}_{K_1x} I_{K_1zK_2\alpha_2\ldots K_M\alpha_M} \right) \right],$$

$$(K_2\alpha_2) \geqslant (K_3\alpha_3) \geqslant \ldots (K_M\alpha_M); \quad K_2\alpha_2, K_3\alpha_3, \ldots, K_M\alpha_M \neq 1x, 1y, 1z, 2x, \tag{23a}$$

$$I_{2x2xK_3\alpha_3\ldots K_M\alpha_M} = \frac{1}{\tilde{P}_{2z}} \left[I_{zx2xK_3\alpha_3\ldots K_M\alpha_M} + \tilde{P}_{2x} I_{2x2zK_3\alpha_3\ldots K_M\alpha_M} - \sum_{K_2=3}^{N} \left(\tilde{P}_{K_2z} I_{2xK_2xK_3\alpha_3\ldots K_M\alpha_M} - \tilde{P}_{K_2x} I_{2xK_2z\ldots K_M\alpha_M} \right) \right],$$

$$(K_3\alpha_3) \geqslant \ldots \geqslant (K_M\alpha_M); \quad K_3\alpha_3, \ldots, K_M\alpha_M \neq 1x, 1y, 1z, 2x, \tag{23b}$$

$$\vdots$$

$$I_{2x2x2x\ldots2x} = \frac{1}{\tilde{P}_{2z}} \left[I_{zx2x2x\ldots2x} + \tilde{P}_{2x} I_{2x2x\ldots2z} - \sum_{K_M=3}^{N} \left(\tilde{P}_{K_Mz} I_{2x2x\ldots K_Mx} - \tilde{P}_{K_Mx} I_{2x2x\ldots K_Mz} \right) \right]. \tag{23c}$$

In eqs. (23) we are permuting $M-1$ indices through $3N-3$ degrees of freedom. Therefore we have $\binom{3N-3+M-2}{M-1}$ relations. Similarly for the $2y$ coordinate we have

$$I_{2yK_2\alpha_2\ldots K_M\alpha_M} = \frac{1}{\tilde{P}_{2z}}\Bigg[-I_{yzK_2\alpha_2\ldots K_M\alpha_M} + \tilde{P}_{2y} I_{2zK_2\alpha_2\ldots K_M\alpha_M} - \sum_{K_1=3}^{N}\left(\tilde{P}_{K_1z} I_{K_1yK_2\alpha_2\ldots K_M\alpha_M} - \tilde{P}_{K_1y} I_{K_1zK_2\alpha_2\ldots K_M\alpha_M}\right)\Bigg],$$

$$(K_2\alpha_2) \geqslant (K_3\alpha_3) \geqslant \ldots \geqslant (K_M\alpha_M); \quad K_2\alpha_2,\ K_3\alpha_3,\ldots,K_M\alpha_M \neq 1x,\ 1y,\ 1z,\ 2x,\ 2y, \tag{24a}$$

$$I_{2y2yK_3\alpha_3\ldots K_M\alpha_M} = \frac{1}{\tilde{P}_{2z}}\Bigg[-I_{yz2yK_3\alpha_3\ldots K_M\alpha_M} + \tilde{P}_{2y} I_{2y2zK_3\alpha_3\ldots K_M\alpha_M} - \sum_{K_2=3}^{N}\left(\tilde{P}_{K_2z} I_{2yK_2yK_3\alpha_3\ldots K_M\alpha_M} - \tilde{P}_{K_2y} I_{2yK_2zK_3\alpha_3\ldots K_M\alpha_M}\right)\Bigg],$$

$$(K_3\alpha_3) \geqslant (K_4\alpha_4) \geqslant \ldots \geqslant (K_M\alpha_M); \quad K_3\alpha_3,\ldots,K_M\alpha_M \neq 1x,\ 1y,\ 1z,\ 2x,\ 2y, \tag{24b}$$

$$\vdots$$

$$I_{2y2y2y\ldots2y} = \frac{1}{\tilde{P}_{2z}}\Bigg[-I_{yz2y2y2y\ldots2y} + \tilde{P}_{2y} I_{2y2y\ldots2z} - \sum_{K_M=3}^{N}\left(\tilde{P}_{K_Mz} I_{2y2y2y\ldots K_My} - \tilde{P}_{K_My} I_{2y2y\ldots K_Mz}\right)\Bigg]. \tag{24c}$$

with $\binom{3N-4+M-2}{M-1}$ relations. In earlier work [10,11] we showed that, in the first, second, and third derivative cases, if $1x$, $1y$, $1z$, $2x$, and $2y$ are chosen as dependent coordinates then $2z$ cannot be chosen as a dependent coordinate. We therefore look for another dependent coordinate on atom 3.

