Translational and rotational symmetries in integral derivatives

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(Received 2 November 1984; accepted 5 February 1985)

Based upon 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 is presented. Due to the unitary form of the operators corresponding to finite translations and rotations, this analysis is generally applicable to all orders of integral derivatives. It is shown that the number of dependent integral derivatives is equal to the number of such independent relations. These dependent integral derivatives can thus be straightforwardly determined in terms of the remaining derivatives which must be explicitly calculated. For example, out of a total of 21, 45, and 78 second-derivative integrals for the two-, three-, and four-center cases, respectively, only 1, 6, and 21 such integral derivatives need be explicitly calculated. The set of such independent and dependent integral derivatives can be chosen in a manner which imposes no restrictions on the allowable geometries of the nuclear positions. The special case of colinear nuclear centers is also separately analyzed.

I. 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. The applications of such derivative methods to finding stationary points on energy surfaces and to following the course of chemical reactions have provided very useful new chemical information.

The evaluation of derivatives of the molecular electronic energy involves calculation of derivatives of one- and two-electron integrals with respect to the nuclear coordinates of the basis functions occurring in the integrals. For example, the first derivative (gradient) of the multiconfigurational self-consistent field (MCSCF) energy can be written as follows[1]:

$$E^{(1)} = \sum_{\mu\nu}\sum_{rs} C_{\mu r}\, C_{\nu s}\, \{\langle d_{rs}\rangle \nabla h_{\mu\nu} - \varepsilon_{rs}\nabla S_{\mu\nu}\} + \frac{1}{2}\sum_{\mu\nu\lambda\sigma}\sum_{rspq} C_{\mu r} C_{\nu s} C_{\lambda p} C_{\sigma q}\langle d_{rspq}\rangle \nabla(\mu\nu|\lambda\sigma). \quad (1)$$

Here $C_{\mu r}$ is the coefficient relating the rth molecular orbital to the μth atomic basis function. $\nabla h_{\mu\nu}$, $\nabla S_{\mu\nu}$, and $\nabla(\mu\nu|\lambda\sigma)$ are derivatives of the atomic-basis one- and two-electron integrals with respect to nuclear coordinates. The $\langle d_{rs}\rangle$ and $\langle d_{rspq}\rangle$ are symmetrized one- and two-particle density matrix elements for the MCSCF wave function.

Since a large number of integral derivatives need to be calculated in order to implement any such energy-derivative expressions, efficient computation of these derivatives is very important. To appreciate the scope of the problem, consider the first and second derivatives of four-center two-electron integrals arising in a calculation involving n primitive (Gaussian) atomic basis functions. Since the only nonzero derivatives result when such an integral is differentiated with respect to the x, y, or z coordinates of the four nuclear centers occurring in the integral, there are only $12\times n^4$ first derivative integrals. Considering symmetries of the form $\partial^2 I/\partial P_{K\alpha}\,\partial P_{L\beta} = \partial^2 I/\partial P_{L\beta}\,\partial P_{K\alpha}$, where $P_{K\alpha}$ is the αth (x, y, or z) coordinate of the K th atomic center, one can easily show that there are only $78\times n^4$ second derivative integrals. In the N-center integral case ($N = 2,3,4$) one has $3N$ first derivatives and $3N(3N+1)/2$ second derivatives of each of the n^4 integrals.

The purpose of this paper is to show that, due to the fact that integrals and integral derivatives remain invariant under translation and rotation of *all* of the centers appearing in the integral, there exist certain relations among the integral derivatives and that these relations can be exploited for savings in computational effort. The essential fact is that not all of the integral derivatives are independent. For example, among the total of 21 second derivatives of any two-center integral, it can be shown that *only one* is independent. The other 20 integrals can be found from the symmetry relations. Thus the practical importance of this work is contained in the relations which we provide for evaluating many integral derivatives in terms of a few independent ones.

Translational invariance properties relating the first-order integral derivatives using infinitesimal translation operators have been dealt with by Komornicki *et al.*[2] and Dupuis *et al.*[3] Translational invariance of second- and higher-order derivatives has also been examined.[4–6] Kahn,[7] using infinitesimal rotations of the nuclear coordinates, has obtained relationships among the first derivative integrals. Vincent *et al.*[8,9] obtained relationships among integral derivatives by differentiating Kahn's results which are based on infinitesimal operators. Page *et al.*[10] have derived relationships by defining arbitrary external coordinates along which the gradient is zero. The present work provides a complete analysis of the invariance properties for first and second integral derivatives. We provide a method for treating the redundancy of invariance conditions. Such a treatment is absent from earlier work. Furthermore the method developed here is generally applicable for the construction of invariance conditions and redundancy analysis of integral derivatives of any order. Rotational invariance conditions are geometry dependent in the sense that poorly chosen conditions impose many geometrical constraints on the molecule.

 0021-9606/85/104566-11$02.10

We present a systematic method to choose the conditions in a manner which imposes no restriction on the allowable geometries of the nuclear positions.

In Sec. II we derive representations of the rotation and translation operators appropriate for generating expressions for the derivatives of the integrals. These operators are then used to derive the essential invariance relations involving the first and second integral derivatives. In Sec. III we provide systematic methods for finding the independent integral derivatives and for calculating explicitly the remaining (dependent) integral derivatives using symmetry relations.

II. THEORETICAL DEVELOPMENT

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

$$I = I\{G_1(\mathbf{P}_1,\mathbf{r}_1), G_2(\mathbf{P}_2,\mathbf{r}_2),\ldots, G_N(\mathbf{P}_N,\mathbf{r}_N)\}, \tag{2}$$

where the Cartesian Gaussian function parametrized in terms of the center $\mathbf{P}_K$ is given as

$$G_K(\mathbf{P}_K,\mathbf{r}_K) = A(\xi,n_x,n_y,n_z)(X-P_{Kx})^{n_x}(Y-P_{Ky})^{n_y} \times (Z-P_{Kz})^{n_z}\exp(-\xi r_K^2). \tag{3a}$$

Each such G_K is an explicit function of the electron-center relative position vector labeled $\mathbf{r}_K$. This vector gives the location of the electron, whose absolute lab-fixed position is denoted $\mathbf{R}$, relative to the center $\mathbf{P}_K$: $\mathbf{r}_K = \mathbf{R} - \mathbf{P}_K$. Here $\mathbf{R}$ has Cartesian components (X,Y,Z) and the normalization constant A is

$$A(\xi,n_x n_y,n_z) = \left(\frac{2\xi}{\pi}\right)^{3/4}(4\xi)^{1/2(n_x+n_y+n_z)}[(2n_x-1)!!]^{-1/2} \times [(2n_y-1)!!]^{-1/2}[(2n_z-1)!!]^{-1/2}. \tag{3b}$$

Functions belonging to the same shell have identical exponent ξ values and equivalent $(n_x+n_y+n_z)$ sums.

A one-electron integral I involves integration (over $d\,\mathbf{R}$) of products of at most two Gaussian functions. A two-electron integral involves integrations (over $d\,\mathbf{R}$ and $d\,\mathbf{R}'$) of products of up to four Gaussians. The operator H appearing in I would commonly either be independent of the $\{\mathbf{P}_K\}$ or dependent in a way which is symmetric under any rotation or translation (e.g., as in the Coulomb interaction $-\Sigma_K Z_K|\mathbf{R}-\mathbf{P}_K|^{-1}$).

The action of the translation $\hat{T}$ or rotation $\hat{R}$ operators on a Gaussian function is to translate or rotate *every* point $\mathbf{R}$ in space about an axis passing through the lab fixed origin. That is, we consider operations (translations and rotations) which displace the Gaussians as if they were rigid bodies whose shapes are described by the charge density of the Gaussian functions. Then any quantum chemical integral I should remain unchanged when *all* of its Gaussians are displaced in the same manner. We denote these invariances for translations and rotations, respectively, as

$$I\{\hat{T}(G_1,G_2,\ldots)\} = I\{G_1,G_2,\ldots\} \tag{4}$$

and

$$I\{\hat{R}(G_1,G_2,\ldots)\} = I\{G_1,G_2,\ldots\}. \tag{5}$$

A. Representation of operators

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

$$\hat{T} = \exp\{-\mathbf{t}\cdot\nabla_R\}, \tag{6}$$

where $\nabla_R = (\partial/\partial X, \partial/\partial Y, \partial/\partial Z)$ defines the gradient operator at all points $\mathbf{R}$ in space. For two-electron integrals, which depend on two such electronic coordinates $\mathbf{R}$ and $\mathbf{R}'$, the ∇_R operator will be implicitly assumed to operate on both variables (i.e., it is $\nabla_R + \nabla_{R'}$). Since the Gaussians in Eq. (4) are written in terms of their centers $\mathbf{P}_K$ and internal coordinate $\mathbf{r}_k$, and since we are looking for relationships among derivatives of integrals relative to nuclear coordinates, we rewrite the operator ∇_R in terms of the coordinates $\mathbf{P}_K$ and $\mathbf{r}_K$ using the relationship

$$\mathbf{R} = \mathbf{P}_K + \mathbf{r}_K, \quad K = 1,\ldots N, \tag{7}$$

which yields

$$\frac{\partial}{\partial X}G_K(\mathbf{P}_K,\mathbf{r}_K) = -\frac{\partial}{\partial P_{Kx}}G(\mathbf{P}_K,\mathbf{r}_K) = \frac{\partial}{\partial x_K}G_K(\mathbf{P}_K,\mathbf{r}_K). \tag{8a}$$

Using this identity it follows that

$$I\{\nabla_R G_K\} = \left(-\sum_{K=1}^{N}\nabla_{P_K}\right)I\{G_K\}. \tag{8b}$$

Thus the translation operator $\hat{T}$ can be cast in a representation such that

$$I\{\hat{T}G_K\} = \exp\left\{\mathbf{t}\cdot\sum_{K=1}^{N}\nabla_{P_K}\right\}I\{G_K\}. \tag{9}$$

The derivative with respect to $\mathbf{P}_K$ has been pulled outside the integral since it is not an integration variable. Thus the action of the translation operator $\hat{T}$ on any one- or two-electron integral I can be written as involving translation of *each* of the Gaussian centers with their orientations ($\mathbf{r}_1$ coordinates) *unchanged*.

We now follow the same procedure to form a rotation operator which generates rotation described by the angle $\boldsymbol{\phi}=(\phi_x,\phi_y,\phi_z)$ about an axis along the direction $\boldsymbol{\phi}$ through the lab-fixed origin. This operator we write as

$$\hat{R}(\boldsymbol{\phi}) = \exp\{-\boldsymbol{\phi}\cdot\mathbf{L}\}, \tag{10a}$$

where

$$\mathbf{L} = \mathbf{R}\times\nabla_R \tag{10b}$$

and we again think of $\mathbf{L}$ operating on both $\mathbf{R}$ and $\mathbf{R}'$ in the case where I is a two-electron integral. To generate rotations of both the center and orientation of a Gaussian function we must allow $\mathbf{L}$ to operate both on $\mathbf{P}_K$ and $\mathbf{r}_K$. For example, the action of the L_z component on a Gaussian is

$$L_z G_K(\mathbf{P}_K,\mathbf{r}_K) = \left(X\frac{\partial}{\partial Y} - Y\frac{\partial}{\partial X}\right)G_K(\mathbf{P}_K,\mathbf{r}_K) = \left\{-\left(P_{KX}\frac{\partial}{\partial P_{KY}} - P_{KY}\frac{\partial}{\partial P_{KX}}\right) + \left(x_K\frac{\partial}{\partial y_K} - y_K\frac{\partial}{\partial x_K}\right)\right\}G_K(\mathbf{P}_K,\mathbf{r}_K) \equiv \{-L_{zK} + l_{zK}\}G_K(\mathbf{P}_K,\mathbf{r}_K). \tag{11a}$$

Thus the action of the total L_z operator on a Gaussian can be written as the sum of the contributions of the operators L_{zK} which act solely on the nuclear coordinates $\mathbf{P}_K$, and operators l_{zK} which change the orientation (internal coordinate $\mathbf{r}_K$) of the Gaussian keeping fixed the nuclear coordinate $\mathbf{P}_K$. The action of the αth component of the total L operator on an integral is

$$I\{L_\alpha G_K(\mathbf{P}_K,\mathbf{r}_K)\} = \sum_{K=1}^{N} I\{(-L_{\alpha K} + l_{\alpha K})G_K(\mathbf{P}_K,\mathbf{r}_K)\}$$
$$\alpha = x,y,z. \tag{11b}$$

Thus the rotation operator can be represented as

$$\hat{R}(\boldsymbol{\phi}) = \exp\left\{\boldsymbol{\phi}\cdot\sum_{K=1}^{N}(\mathbf{L}_K - \mathbf{l}_K)\right\}, \tag{12}$$

and the effect of a rotation operator $\hat{R}(\boldsymbol{\phi})$ about an axis through the lab fixed coordinate origin can be thought of as the rotation by ϕ of *each* Gaussian center about the same axis followed by rotation of each of the Gaussian shapes about a parallel axis through their centers.

Different components of the L (or l) operators belonging to the same centers do not commute:

$$[L_{xK},L_{yK}] = -L_{zK} \tag{13a}$$

and

$$[l_{xK},l_{yK}] = -l_{zK}. \tag{13b}$$

Also the operators $\mathbf{L}_K$ and $\mathbf{l}_K$ do *not* commute, since from Eq. (8a) it is seen that derivatives with respect to P_K and r_K are related. However, the operators belonging to different centers $\mathbf{L}_K$, $\mathbf{L}_J$ do commute. Of course the components of the translation operators all commute.

B. Invariance relations for integrals

In this section we analyze the consequences of the invariance relations involving any integral I. The translational invariance of Eq. (9) can be developed as follows:

$$\exp\left\{\mathbf{t}\cdot\sum_{K=1}^{N}\nabla_{P_K}\right\}I = I$$
$$= I + \sum_{\alpha=x,y,z} t_\alpha \sum_{K=1}^{N} I_{K\alpha} + \frac{1}{2}\sum_{\alpha\beta} t_\alpha t_\beta \sum_{KJ}^{N} I_{K\alpha J\beta} + \frac{1}{3!}\sum_{\alpha\beta\gamma} t_\alpha t_\beta t_\gamma \sum_{KJM}^{N} I_{K\alpha J\beta M\gamma} + \cdots, \tag{14}$$

where the shorthand notation

$$I_{K\alpha} = \frac{\partial I}{\partial P_{K\alpha}}, \quad \frac{\partial^2 I}{\partial P_{K\alpha}\partial P_{J\beta}} = I_{K\alpha J\beta}, \quad \text{etc.} \tag{15}$$

has been introduced. Since the t_α are independent and of arbitrary magnitudes, the terms of each order must separately vanish. From the first-order terms we therefore have

$$\sum_{K=1}^{N} I_{K\alpha} = 0, \quad \alpha = x,y,z \tag{16}$$

which amount to three relations among the first derivative integrals $\{I_{K\alpha}\}$. Similarly, the second-order terms give

$$\sum_{\alpha\beta} t_\alpha t_\beta \sum_{KJ}^{N} I_{K\alpha J\beta} = 0. \tag{17}$$

However, not all nine relations are independent due to the permutational symmetry of the integrals (e.g., $I_{K\alpha L\beta} = I_{L\beta K\alpha}$, for $K \neq L$, or $\alpha \neq \beta$). In consideration of these symmetries the following two sets of equations can be written

$$\sum_{KJ}^{N} I_{K\alpha J\beta} = 0, \quad \alpha\beta = xy, yz, zy \tag{18a}$$

and

$$2\sum_{K>J}^{N} I_{K\alpha J\alpha} + \sum_{K=1}^{N} I_{K\alpha K\alpha} = 0, \quad \alpha = x,y,z. \tag{18b}$$

Thus these equations give *six relations* among the second derivative integrals. The relations among the third- and higher-order derivatives can also be straightforwardly obtained from Eq. (14).

The usefulness of these kinds of relations can be seen by considering an example of a two-center integral for which Eq. (16) reads $I_{1\alpha} = -I_{2\alpha}$ ($\alpha = x,y,z$). That is, one of the integral derivatives can be found knowing the other (for each α). As will be seen shortly, not all of the translation and rotation constraints of a given order are mutually independent. In the following section we represent a more systematic approach for determining the number of independent constraints of a given order and a method for calculating the dependent integral derivatives from a set of independent ones.

Before moving on to the analysis of the full set of rotation and translation relations of a given order, we need to show how to derive relations from the rotational invariance relation. Using Eq. (12) to allow $\hat{R}$ to act on all of the Gaussians in an integral I and expanding the exponential appearing in Eq. (12) one obtains

$$I\{G_K\} = I\{G_K\} + I\left\{\boldsymbol{\phi}\cdot\sum_K(\mathbf{L}_K - \mathbf{l}_K)G_K\right\} + 1/2I\left\{\left[\boldsymbol{\phi}\cdot\sum_K(\mathbf{L}_K - \mathbf{l}_K)G_K\right] \times\left[\boldsymbol{\phi}\cdot\sum_J(\mathbf{L}_J - \mathbf{l}_J)G_J\right]\right\} + \cdots. \tag{19}$$

Because the components of $\boldsymbol{\phi}$ are independent and arbitrary rotation angles, the first-order terms give

$$\sum_{K=1}^{N} L_{\alpha K} I = \sum_{K=1}^{N} l_{\alpha K} I, \quad \alpha = x,y,z. \tag{20}$$

Here the operator $L_{\alpha K}$ has been pulled outside the integral I since the $\mathbf{P}_K$ are not integration variables ($\mathbf{R}$ and $\mathbf{R}'$ are), and the notation $l_{\alpha K}\, I$ has been introduced to mean that the $l_{\alpha K}$ operator is applied to the vector $\mathbf{r}_K$ in the Gaussian G_K appearing in I. That is, $l_{\alpha K}\, I$ represents $I(l_{\alpha K} G_K)$. These relations show that the first-order effect of rotation of the nuclear *centers* about an axis through the lab-fixed origin on an integral is identical to the rotation of the Gaussian orientations about a parallel axis through the fixed nuclear center.