As a first step we take linear combinations of eq. (22) to form

$$\sum_{K_1=3}^{N} C_{K_1xy} I_{K_1zK_2\alpha_2\ldots K_M\alpha_M} + \sum_{K_1=3}^{N} C_{K_1yz} I_{K_1xK_2\alpha_2\ldots K_M\alpha_M} + \sum_{K_1=3}^{N} C_{K_1zx} I_{K_1yK_2\alpha_2\ldots K_M\alpha_M}$$
$$= \tilde{P}_{2z} I_{xyK_2\alpha_2\ldots K_M\alpha_M} + \tilde{P}_{2y} I_{zxK_2\alpha_2\ldots K_M\alpha_M} + \tilde{P}_{2x} I_{yzK_2\alpha_2\ldots K_M\alpha_M}, \tag{25}$$

where we have introduced the notation

$$C_{K_1\beta\gamma} = \tilde{P}_{2\beta}\tilde{P}_{K_1\gamma} - \tilde{P}_{2\gamma}\tilde{P}_{K_1\beta}, \quad \beta\gamma = xy,\ yz,\ zx. \tag{26}$$

Note that eq. (25) contains no reference to atom 1 or atom 2 in the summation.

If $C_{3yz} = C_{3zx} = C_{3xy} = 0$, it is easy to show that centers 1, 2, and 3 are collinear contrary to assumption. If $C_{3yz} \neq 0$, we can solve eq. (25) for integral derivatives involving the coordinate $3x$:

$$I_{3xK_2\alpha_2\ldots K_M\alpha_M} = \frac{1}{C_{3yz}}\Bigg(-\sum_{K_1=4}^{N} C_{K_1yz} I_{K_1xK_2\alpha_2\ldots K_M\alpha_M} - \sum_{K_1=3}^{N} C_{K_1xy} I_{K_1zK_2\alpha_2\ldots K_M\alpha_M} - \sum_{K_1=3}^{N} C_{K_1zx} I_{K_1yK_2\alpha_2\ldots K_M\alpha_M}$$
$$+ \tilde{P}_{2z} I_{xyK_2\alpha_2\ldots K_M\alpha_M} + \tilde{P}_{2y} I_{zxK_2\alpha_2\ldots K_M\alpha_M} + \tilde{P}_{2x} I_{yzK_2\alpha_2\ldots K_M\alpha_M}\Bigg),$$

$$(K_2\alpha_2) \geqslant (K_3\alpha_3) \geqslant \ldots \geqslant (K_M\alpha_M); \quad K_2\alpha_2,\ K_3\alpha_3,\ldots,\ K_M\alpha_M \neq 1x,\ 1y,\ 1z,\ 2x,\ 2y,\ 3x, \tag{27a}$$

$$
\begin{aligned}
I_{3x3x\dots K_M} = \frac{1}{C_{3yz}} \Bigg(& -\sum_{K_2=4}^{N} C_{K_2yz} I_{3xK_2xK_3\alpha_3\dots K_M\alpha_M} - \sum_{K_2=3}^{N} C_{K_2xy} I_{3xK_2zK_3\alpha_3\dots K_M\alpha_M} \\
& - \sum_{K_2=3}^{N} C_{K_1zx} I_{3xK_2yK_3\alpha_3\dots K_M\alpha_M} + \tilde{P}_{2z} I_{xy3xK_3\alpha_3\dots K_M\alpha_M} \\
& + \tilde{P}_{2y} I_{zx3xK_3\alpha_3\dots K_M\alpha_M} + \tilde{P}_{2x} I_{yz3xK_3\alpha_3\dots K_M\alpha_M} \Bigg),
\end{aligned}
$$

$$
(K_3\alpha_3) \geqslant (K_4\alpha_4) \geqslant \dots \geqslant (K_M\alpha_M); \quad K_3\alpha_3, \dots, K_M\alpha_M \neq 1x, 1y, 1z, 2x, 2y, 3x, \tag{27b}
$$