Before writing the second-order terms, let us write Eq. (20) explicitly in terms of the derivatives of the integrals. The left-hand side of Eq. (20) is

$$\sum_{K=1}^{N} L_{\gamma K} I\{G_K\} = \sum_{K=1}^{N} \left(P_{K\alpha} \frac{\partial}{\partial P_{K\beta}} - P_{K\beta} \frac{\partial}{\partial P_{K\alpha}} \right) I\{G_K\}$$

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

$$\alpha\beta\gamma = xyz,yzx,zxy. \tag{21}$$

To write the right-hand side (RHS) of Eq. (20) let us, for example, consider the case $\gamma = z$ (the other two cases $\gamma = y,x$ follow from cyclic permutations):

$$\text{RHS} = \sum_{K=1}^{N} l_{zK} I\{G_K\}$$

$$= \sum_{K=1}^{N} I\left\{ \left(x_K \frac{\partial}{\partial y_K} - y_K \frac{\partial}{\partial x_K} \right) G_K \right\}. \tag{22}$$

Now since

$$x_K \frac{\partial}{\partial y_K} G_K(\mathbf{P}_K,\mathbf{r},n_x,n_y,n_z,\xi)$$

$$= n_y \left(\frac{2n_x+1}{2n_y-1} \right)^{1/2} G_K(\mathbf{P}_K,\mathbf{r}_K,n_x+1,n_y-1,n_z,\xi)$$

$$- (2n_x+1)^{1/2}(2n_y+1)^{1/2}$$

$$\times G_K(\mathbf{P}_K,\mathbf{r}_K,n_x+1,n_y+1,n_z,\xi) \tag{23}$$

it can be seen that l_{zK} transforms a Gaussian into a linear combination of two Gaussians belonging to the same shell:

$$\text{RHS} = \sum_{K=1}^{N} \left\{ n_y \left(\frac{2n_x+1}{2n_y-1} \right)^{1/2} I_K(n_x+1,n_y-1) \right.$$

$$\left. - n_x \left(\frac{2n_y+1}{2n_x-1} \right)^{1/2} I_K(n_x-1,n_y+1) \right\}. \tag{24}$$

Here $I_K(n_x+1,n_y-1)$ means that the Kth Gaussian $G_K\{n_x,n_y,n_z\}$ in the integral I has been replaced by $G_K\{n_x+1,n_y-1,n_z\}$ with n_z unchanged and with proper normalization included. The point that these integrals are of the same shell is quite computationally important because such integrals are automatically calculated within the same integral-evaluation routines which evaluate $I_K(n_x,n_y,n_z)$. In general the right-hand side of Eq. (20) can be written as

$$\text{RHS} = \sum_{K=1}^{N} \{A_{\alpha\beta} I_K(n_\alpha+1,n_\beta-1)$$

$$- A_{\beta\alpha} I_K(n_\alpha-1,n_\beta+1)\} \equiv I_{\alpha\beta} \tag{25}$$

with $\alpha\beta$ chose in cyclic order ($\alpha\beta = yz,zx,xy$), and

$$A_{\beta\alpha} = n_\alpha \left(\frac{2n_\beta+1}{2n_\alpha} \right)^{1/2}. \tag{26}$$

Thus combining the results of Eqs. (21) and (25), the working relations expressed in Eq. (20) can be rewritten explicitly to yield the three first-order rotational invariance conditions:

$$\sum_{K=1}^{N} (P_{K\alpha} I_{K\beta} - P_{K\beta} I_{K\alpha}) = I_{\alpha\beta}, \quad \alpha\beta = yz,zx,xy. \tag{27}$$

Kahn[7] also arrived at this equation based on a different set of arguments.

The second-order rotational conditions from Eq. (19) are

$$\sum_{KJ}^{N} \sum_{\alpha\beta} \phi_\alpha \phi_\beta [L_{\alpha K} - l_{\alpha K}][L_{\beta J} - l_{\beta J}] I = 0, \quad \alpha,\beta = x,y,z \tag{28}$$

which, because the ϕ_α and ϕ_β are independent, reduce to

$$\sum_{KJ}^{N} L_{\alpha K} L_{\beta J} I = -\sum_{KJ}^{N} (l_{\alpha K} l_{\beta J} - l_{\alpha K} L_{\beta J} - L_{\alpha K} l_{\beta J}) I,$$

$$\alpha,\beta = x,y,z. \tag{29}$$

All of these *nine* conditions are *not* independent! To see the hidden dependence let us subtract $\Sigma_{KJ}\, L_{\beta J}\, L_{\alpha K}$ thereby obtaining

$$\sum_{JK}^{N} [L_{\alpha K}, L_{\beta J}] I = -\sum_{JK}^{N} \{[l_{\alpha K}, l_{\beta J}] I - [l_{\alpha K}, L_{\beta J}] I$$

$$- [L_{\alpha K}, l_{\beta J}] I\} \tag{30}$$

which, from the commutation relations of Eq. (13), is a first-order expression in L. This clearly displays the lack of independence of Eqs. (29). In fact Eq. (29) contains only *six* independent conditions for $\alpha\beta$: *xx,yy,zz,xy, yz,zx*.

To write Eq. (29) in a manner which makes clear how these results can be used to relate some second integral derivatives to others, let us first examine the right-hand side of Eq. (29). From Eqs. (22) and (25) it should be clear that the term $l_{\alpha K}\, l_{\beta J}\, I$ can be evaluated in terms of integrals belonging to the same shell as the original integral I

$$l_{\alpha K} l_{\beta J} I = l_{\alpha K}\{A_{\sigma\gamma} I_J(n_\sigma+1,n_\gamma-1)$$

$$- A_{\gamma\alpha} I_J(n_\sigma-1),n_\gamma+1)\}, \quad \beta\sigma\gamma = xyz,yzx,zxy. \tag{31a}$$

Application of $l_{\alpha K}$ to I_J $(n_\alpha \pm 1, n_\gamma \mp 1)$ can be achieved by using Eqs. (22) and (23) once again. For $K \neq J$ we have

$$l_{\alpha K} I_J(n_\sigma+1,n_\gamma-1)$$

$$= A_{\mu\nu} I_{JK}(n_\sigma+1,n_\gamma-1;n_u+1,n_\nu-1)$$

$$- A_{\nu\mu} I_{JK}(n_\sigma+1,n_\gamma-1;n_\mu-1,n_\nu+1),$$

$$\alpha\mu\nu = xyz,yxz,zxy. \tag{31b}$$

For $K = J$ the analysis is similar although there are special cases of $\alpha = \beta$ and $\alpha \neq \beta$. The essential point is that $l_{\alpha K}\, l_{\beta J}\, I$ does *not* require the evaluation of integral derivatives; it is simply another integral belonging to the same shell as the original integral I.

We can now rewrite the six independent relations of Eq. (29), in which the left-hand side will only involve second derivatives of integrals, by explicitly writing out the quantity $\Sigma_{KJ}\, L_{\mu K}\, L_{\nu J}\, I$. Then for $\mu = \nu$ we have

$$\sum_{K>J}^{N} \{2P_{K\alpha} P_{J\alpha} I_{K\beta J\beta} + 2P_{K\beta} P_{J\beta} I_{K\alpha J\alpha}\}$$

$$- \sum_{KJ}^{N} 2P_{K\alpha} P_{J\beta} I_{K\beta J\alpha} + \sum_{K=1}^{N} \{P_{K\alpha}^2 I_{K\beta K\beta}$$

$$+ P_{K\beta}^2 I_{K\alpha K\alpha}\} = I_{\alpha\beta\alpha\beta}, \tag{32a}$$

where

$$I_{\alpha\beta\alpha\beta} = \hat{I}_{\alpha\beta\alpha\beta} + \sum_{K=1}^{N} \{P_{K\alpha} I_{K\alpha} + P_{K\beta} I_{K\beta}\},$$

$$\alpha\beta = xy,yz,zx$$

and for $\mu \neq \nu$

$$\sum_{KJ}^{N} \{P_{K\alpha} P_{J\gamma} I_{K\beta J\sigma} - P_{K\alpha} P_{J\sigma} I_{K\beta J\gamma} - P_{K\beta} P_{J\gamma} I_{K\alpha J\sigma} + P_{K\beta} P_{J\sigma} I_{K\alpha J\gamma}\} = I_{\alpha\beta\gamma\sigma}, \quad (32b)$$

where

$$I_{\alpha\beta\gamma\sigma} = \hat{I}_{\alpha\beta\gamma\sigma} - \sum_{K=1}^{N} P_{K\beta} I_{K\gamma},$$

$$(\alpha\beta) \neq (\lambda\sigma): yz,zx,xy.$$

Here $\hat{I}$ is the right-hand side of Eq. (29). The additional terms of the right-hand side of Eq. (32a) and (32b) are the first derivative terms from the left-hand side of Eq. (29).

In summary Eq. (32) expresses relationships among various second-integral derivatives $\{I_{K\alpha J\beta}\}$. The matrix of coefficients multiplying the $I_{K\alpha J\beta}$ involves only geometrical information $\{P_{K\gamma}\}$ relating to the positions of the N centers in I. As a result the relations given in Eq. (32) are equally valid for *all* integral derivatives involving the same N centers.

C. Invariance relations for derivatives of integrals

So far we have derived relations among the first- and second-order derivatives of integrals based on the fact that an integral is translationally and rotationally invariant. Additional relations among the second- and higher-order integral derivatives can be obtained if we recognize that the derivatives $\partial I / \partial P_{J\mu} (J = 1,N; \mu = x,y,x)$ themselves are also invariant under $\hat{T}$ and $\hat{R}$:

$$\hat{T}\left(\frac{\partial I}{\partial P_{J\mu}}\right) = \frac{\partial I}{\partial P_{J\mu}}, \quad (33)$$

$$\hat{R}\left(\frac{\partial I}{\partial P_{J\mu}}\right) = \frac{\partial I}{\partial P_{J\mu}}. \quad (34)$$

It should be noted that the invariance condition $\hat{R}\hat{T}I = I$ does not contribute independent relations since, from Eq. (34), $\hat{R} \sum_J (\partial I / \partial P_{J\mu})$ is the second-order term of $\hat{R}\hat{T}I$. It is straightforward to write down explicitly the resulting relations involving the second integral derivatives by substituting $I_{J\mu}$ for I in Eqs. (16) and (27):

$$\sum_{K=1}^{N} I_{K\alpha J\mu} = 0, \quad \alpha,\mu = x,y,z; J = 1,N \quad (35)$$

and

$$\sum_{K=1}^{N} \{P_{K\alpha} I_{K\beta J\mu} - P_{K\beta} I_{K\alpha J\mu}\} = I_{\alpha\beta J\mu}, \quad \begin{matrix} \alpha\beta = yz,zx,xy, \\ \mu = x,y,z; J = 1,N, \end{matrix} \quad (36a)$$

where

$$I_{\alpha\beta J\mu} = \sum_{K=1}^{N} l_{\gamma K} I_{J\mu}\{G_K\}, \quad \alpha\beta\gamma = xyz,yzx,zxy. \quad (36b)$$

Vincent *et al.*[8] have derived relations similar to Eq. (36). Their expressions are more complicated since they contain extra first derivative terms. Note that each of Eqs. (35) and (36) yield $3 \times 3N$ relations among the second integral derivatives.

Summarizing the development so far, we have obtained translational and rotational invariance relations to first order. Those pertaining to the first derivatives of the integrals are shown in Eqs. (16) and (27) and amount to a total of six relations. For the second-order integral derivatives, the relations consist of six second-order translational invariance relations [Eq. (18)], $3 \times 3N$ relations arising from first-order translational invariance of the first derivative integrals [Eq. (35)], $3 \times 3N$ relations arising from the first-order rotational invariance of the first derivatives [Eq. (36)], and six second-order rotational invariance relations [Eqs. (32)]. Thus we have a *total* of $6(3N + 2)$ relations involving $3N(3N + 1)/2$ second integral derivatives and a total of six relations among the $3N$ first integral derivatives.

III. IMPLEMENTATION

In this section we deal with how to make use of the symmetry equations in reducing the number of (independent) first- and second-order derivative integrals that need to be explicitly calculated. Out of the $3N$ displacements of the N nuclei, $N' = 3N - 6$ ($3N - 5$ for collinear geometries) of these displacements lead to independent first order derivatives; $N'(N' + 1)/2$ arise in independent second derivatives. Given that there are six symmetry relations among the $3N$ first integral derivatives, one might decide to explicitly calculate *any* $(3N - 6)$ derivatives and to obtain the remaining six via our symmetry relations. However, this procedure *cannot* directly be applied since the symmetry relations of Eqs. (16) and (27) are not always an independent set, and it is not possible to make arbitrary choices of the $(3N - 6)$ integrals to be evaluated explicitly. Similar problems arise again in the case of second-derivative integrals where the number of symmetry relations $[6(3N + 2)]$ *exceeds* the total number of integrals $[3N(3N + 1)/2]$. Clearly more needs to be said before the above symmetry relations can be implemented in a manner which eliminates redundancies and clarifies which derivatives can be chosen as independent.

The first-order relations of Eqs. (16) and (27), as well as the second-order relations of Eqs. (18), (32), (35), and (36), respectively, constitute systems of m simultaneous inhomogeneous linear equations in n integral derivatives as the variables. The coefficient matrix $(m \times n)$ depends only upon the geometry of the N Gaussian centers $\{P_K\}$. The problem is to first reduce the respective linear system of equations to one containing only r $(\leqslant m)$ independent relations, where r is the rank of the system of equations. The next step is to write r dependent integrals in terms of the $n - r$ independent ones.[11] In the following subsection we detail steps involved in such calculations.

A. First derivative (gradient) integrals

We can simplify the set of linear equations given in Eqs. (16) and (27) by first solving Eq. (16) for $I_{N\alpha}$:

$$I_{N\alpha} = -\sum_{K=1}^{N-1} I_{K\alpha}, \quad \alpha = x,y,z. \quad (37)$$

Eliminating the derivative $I_{N\alpha}$ from Eq. (27), we obtain

$$\sum_{K=1}^{N-1} \{\hat{P}_{K\alpha} I_{K\beta} - \hat{P}_{K\beta} I_{K\alpha}\} = I_{\alpha\beta}, \quad \alpha\beta = xy,yz,zx \quad (38)$$

which constitute three *independent* relations in terms of the

$3(N-1)$ gradient integrals $I_{K\alpha}$ $(K=1,N-1)$. Here $\hat{P}_{K\alpha}$ is defined by $\hat{P}_{K\alpha}=P_{K\alpha}-P_{N\alpha}$. Equations (38) can be solved separately for the $I_{K\alpha}$ $(K=1,N-1)$ after which Eq. (37) gives the $I_{N\alpha}$. The special case in which all of the centers are collinear must be treated separately, since only two of the three relations in Eq. (38) are then independent due to the identity $\hat{P}_{1x}E_{yz}+\hat{P}_{1y}E_{zx}+\hat{P}_{1z}E_{xy}=0$, where $E_{\alpha\beta}$ represents the left- or right-hand side of Eq. (38). Thus for collinear centers ($\hat{P}_{1y}\neq 0$), instead of Eq. (38) we use the following *two* independent relations

$$\sum_{K=1}^{N-1}(\hat{P}_{K\alpha}I_{K\beta}-\hat{P}_{K\beta}I_{K\alpha})=I_{\alpha\beta},\quad \alpha\beta=xy,yz. \tag{39}$$

Recall that the $I_{\alpha\beta}$ defined in Eq. (25) involve integrals from the same shell as the original integral I. The independent gradient integrals which must be calculated explicitly are *solely* determined through the solution of Eq. (38) or (39). There are a total of $3N-6$ ($3N-5$ for collinear centers) such independent gradient integrals. Equation (37) can then be used to uniquely determine the $I_{N\alpha}$. To make perfectly clear the steps to be followed in achieving and implementing the final working equations, let us consider in further detail the particular case where I involves three Gaussian centers.

1. Three center case

In this case we have in Eqs. (37) and (38) a total of six relations involving $(3N)$ nine integral derivatives. We begin by writing explicitly the three relations given by Eq. (38) in terms of the six integral derivatives $I_{K\alpha}$ $(K=1,2;\ \alpha=x,y,z)$ as

$$\begin{bmatrix} -\hat{P}_{1y} & \hat{P}_{1x} & 0 & -\hat{P}_{2y} & \hat{P}_{2x} & 0 \\ 0 & -\hat{P}_{1z} & \hat{P}_{1y} & 0 & -\hat{P}_{2z} & \hat{P}_{2y} \\ \hat{P}_{1z} & 0 & -\hat{P}_{1x} & \hat{P}_{2z} & 0 & -\hat{P}_{2x} \end{bmatrix} \begin{bmatrix} I_{1x} \\ I_{1y} \\ I_{1z} \\ I_{2x} \\ I_{2y} \\ 1_{2z} \end{bmatrix} = \begin{bmatrix} I_{xy} \\ I_{yz} \\ I_{zx} \end{bmatrix}. \tag{40}$$

Using elementary row operations, we can transform this system of equations to lower row-echelon form

$$\begin{bmatrix} -\hat{P}_{1y} & \hat{P}_{1x} & 0 & -\hat{P}_{2y} & \hat{P}_{2x} & 0 \\ 0 & -\hat{P}_{1z} & \hat{P}_{1y} & 0 & -\hat{P}_{2z} & P_{2y} \\ 0 & 0 & 0 & \begin{pmatrix} \hat{P}_{1y} & \hat{P}_{2z} \\ -\hat{P}_{1z} & \hat{P}_{2y} \end{pmatrix} & \begin{pmatrix} \hat{P}_{1z} & \hat{P}_{2x} \\ -\hat{P}_{2z} & \hat{P}_{1x} \end{pmatrix} & \begin{pmatrix} \hat{P}_{1x} & \hat{P}_{2y} \\ -\hat{P}_{2x} & \hat{P}_{1y} \end{pmatrix} \end{bmatrix} \begin{bmatrix} I_{1x} \\ I_{1y} \\ I_{1z} \\ I_{2x} \\ I_{2y} \\ I_{2z} \end{bmatrix} = \begin{bmatrix} I_{xy} \\ I_{yz} \\ \hat{P}_{1x}I_{yz} \\ +\hat{P}_{1z}I_{xy} \\ +\hat{P}_{1y}I_{zx} \end{bmatrix} \tag{41}$$

In obtaining Eq. (41) from Eq. (40) we assumed that there existed nonzero pivot elements in each of the rows of the rectangular coefficient matrix of Eq. (40). In particular we assume that the centers have been numbered and the axes labeled such that $\hat{P}_{1y}$ is a nonzero pivot element. The numbering of the two centers $(K=1,2)$ and of the direction $(\alpha=x,y,z)$ is arbitrary. Thus our *choice* of $\hat{P}_{1y}\neq 0$ means that we *assume* that the centers and directions are chosen such that at least one center has a different y component from center N.