$\vdots$

$$
\begin{aligned}
I_{3x3x\dots 3x} = \frac{1}{C_{3yz}} \Bigg(& -\sum_{K_M=4}^{N} C_{K_Myz} I_{3x3x\dots K_Mx} - \sum_{K_M=3}^{N} C_{K_Mxy} I_{3x3x\dots K_Mz} \\
& - \sum_{K_M=3}^{N} C_{K_Mzx} I_{3x3x\dots K_My} + \tilde{P}_{2z} I_{xy3x3x\dots 3x} + \tilde{P}_{2y} I_{zx3x3x\dots 3x} + \tilde{P}_{2x} I_{yz3x3x\dots 3x} \Bigg).
\end{aligned} \tag{27c}
$$

Likewise if $C_{3zx} \neq 0$ we can solve for integral derivatives involving $3y$, and if $C_{3xy} \neq 0$ we can solve for integral derivatives involving $3z$. Eqs. (27) contain $\binom{3N-5+M-2}{M-1}$ relations.

Thus, assuming $\tilde{P}_{2z} \neq 0$ and $C_{3yz} \neq 0$, the procedure for using translational and rotational invariance for the non-collinear case is to explicitly evaluate all integral derivatives involving the coordinates P_{2z}, P_{3y}, P_{3z}, $P_{K\alpha}$ ($K = 4, N$; $\alpha = x, y, z$) and then use eqs. (18)–(20), (23), (24), and (27) to solve for the remaining integral derivatives. Using eq. (21) it is straightforward to show that there are $[\binom{3N+M-1}{M} - \binom{3N-6+M-1}{M}]$ relations in eqs. (18)–(20), (23), (24) and (27) as expected. For the collinear case eqs. (27) involve division by zero and therefore are not valid. Thus for the collinear case one uses the $[\binom{3N+M-1}{M} - \binom{3N-5+M-1}{M}]$ Mth-order relations given in eqs. (18)–(20) and (23), (24). The results of eqs. (23), (24) and (27) are an improvement over our earlier work [10,11] where the results of rotational invariance were left as a system of linear equations to be solved. We, in fact, have a complete implementation of computer code for rotational and translational invariance of first integral derivatives.

Use of the rotational conditions of eqs. (23), (24) and (27) for Mth-order integral derivatives requires knowing $(M-1)$th-order integral derivatives. This, in fact, poses no difficulty. Using third energy derivatives as an example [12,13], calculation of the third derivatives of the energy requires knowing first, second, and third integral derivatives. Thus one can calculate the integral and the first, second, and third integrals derivatives with respect to the *independent* coordinates. Knowing the values of the integral and the independent first integral derivatives one can calculate, using translational and rotational invariance, the dependent first integral derivatives. One can then calculate the dependent second integral derivatives followed by the dependent third integral derivatives.

4. Discussion

In this section we will examine the independence and completeness of the relations in eqs. (18)–(20), (23), (24) and (27). For example, it should be noted that there are fewer conditions in eqs. (23), (24) and (27) than in eq. (22). The question arises as to whether the excess relations in eq. (22) yield additional information.

If we denote a relation in eq. (22) by $E_{\beta_1\gamma_1K_2\alpha_2K_3\alpha_3\dots K_M\alpha_M}$ for the given values of β_1, γ_1, K_2, α_2, etc., we note that the $2\binom{3N-3+M-3}{M-2} + \binom{3N-4+M-3}{M-2}$ relations from eq. (22) that were *not* used in constructing eqs.

(22), (24), and (27) are of the form $E_{yz2xK_3\alpha_3\ldots K_M\alpha_M}$, $E_{xy2xK_3\alpha_3\ldots K_M\alpha_M}$, and $E_{xy2yK_3\alpha_3\ldots K_M\alpha_M}$. The relation $E_{yz2xK_3\alpha_3\ldots K_M\alpha_M}$ was not used since eqs. (24) were restricted never to contain an integral derivative with respect to $2x$. Likewise, $E_{xy2xK_3\alpha_3\ldots K_M\alpha_M}$ and $E_{xy2yK_3\alpha_3\ldots K_M\alpha_M}$ were not used since eqs. (27) were restricted never to contain an integral derivative with respect to $2x$ or $2y$. A straightforward calculation shows that

$$2\binom{3N-3+M-3}{M-2}+\binom{3N-4+M-3}{M-2}+\binom{3N-3+M-1}{M}-\binom{3N-6+M-1}{M}$$
$$=3\binom{3N-3+M-2}{M-1}. \tag{28}$$

Thus, there are no other relations in eq. (22) that were not used in constructing eqs. (23), (24) and (27).