From this lower-echelon form it is possible to say that (I_{1y}) and any two of (I_{2x},I_{2y},I_{2z}) are independent integral derivatives. Moreover the rank of the above coefficient matrix is three which shows that all three relations of Eq. (40) are independent. Considering permutations among the center indices (1,2,3) and among the components (x,y,z), one deduces that any independent set of integral derivatives must be of the form $I_{K\alpha},I_{J\beta}$, and $I_{J\gamma}$ $(K\neq J;\ \beta\neq\gamma)$. That is, any choice of independent integral derivatives must span at least two centers.

Taking a particular *choice* for the independent integral derivatives (I_{1y},I_{2y},I_{2z}), Eq. (40) can be rewritten in a partitioned form as

$$\mathsf{A}\begin{bmatrix} I_{1x} \\ I_{1z} \\ 1_{2x} \end{bmatrix} = \begin{bmatrix} I_{xy} \\ I_{yz} \\ I_{zx} \end{bmatrix} - \mathsf{B}\begin{bmatrix} I_{1y} \\ I_{2y} \\ I_{2z} \end{bmatrix}. \tag{42}$$

The square matrix A has the dimension $r(=3)$ equal to the rank of the coefficient matrix of Eq. (40), which is also equal to the number of relations in Eq. (39). The rectangular matrix B has dimensions $r\times\{3(N-1)-r\}$. The columns of the A and B matrices are the corresponding columns of the coefficient matrix in Eq. (40) multiplying the appropriate integral derivatives:

$$\mathsf{A}=\begin{bmatrix} -\hat{P}_{1y} & 0 & -\hat{P}_{2y} \\ 0 & \hat{P}_{1y} & 0 \\ \hat{P}_{1z} & -\hat{P}_{1x} & \hat{P}_{2z} \end{bmatrix}, \tag{43a}$$

$$\mathsf{B}=\begin{bmatrix} \hat{P}_{1x} & \hat{P}_{2x} & 0 \\ -\hat{P}_{1z} & -\hat{P}_{2z} & \hat{P}_{2y} \\ 0 & 0 & -\hat{P}_{2x} \end{bmatrix}. \tag{43b}$$

Equation (42) allows the dependent integral derivatives (I_{1x},I_{1z},I_{2x}) to be obtained directly in terms of the independent ones (I_{1y},I_{2y},I_{2z}) via a straightforward solution of the simultaneous linear equations.

Notice that A and B matrix elements involve only geometrical variables and therefore need to calculated only once for a given set of H centers regardless of what orbitals on those centers are involved. However, the elements I_{xy}, I_{yz}, and I_{zx} must be calculated for each integral derivative. Computational simplifications arise in evaluating I_{1x}, I_{1y}, and I_{2z} from Eq. (42) rather than by direct calculation because, as seen from Eqs. (22)–(24), the elements I_{xy}, I_{yz}, and I_{zx} involve linear combinations of integrals in which one Gaussian has been replaced by another from the same *shell*. Once the set of $I_{K\alpha}$ ($K=1$, $N=1$) are in hand, the remaining three integrals $I_{N\alpha}$ can directly be obtained from Eq. (37).

To deal with the case when all three centers are collinear, one must use Eq. (39) instead of Eq. (38) along with Eq. (37). The corresponding explicit form of Eq. (39) is identical to Eq. (40) but without the bottom row. The coefficient matrix then is already in a lower echelon form of rank two and any four out of the five integral derivatives I_{1y}, I_{1z}, I_{2x}, and I_{2z} are independent. Choosing I_{1y}, I_{2x}, I_{2y}, and I_{2z} with $\hat{P}_{1y}\neq 0$ to be independent, the transformation equation [analogous to Eq. (42)] from which the remaining integral derivatives I_{1x} and I_{1z} can be obtained is

$$\begin{bmatrix} -\hat{P}_{1y} & 0 \\ 0 & \hat{P}_{1y} \end{bmatrix} \begin{bmatrix} I_{1x} \\ I_{1x} \end{bmatrix} = \begin{bmatrix} I_{xy} \\ I_{yz} \end{bmatrix} - \begin{bmatrix} \hat{P}_{1x} & -\hat{P}_{2y} & \hat{P}_{2x} & 0 \\ -P_{1z} & 0 & -\hat{P}_{2z} & P_{2y} \end{bmatrix} \begin{bmatrix} I_{1y} \\ I_{2x} \\ I_{2y} \\ I_{2z} \end{bmatrix}. \tag{44}$$

It should be mentioned that the transformation equations for the special cases when all three centers lie along a coordinate axis (the y axis as explained above) or parallel to the coordinate plane are contained in Eq. (44) as special cases. For all three centers lying along the y axis ($P_{1y}\neq 0$), the x- and z-coordinates vanish and Eq. (44) reduces to

$$\begin{bmatrix} -\hat{P}_{1y} & 0 \\ 0 & \hat{P}_{1y} \end{bmatrix} \begin{bmatrix} I_{1x} \\ I_{1z} \end{bmatrix} = \begin{bmatrix} I_{xy} \\ I_{yz} \end{bmatrix} - \begin{bmatrix} -\hat{P}_{2y} & 0 \\ 0 & \hat{P}_{2y} \end{bmatrix} \begin{bmatrix} I_{2x} \\ I_{2z} \end{bmatrix}, \tag{45}$$

which clearly displays the necessary equivalence between the x and z directions for this special case.

In summary our main conclusion regarding the translational and rotational invariance in the three-center case is that, out of nine possible integral derivatives, only three (four for collinear centers) need to be calculated explicitly; the remaining six (five for collinear centers) can be found from the symmetry relations. We will now simply state the conclusions of analogous analyses of the two- and four-center cases pertaining to the first derivative integrals.

2. Two-center integral gradients

For this obviously collinear case, the two relations in Eq. (39) involving the three integral derivatives (I_{1x}, I_{1y}, and I_{1z}) are already in lower row-echelon form. The rank of the coefficient matrix is two and either I_{1z} or I_{1y} can be chosen to be an independent gradient. Because of permutational symmetry between the two centers and among the components (x,y,z), any *one* of the gradients $I_{K\alpha}$ can be chosen to be independent. Again assuming that the centers and axes are chosen such that $\hat{P}_{1y}\neq 0$ and choosing I_{1y} to be the independent integral which is explicitly calculated, the result analogous to Eq. (42) reads

$$\begin{bmatrix} -\hat{P}_{1y} & 0 \\ 0 & \hat{P}_{1y} \end{bmatrix} \begin{bmatrix} I_{1x} \\ I_{1z} \end{bmatrix} = \begin{bmatrix} I_{xy} \\ I_{yz} \end{bmatrix} - \begin{bmatrix} \hat{P}_{1x} \\ -\hat{P}_{1z} \end{bmatrix} I_{1y} \tag{46}$$

from which the elements I_{1x} and I_{1z} can be calculated. Equation (37) can then be used to give the remaining integral derivatives $I_{2\alpha} = -I_{1\alpha}$ ($\alpha = x,y,z$).

3. Four-center integral gradients

Writing Eq. (38) for the four-center case, one has three relations involving nine integral derivatives $I_{K\alpha}$ ($K=1,2,3$; $\alpha = x,y,z$). Transformation to the lower row-echelon form shows that the rank of the coefficient matrix is three. For noncollinear geometries, the six independent derivatives are of the form $I_{K\alpha}$, $I_{L\beta}$, $I_{L\gamma}$ ($K\neq L, \beta\neq\gamma$), and $I_{J\mu}$ ($J\neq K$ or L, $\mu = x,y,z$). Again assuming that centers and directions are chosen such that $\hat{P}_{1y}\neq 0$, we can select I_{1y}, I_{2y}, I_{2z}, I_{3x}, I_{3y}, and I_{3z} as the six independent derivatives. The transformation equation analogous to Eq. (42) from which I_{1x}, I_{1z}, and I_{2x} are obtained has the same 3×3 A matrix and a 3×6 B matrix whose columns correspond to the six independent derivatives. As before, these A and B matrices are extracted directly from the columns of the coefficient matrix appearing in Eq. (38). Equation (37) then gives the remaining integral derivatives I_{4x}, I_{4y}, and I_{4z}.

Again, for the collinear four-center case, two relations of Eq. (39) are already in the echelon form. The seven independent integral derivatives can be chosen (again with $\hat{P}_{1y}\neq 0$) to be I_{1y} and $I_{K\alpha}$ ($K=2$, $N-1$; $\alpha = x,y,z$). These integral derivatives determine all of the remaining (dependent) integrals.

B. Second Derivative (Hessian) Integrals

We can now perform a similar analysis for the relations in Eqs. (18), (32), (35), and (36) involving the so-called Hessian integrals. Before we begin to perform the row-echelon reduction, we note that the computational effort in setting up or utilizing these symmetry relations arises mainly through the calculation of the right-hand sides (the $I_{\alpha\beta\lambda\sigma}$ or $I_{\alpha\beta J\mu}$) of the equations which arise via the rotational invariance of I of $I_{J\mu}$. The elements of the left-hand side coefficient matrix only involve the geometrical coordinates of the

N centers and need to calculated only once for any given nuclear positions. Thus they remain valid and unchanged for all of the integrals involving basis functions of the same centers. The right-hand side elements of Eqs. (18) and (35) corresponding to the translational symmetries are zero. On the other hand, the right-hand side of Eqs. (36) and (32) are given, respectively, in Eqs. (36) and (31)–(32). As mentioned earlier, their calculation involves generating linear combinations of integrals or first integral derivatives in which a Gaussian is replaced by another from the same shell; thus although the evaluation of these right-hand side elements is the most computationally difficult step in implementing the symmetry relations treated here, such calculations are considerably easier than the explicit evaluation of additional second integral derivatives.

As pointed out earlier, the number of second-order symmetry relations $[6(3N+2)]$ is much larger than the number of Hessian integrals $[3N(3N+1)/2]$ for $N \leqslant 4$. Hence, not all of the symmetry relations are independent. Therefore whenever it is possible to locate and discard dependent relations, it should be done. This will considerably simplify computational effort in two ways. One saves by not having to calculate the right-hand sides belonging to such relations; moreover dealing with fewer equations gives rise to a considerably simplified analog of Eq. (42). Thus our aim is to discard *all* such dependent relations and to work with only the independent ones.

To illustrate such a reduction, we note that by substituting Eq. (35) into Eq. (18) we obtain a trivial identity

$$\sum_{KJ}^{N} I_{K\alpha J\beta} = \sum_{J=1}^{N}\left\{\sum_{K=1}^{N-1} I_{K\alpha J\beta} + I_{N\alpha J\beta}\right\} = \sum_{J=1}^{N}\left\{\sum_{K=1}^{N-1} I_{K\alpha J\beta} - \sum_{K=1}^{N-1} I_{K\alpha J\beta}\right\} = 0.$$

This means that the second-order translation relations of Eq. (18) are *not* independent of Eq. (35). Similarly, by substituting Eq. (36) into Eq. (32), it is found that the relations of Eq. (32) are also not independent. Hence, Eqs. (18) and (32) can be eliminated from further consideration. As a result of the above observations, we need only work with $9N$ relations from each of Eqs. (35) and (36).

The next stage of simplification involves rewriting the relations of Eqs. (35) and (36) in a partitioned form with the integrals derivatives $I_{N\alpha J\beta}$ ($J=1, N$; $\alpha, \beta = x, y, z$) separated from the complementary set involving derivatives on the remaining centers $I_{K\alpha J\beta}$ ($K, J = 1, N-1$). We begin by rewriting the independent relations of Eq. (35) as

$$I_{N\alpha J\mu} = -\sum_{K=1}^{N-1} I_{K\alpha J\mu}, \quad \begin{matrix} J = 1, N-1, \\ \alpha, \mu = x, y, z \end{matrix} \tag{47a}$$

and

$$\sum_{K=1}^{N} I_{N\mu K\alpha} = 0, \quad \alpha\mu = xx, yy, zz, xy, yz, zx. \tag{47b}$$

These are a total of $9(N-1)+6$ relations involving the same number $9(N-1)+6$ of integral derivatives involving the Nth center. Using these equations, it is straightforward to eliminate from Eq. (36) Hessian integrals involving the Nth center:

$$\sum_{K=1}^{N-1} (\hat{P}_{K\alpha} I_{K\beta J\mu} - \hat{P}_{K\beta} I_{K\alpha J\mu}) = I_{\alpha\beta J\mu}, \quad \begin{matrix} \alpha\beta = xy, yz, zx, \\ \mu = x, y, z, \\ J = 1, N-1, \end{matrix} \tag{48}$$

where $\hat{P}_{K\alpha} = P_{K\alpha} - P_{N\alpha}$.

The relations in Eq. (48) still contain dependencies which can be exposed by noting the following three independent relations among the relations (RAR) of Eq. (48):

$$\sum_{J=1}^{N-1} \{\hat{P}_{J\gamma} E_{\alpha\beta J\beta} + \hat{P}_{J\alpha} E_{\beta\gamma J\beta} - \hat{P}_{J\beta}(E_{\alpha\beta J\gamma} + E_{\beta\gamma J\alpha})\} = 0, \quad \alpha\beta\gamma = xyz, yzx, zxy. \tag{49}$$

Here $E_{\alpha\beta J\gamma}$ represents the left- or right-hand side of a relation in Eq. (48) for the given values of α, β, γ, and J. These three RAR's can be verified quite easily by simple substitution. Based on these three RAR's it is possible to discard three of the relations of Eq. (48). One particular choice, which imposes the minimum number of constraints on the allowable geometries of the N centers, is to discard the three relations of the form $E_{\alpha\beta J\gamma}$, $E_{\gamma\alpha J\gamma}$, and $E_{\gamma\alpha J\alpha}$ for a value of J for which some $\hat{P}_{J\beta} \neq 0$. Analogous to our treatment of the gradient integrals (in which $\hat{P}_{1y} \neq 0$, was assumed) we choose $J=1$ and $\beta = y$ so that the relations E_{xy1z}, E_{zx1z}, and E_{zx1x} are discarded. Equation (48) then becomes

$$\sum_{K=1}^{N-1} (\hat{P}_{K\alpha} I_{K\beta J\mu} - \hat{P}_{K\beta} I_{K\alpha J\mu}) = I_{\alpha\beta J\mu}, \quad \alpha\beta = xy, yz, zx, \quad \mu = x, y, z; J = 1, N-1, \quad (E_{xy1z}, E_{zx1z}, E_{zx1x}). \tag{50}$$

The discarded conditions E_{xy1z}, E_{zx1z}, E_{zx1x} are enclosed in parentheses above. Equation (50) represents a set of $(9N'-3)$ *independent* relations involving $3N'(3N'+1)/2$ Hessian integrals where $N' = N-1$. Therefore $\{3N'(3N'+1)/2-(9N'-3)\}$ integrals are truly independent and need to be calculated explicitly, while $(9N'-3)$ integrals can be obtained in terms of these from the symmetry relations of Eq. (50). Note that $\{3N'(3N'+1)/2–(9N'-3)\}$ equals $\{(3N-6)(3N+6+1)/2\}$, the number of independent integral derivatives predicted at the beginning of this section. A specific choice of these independent Hessian integrals can be made from the echelon form of the coefficient matrix of Eq. (50).

The case of collinear centers must again be considered separately. Due to the reduced geometrical flexibility, fewer Hessian integrals are determined through the symmetry relations. In addition to the three RAR's given in Eq. (49) the constraints due to the collinear centers can be represented by the $3(N-1)$ RAR's of Eq. (46) as

$$\hat{P}_{Kz} E_{xyJ\mu} + \hat{P}_{Kx} E_{yzJ\mu} + \hat{P}_{Ky} E_{zxJ\mu} = 0, \quad \begin{matrix} J = 1, N-1, \\ \mu = x, y, z, \\ K \text{ fixed}. \end{matrix} \tag{51}$$

From the total of $3N$ RAR's only $3N-2$ can be shown to be independent and be discarded. For $\hat{P}_{1y} \neq 0$ we chose to discard the relations E_{xy1y} and $E_{zxJ\mu}$ ($J = 1, N-1$; $\mu = x, y, z$) from Eq. (46). The final set of $\{6(N-1)-1\}$ *independent* relations for the collinear centers can be represented as

$$\sum_{K=1}^{N-1}(\hat{P}_{K\alpha}I_{K\beta J\mu}-\hat{P}_{K\beta}I_{K\alpha J\mu})=I_{\alpha\beta J\mu},$$
$$\alpha\beta=xy,yz,$$
$$\mu=x,y,z;J=1,N-1, \quad (52)$$
$$(E_{xy1z}).$$

For collinear centers thus $\{3N'(3N'+1)/2-6N'+1\}$ integrals will be independent and $6N'-1$ integrals will be calculated in terms of these from Eq. (52). Note that $\{3N'(3N'+1)/2-6N+1\}$ equals $\{(3N-5)(3N-5+1)/2\}$. A specific choice of these independent integrals will be made from the echelon form of Eq. (52).

The plan for the solution of Eqs. (47) and (50) [or (52) for collinear centers] is as follows. First we perform the row reduction of Eq. (50) [or Eq. (52)] and obtain equations giving the dependent Hessian integrals in terms of the explicitly calculated independent ones. Knowing the values of these integral derivatives, the remaining integrals (i.e., those involving center N) can be obtained from Eqs. (47). It is straightforward to show that the $9(N-1)+6$ relations of Eq. (47) (involving the same number of integrals) are *all* independent. This means that the independent integral derivatives are *solely* determined through the solutions of Eq. (50) [or Eq. (52) for collinear centers].