There exist certain relations among the relations (RARs) of eq. (22):

$$\sum_{K_2=2}^{N}\Big[\tilde{P}_{K_2\sigma}E_{\beta\gamma K_2\gamma K_3\alpha_3\ldots K_M\alpha_M}+\tilde{P}_{K_2\beta}E_{\gamma\sigma K_2\gamma K_3\alpha_3\ldots K_M\alpha_M}$$
$$-\tilde{P}_{K_2\gamma}\big(E_{\beta\gamma K_2\sigma K_3\alpha_3\ldots K_M\alpha_M}+E_{\gamma\sigma K_2\beta K_3\alpha_3\ldots K_M\alpha_M}\big)\Big]=0,$$
$$\beta\gamma\sigma=xyz,\ yzx,\ zxy;\quad K_3,\ K_4,\ldots,K_M=2,\ N;\quad \alpha_3,\ \alpha_4,\ldots,\alpha_M=x,\ y,\ z;$$
$$(K_3\alpha_3)\geqslant(K_4\alpha_4)\geqslant\ldots\geqslant(K_M\alpha_M). \tag{29}$$

These RARs are generalizations of RARs that were discovered in earlier papers [10,11] for the second and third derivative cases. Eq. (29) can be verified by substitution of the left- or right-hand side of eq. (22) for the given values of β, γ, σ, K_2, K_3, α_3, etc.

If we set $\beta\gamma\sigma=yzx$ in eq. (29) we can solve for all of the relations of the form $E_{yz2xK_3\alpha_3\ldots K_M\alpha_M}$. If we set $\beta\gamma\sigma=zxy$ we can solve for $E_{xy2xK_3\alpha_\beta\ldots K_M\alpha_M}$. If we set $\beta\gamma\sigma=xyz$ we can solve for $E_{xy2yK_3\alpha_3\ldots K_M\alpha_M}$. This last step required the knowledge of the $E_{yz2xK_3\alpha_3\ldots K_M\alpha_M}$. Also solving for the relations in each of the above steps required only division by $\tilde{P}_{2z}$ which we have already assumed to be non-zero. Thus the excess relations in eq. (22) give no additional information.

Likewise, it would appear at first glance that there are more relations in eq. (12) than there are in eqs. (18)–(20). However, the conditions in eq. (12) are not unique. A given condition may be repeated several times. It can be shown, in fact, that the number of unique relations in eq. (12) is equal to the number of relations in eqs. (18)–(20).

We now wish to show the independence of our working relations in eqs. (18)–(20), (23), (24) and (27). We first note the relation in eq. (18c) is independent of all other working relations since it is the only relation that contains $I_{1x1x\ldots1x}$. We can then work in reverse order through eqs. (18) finding each relation to be independent of all the others since it contains an integral derivative on the right-hand side that is not in the relations above it in eqs. (18) or in eqs. (19), (20) and (23), (24) or (27). What we have achieved is a kind of symbolic echelon form. Likewise, we can work in reverse order through eqs. (19) followed by eqs. (20), (23), (24) and (27). Thus we can conclude that our working relations are independent.

5. Conclusion

In this paper we have given useful working relations which allow one to evaluate certain integral derivatives in terms of others. The working relations for the non-collinear case are embodied in eqs. (18)–(20), (23), (24) and (27).

For ease of notation geometrical constraints were introduced into the derivation of eqs. (23), (24) and (27), but, in fact, these constraints can be satisfied for arbitrary nuclear geometry by appropriate renaming of coordinate axes. For an N-center integral there are $[\binom{3N+M-1}{M} - \binom{3N-6+M-1}{M}]$ Mth-order relations in eqs. (18)–(20), (23), (24) and (27).

For the collinear case eqs. (27) involve division by zero and therefore are not valid. Thus for the collinear case one uses the $[\binom{3N+M-1}{M} - \binom{3N-5+M-1}{M}]$ Mth-order relations given in eqs. (18)–(20) and (23), (24).

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