1. Three-center Hessian integrals

For this case, Eq. (50) gives 15 independent relations involving 21 Hessian integrals. The coefficient matrix for this case is given in the Appendix. The six independent integrals inferred from the echelon form of the coefficient matrix can be chosen to be I_{1y1y}, I_{2y1y}, I_{2y2y}, I_{2z1y}, I_{2z2y}, and I_{2x2x} whenever $\hat{P}_{1y}\neq 0$ and $\hat{P}_{1y}\hat{P}_{2z}-\hat{P}_{1z}\hat{P}_{2y}\neq 0$. In general based on the permutational symmetry among the centers (1,2,3) and among the components (x,y,z), one may deduce that, for $\hat{P}_{K\alpha}\neq 0$ and $\hat{P}_{K\alpha}\hat{P}_{L\beta}-\hat{P}_{K\beta}\hat{P}_{L\alpha}\neq 0$, the six independent integrals arise from action of unique pairs of differential operators $\partial P_{K\alpha}$, $\partial P_{L\alpha}$, $\partial P_{L\beta}$, and $\partial P_{J\mu}$ ($J=1,N-1$; $\mu=x,y,z$; $J\neq K\neq L$; $\alpha\neq\beta$). The corresponding 15 dependent integrals are of the form $I_{K\alpha J\beta}$ [$K=1,N-1$; $\alpha=x,y,z$; $J=1$; $\beta=x,z$; $(K\alpha)\geqslant(J\beta)$]. From the coefficient matrix given in the Appendix, it is straightforward to write down the columns corresponding to these dependent and independent Hessian integrals which constitute the elements of the corresponding A (15×15) and B (15×6) matrices. Once A and B are in hand, the dependent integral derivatives can be evaluated. The remaining dependent integrals of the form $I_{N\alpha L\beta}$ are directly calculated from Eq. (47).

It should be emphasized that the conditions $\hat{P}_{K\alpha}\neq 0$ and $\hat{P}_{K\alpha}\hat{P}_{J\beta}-\hat{P}_{K\beta}\hat{P}_{J\alpha}\neq 0$ are *not* restrictions on the geometry in the nonlinear case. One of the three elements $\hat{P}_{Kx}$, $\hat{P}_{Ky}$, or $\hat{P}_{Kz}$ is nonzero since atom K and atom N do not have the same center; thus $\hat{P}_{K\alpha}\neq 0$ for some α. For some atom J the atoms N, K, and J are not collinear by assumption. Then if

$$\frac{\hat{P}_{K\alpha}}{\hat{P}_{J\alpha}}=\frac{\hat{P}_{K\mu}}{\hat{P}_{J\mu}}$$

and

$$\frac{\hat{P}_{K\alpha}}{\hat{P}_{J\alpha}}=\frac{\hat{P}_{K\nu}}{\hat{P}_{J\nu}},\ \alpha\mu\nu=xyz,zxy,yzx,$$

the three atoms are collinear, contrary to assumption. Therefore we can let $\beta=\mu$ or ν depending on which of the above is not true. The consequences of the above conditions are presented in more detail in the Appendix.

To deal with the case of collinear centers we analyze Eq. (52) [instead of Eq. (50)] which yields 11 independent relations involving the same 21 Hessian integrals. The 10 independent integrals, as inferred from the echelon form of the coefficient matrix (again for $\hat{P}_{1y}\neq 0$), can be constructed by applying unique pairs of the differential elements ∂P_{1y}, ∂P_{2x}, ∂P_{2y}, and ∂P_{2z} to I. From here on, one follows the standard procedure to obtain all the remaining dependent Hessian integrals.

In general taking into account the 24 Hessian integrals $I_{N\alpha L\beta}$ obtainable from Eq. (47), one must calculate only six (ten for collinear centers) Hessian integrals explicitly out of the total of 45; the remaining 39 (35 for collinear centers) are obtained from the symmetry relations. In what follows we now give a slightly condensed description of the four- and two-center cases.

2. Four-center Hessian integrals

Equation (50) for this case produces 24 independent relations involving 45 Hessian integrals. From the echelon form of the coefficient matrix, the 21 independent Hessian integrals can be chosen to be constructed by applying all pairs of the differential elements ∂P_{1y}, ∂P_{2y}, ∂P_{2z}, ∂P_{3x}, ∂P_{3y}, and ∂P_{3z} to I ($\hat{P}_{1y}\neq 0$ and $\hat{P}_{1y}\hat{P}_{2z}-\hat{P}_{1z}\hat{P}_{2y}\neq 0$). The 24 dependent integrals can then be found in terms of these by using an analog of Eq. (42) in which the A(24×24) and B(24×21) matrices are straightforwardly obtained from the corresponding columns of the coefficient matrix.

For four collinear centers, Eq. (52) involves 17 relations. For $\hat{P}_{1y}\neq 0$ the 28 independent integrals are obtained by using all pairs of the differentials ∂P_{1y} and $\partial P_{K\alpha}$ ($K=2,3$; $\alpha=x,y,z$).

In summary, taking into account the additional 33 dependent Hessian integrals determined by Eq. (47), we conclude that out of the total of 78 Hessian integrals for $N=4$, only 21 (28 for collinear centers) need be calculated explicitly while the remaining 57 (50 for collinear centers) are determined through symmetry relations.

3. Two-center Hessian integrals

For this obviously collinear case, Eq. (52) gives five independent relations involving six Hessian integrals. For $\hat{P}_{1y}\neq 0$, the one independent integral can be chosen to be I_{1y1y} which determine the remaining five. Taking into account the additional 15 dependent integrals determined by Eq. (47), we conclude that out of a total of 21 Hessian integrals only one needs to be calculated explicitly.

IV. DISCUSSION AND CONCLUSION

In this paper we have given useful working relations which allow one to evaluate certain first and second integral derivatives in terms of others. With respect to the first deri-

vative or gradient integrals, the basic symmetry relations are embodied in Eqs. (37) and (38) [or Eq. (39) for collinear centers]. The $(3N-6)$ independent integral derivatives can be chosen to be of the form $I_{K\alpha}$, $I_{L\alpha}$, $I_{L\gamma}$, and $I_{J\mu}$ $(J=1,N-1;\mu=x,y,z;K\neq L\neq J)$ for nonlinear geometries. For linear geometries the $(3N-5)$ independent integral derivatives are of the form $I_{K\alpha}$ and $I_{J\mu}$ $(J=1,N-1;\mu=x,y,z;J\neq K)$. Though these choices are not unique they provide maximum flexibility in choosing the coordinates of the centers.

Similarly for the Hessian integral derivatives we have provided working results in Eqs. (47) and (50) [or Eq. (52) for collinear centers]. For nonlinear geometries, the $3N'(3N'+1)/2-(9N'-3)$ independent Hessian integrals $(N'=N-1)$ can be constructed from unique pairs of the differential elements $\partial P_{K\alpha}$, $\partial P_{L\alpha}$, $\partial P_{L\gamma}$, and $\partial P_{J\mu}$ $(J=1,N-1;\mu=x,y,z;K\neq L\neq J)$ acting on I. For collinear geometries on the other hand, the $\{3N'(3N'+1)/2-6N'+1\}$ independent Hessian integrals for $(P_{K\alpha}\neq 0)$ can be constructed from pairs of $\partial P_{K\alpha}$ and $\partial P_{J\mu}$ $(J=1,N-1;\mu=x,y,z;J\neq K)$ acting on I. The savings gained in computing second integral derivatives is very impressive. For the two- , three- , and four-center integral cases there exist a total of 21, 45, and 78 second derivatives of which only 1, 6, and 21 need to be explicitly evaluated!

Obtaining relations among the third and higher derivatives of integrals is straightforward. If $\hat{S}^{(n)}$ refers to the nth order representation of the symmetry operation $\hat{T}$ or $\hat{R}$, and $I^{(n)}$, denotes the nth nuclear derivative of the integral, then a complete set of relations of the nth derivative come from the combinations $S^{(n)}I^{(0)}$, $S^{(n-1)}I^{(1)},\ldots,S^{(1)}I^{(n-1)}$. In particular considering the case of third derivative integrals, from the total of $M=3N(3N+1)(3N+2)/3!$ such integrals, $M'=N'(N'+1)(N'+2)/3!$ are independent, where $N'=(3N-6)$ [or $(3N-5)$ for collinear centers]. Taking the cue from the gradient and Hessian integrals, the translational conditions $\hat{T}^{(1)}I^{(2)}$ determine the integrals $I_{N\alpha J\mu L\nu}$ $(J,L=1,N)$ while the rotational conditions $\hat{R}^{(1)}I^{(2)}$ yield

$$\sum_{K=1}^{N-1}(\hat{P}_{K\alpha}I_{K\beta J\mu L\nu}-\hat{P}_{K\beta}I_{K\alpha J\mu L\nu})=I_{\alpha\beta J\mu L\nu},$$
$$\alpha\beta=xy,yz,zx,$$
$$\mu,\nu=x,y,z,$$
$$J,L=1,N-1;(J\mu)\geqslant(L\nu).$$

For $\hat{P}_{K\alpha}\neq 0$ the M' independent third derivative integrals can be obtained from unique combinations of N' differential elements

$$\partial P_{K\alpha},\partial P_{J\alpha},\partial P_{J\beta},\partial P_{L\mu}(L=1,N-1;\mu=x,y,z;K\neq J\neq L).$$

The integral derivatives needed for *ab initio* quantum chemical applications involve the contracted Gaussian functions. Since the contractions (linear combinations) are performed over the *same* center and because the derivative $\nabla^{(n)}$ is a linear operator, the derivatives of contracted-Gaussian based integrals are easily obtained $\nabla^{(n)}I(i,j,k,l)=\Sigma_{\mu\nu\lambda\sigma}C_{\mu i}C_{\nu j}C_{\lambda K}C_{\sigma l}\nabla^{(n)}I(\mu\nu\lambda\sigma)$, where $I(\mu\nu\lambda\sigma)$ refers to the orbital indices of the integral involving primitive Gaussians. That means, for the integral set $\{I(\mu\nu\lambda\sigma)\}$ which maps onto the contracted integral $I(ijkl)$, if $\{I(\mu\nu\lambda\sigma)\}$ is dependent (independent) so is $I(ijkl)$. Dupuis *et al.*[3] and Vincent *et al.*[8] have suggested, for translational and rotational invariance, that a sum over all the derivatives arising from four shells of integrals multiplied by the appropriate density matrix element be used instead of the individual integrals. This approach greatly reduces the number of times that invariance conditions must be applied.

Although the set of first- and second-order relations obtained here are based upon the straightforward application of the translational and rotational invariance of any integral (or integral derivative), the identification of the independent and dependent variables as well as the determination of the number of independent equations required substantial analysis. In fact, the reduction of the working equations, via elementary row operations, to generate lower row-echelon and ultimately reduced row-echelon forms became sufficiently complicated in the three- and four-center second integral derivative cases that these operations were carried out analytically on the computer using the algebraic programming language REDUCE.[12] In particular the nontransparent relations given in Eq. (49) were discovered using REDUCE. Also the REDUCE codes were used to check our hand evaluations for the first derivative and two-center second derivative cases.

ACKNOWLEDGMENTS

The authors wish to acknowledge the National Science Foundation (grant no. 8206845) and the Army Research Office (Grant No. DAAG2984K0086) for their support.

APPENDIX

In what follows we are using the three-center case as an example. The N-center case is completely analogous and we will simply state the general case. For quantum chemical integrals $N\leqslant 4$, but we do not make that restriction in the following.

Equation (50) is a system of linear equations. In Table I we give the coefficient matrix for the three-center case where we have used the abbreviation μ_J for $\hat{P}_{J\mu}$. The variable names have been written above each column, and we have used $E_{\alpha\beta J\mu}$ to label the relations on the left of the matrix. The right-hand side of $E_{\alpha\beta J\mu}$ is $I_{\alpha\beta J\mu}$. It should be noted that E_{zx1x}, E_{xy1z}, and E_{zx1z} have been removed since we have earlier shown them to be redundant.

One method of solving the relations is Gaussian elimination. The first 11 rows are already in upper triangular form and would not be changed in the downward reduction. The bottom four relations, however, would be transformed. In general there will be $3(N-2)+1$ analogous relations for N-center case $(N\geqslant 3)$, and in general these will be transformed by downward elimination into

$$\sum_{K=2}^{N-1}C_{Kzx}I_{KyJ\mu}+\sum_{K=2}^{N-1}C_{Kxy}I_{KzJ\mu}+\sum_{K=2}^{N-1}C_{Kyz}I_{KxJ\mu}=\hat{P}_{1z}I_{xyJ\mu}+\hat{P}_{1y}I_{zxJ\mu}+\hat{P}_{1x}I_{yzJ\mu},$$
$$J\mu=1y,L\nu,\quad L=2,N-1;\ N=3,4,\ldots,\quad \nu=x,y,z, \tag{53}$$

TABLE I. The coefficient matrix for the three center rotational invariance conditions.

	I_{1x1x}	I_{1x1z}	I_{1x2x}	I_{1x2z}	I_{1x1y}	I_{1y1z}	I_{1x2y}	I_{1x2z}	I_{2x2x}	I_{1z2z}	I_{2x2y}	I_{1y2x}	I_{1y2z}	I_{2y2x}	I_{2x2z}	I_{1y1y}	I_{1y2y}	I_{2y2y}
E_{xy1x}	$-Y_1$	0	$-Y_2$	0	X_1	0	X_2	0	0	0	0	0	0	0	0	0	0	0
E_{yz1x}	0	Y_1	0	0	$-Z_1$	0	$-Z_2$	Y_2	0	0	0	0	0	0	0	0	0	0
E_{yz1z}	0	0	0	0	0	$-Z_1$	0	0	Y_2	0	0	0	0	0	0	0	0	0
E_{xy2x}	0	0	$-Y_1$	0	0	0	0	0	0	$-Y_2$	X_2	X_1	0	0	0	0	0	0
E_{yz2x}	0	0	0	Y_1	0	0	0	0	0	0	$-Z_2$	$-Z_1$	0	0	0	0	0	0
E_{xy1y}	0	0	0	0	$-Y_1$	0	0	0	0	0	0	$-Y_2$	0	Y_2	0	X_1	X_2	0
E_{yz1y}	0	0	0	0	0	Y_1	0	0	0	0	$-Y_2$	0	0	0	0	$-Z_1$	$-Z_2$	0
E_{xy2y}	0	0	0	0	0	0	$-Y_1$	0	0	0	0	0	X_1	X_2	0	0	X_1	X_2
E_{yz2y}	0	0	0	0	0	0	0	Y_1	0	0	0	0	$-Z_1$	$-Z_2$	Y_2	0	$-Z_1$	$-Z_2$
E_{xy2z}	0	0	0	0	0	0	0	0	$-Y_2$	Y_1	0	0	$-X_1$	$-X_2$	0	0	0	0
E_{yz2z}	0	0	0	0	0	0	0	$-Y_1$	0	0	0	0	0	0	$-Y_2$	0	0	0
E_{zx2x}	0	0	Z_1	0	0	0	0	0	Z_2	0	0	$-X_2$	0	0	0	0	0	0
E_{zx2z}	0	0	0	$-X_1$	0	0	0	0	0	Z_1	Z_2	0	0	0	0	0	0	0
E_{zx1y}	0	0	0	0	Z_1	$-X_1$	0	0	0	0	0	0	$-X_2$	0	0	0	0	0
E_{zx2y}	0	0	0	0	0	0	Z_1	$-X_1$	0	0	0	0	0	$-X_2$	0	0	0	0
E_{xz2z}	0	0	0	0	0	0	0	0	Z_1	$-X_1$	0	0	0	0	$-X_2$	0	0	0

where we have introduced the notation

$$C_{K\alpha\beta} = \hat{P}_{1\alpha}\,\hat{P}_{K\beta} - \hat{P}_{1\beta}\,\hat{P}_{K\alpha}, \quad \alpha\beta = xy, yz, zx.$$

For the three-center case $J\mu$ takes the four values $1y, 2x, 2y, 2z$.

For the linear case Eq. (53) yields the trivial relation $0 = 0$. Since the two-center case is always linear there is no analogous set of relations. For the nonlinear case at least one of the terms of the left-hand side of Eq. (53) will be nonzero.

Let us assume for example that $(\hat{P}_{1x}\,\hat{P}_{2y} - \hat{P}_{1y}\,\hat{P}_{2x})$ is nonzero. Then $I_{2zJ\mu}$ does not need to be calculated explicitly for each of the relations in Eq. (53). These relations can be applied in any order with one exception. To solve for I_{2z2z} ($J\mu = 2z$) requires knowing I_{2x2z} and I_{2y2z} which first need to be calculated from two of the other relations. It should be emphasized that in using downward elimination to arrive at Eq. (53) the only nonzero pivot element that was assumed was $\hat{P}_{1y}$.

Next let us look at rows 4–11 in Table I. These correspond in the general case to the relations

$$-\sum_{K=1}^{N-1}(\hat{P}_{Ky}\,I_{KxJ\mu} - P_{Kx}\,I_{KyJ\mu}) = I_{xyJ\mu}, \tag{54a}$$

$$\sum_{K=1}^{N-1}(\hat{P}_{Ky}\,I_{KzJ\mu} - \hat{P}_{Kz}\,I_{KyJ\mu}) = I_{yzJ\mu}, \tag{54b}$$

$$J\mu = 1y, L\nu, \quad \begin{matrix} L = 2, N-1; N = 2,3,4,\ldots, \\ \nu = x, y, z. \end{matrix}$$

For the two-center case the above yields two relations. For the three-center case we get eight relations. In general Eqs. (54) yield $6(N-2)+2$ relations. Since $\hat{P}_{1y} \neq 0$ Eq. (54a) can be solved for $I_{1xJ\mu}$ and Eq. (54b) for $I_{1zJ\mu}$. Thus these $6N-10$ integrals do not need to be explicitly calculated. Also these relations can be applied in any order. This can be seen for the three-center case from the diagonal block (row 4–11 and column 4–11) of Table I. This is true in general.

Next the first three rows of the coefficient matrix correspond to the relations

$$\sum_{K=1}^{N-1}(\hat{P}_{K\alpha}\,I_{K\beta\,1\mu} - \hat{P}_{K\beta}\,I_{K\alpha 1\mu}) = I_{\alpha\beta\,1\mu}, \tag{55}$$

$$\alpha\beta\mu = xyx, yzx, yzz.$$

These can be solved for I_{1x1x}, I_{1x1z}, and I_{1z1z}, respectively.

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