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Symmetry-adapted integral derivatives

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A procedure, based on double coset decompositions, is described for reducing formulas for derivatives (with respect to nuclear coordinates) of integrals over symmetry-adapted orbitals to symmetry-distinct integral derivatives over atomic orbitals. The procedure is applicable to any finite point group and to integral derivatives of any order.

Key words: Analytical derivatives — Symmetry — Integral Processing — Coupled perturbed methods — Double cosets

1. Introduction

The transformation of two-electron integrals from an atomic orbital (AO) to a molecular orbital (MO) basis is, formally, one of the most time-consuming steps in beyond-SCF calculations: its N^5 behavior (for N orbitals) has the highest power dependence of any step in the calculation, at least if the CI expansion is of single and double excitation type. Consequently, the exploitation of symmetry in the transformation is of vital importance in reducing the computational labor, which then behaves as N_m^5, where N_m is some average of the number of functions of each symmetry species [1]. Even one element of symmetry can effect an order of magnitude reduction in the total labor. Most commonly, this exploitation of symmetry involves the generation of integrals over symmetry-adapted orbitals (SO) as an intermediate step, using a list of symmetry-distinct AO integrals [1-4]. The transformation is then carried out from the SO basis to the MO basis. It is also possible to consider a scheme which bypasses the *explicit* generation of SO

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integrals, going directly from distinct AO integrals to MO integrals but retaining the advantages of symmetry blocking [5–7]. Whether SO integrals are formed explicitly or not, formulas for generating them from distinct AO integrals are required in developing a computational scheme; such formulas have been devised by a number of authors [2–4], but the most convenient and most elegant formulation is that of Davidson [3]. The latter work is based on double coset decompositions (DCD) and it is this approach that we shall follow in the present work.

While the symmetry processing and transformation of integrals has been explored in detail, there has been much less discussion of the transformation of integral *derivatives.* Integrals differentiated with respect to nuclear coordinates are required in "analytical derivative" schemes for computing molecular properties such as gradients and force constants (see, e.g. [8–11] and references therein). In many applications [8, 11–14], MO integral derivatives appear contracted with reduced density matrices in expressions which can be represented in a simple way as

$$\sum_p \sum_q \sum_r \sum_s P_{pqrs}[pq|rs]' \tag{1}$$

where the prime on the integral indicates differentiation (not necessarily only to first order) and P is the second-order reduced density matrix. The sum in (1) is over MO indices. Transforming P into the AO basis gives

$$\sum_\mu \sum_\nu \sum_\lambda \sum_\sigma P_{\mu\nu\lambda\sigma}[\mu\nu|\lambda\sigma]'. \tag{2}$$

By this means it is possible not only to avoid transforming the integral derivatives but also, by rewriting (2) in terms of *distinct* AO integral derivatives only [14], to avoid having to consider explicitly their symmetry properties. This procedure is described in detail in [14]. Obviously, this approach can also be used in cases in which P is a direct product of first-order reduced density matrices, as in SCF or GVB methods [15].

In expressions for more complicated cases, however, such as those which determine perturbed MCSCF or CI wave functions [11], terms such as

$$R_{pq} = \sum_r \sum_s \sum_t P_{prst}[qr|st]' \tag{3}$$

arise. This is obviously not the simple index contraction above, and it is not possible to approach the construction of R, say, in the straightforward manner of [14]. Indeed, it has recently been suggested [11] that there will be little alternative to transforming integral *derivatives* to the MO basis. As a consequence it is desirable to derive formulas for symmetry-adapted integral derivatives, that is, SO integral derivatives, in order to reduce the transformation labor as outlined above.

In order to achieve maximum simplicity in the formulas for SO integral derivatives we shall employ symmetry-adapted nuclear coordinates. It is simple to obtain final quantities, such as gradients or force constants, etc. in terms of the original nuclear coordinates if other computational considerations should require it [16].

In the following section we define a number of terms and discuss how SOs are generated from AOs and how differentiation operators act on AOs. In Sect. 3 formulas for one- and two-electron integral derivatives are derived in terms of distinct AO integral derivatives for any (finite) point group. In Sect. 4 these formulas are rewritten explicitly for the special case of D_{2h} and its subgroups: a number of programs restrict treatment of symmetry to these groups because of the many simplifications which ensue. Application of the methods of this work to higher derivatives is considered in Sect. 5 and conclusions are given in Sect. 6.

2. Definitions

In order to take maximum advantage of Davidson's work on SO integrals [3] we will use the same notation as far as possible. $\mathscr{G}$ denotes the molecular point group, which is restricted to be finite (of order $|\mathscr{G}|=g$) with elements G. For each nucleus A, B, $C\ldots$ in the molecule there exists a subgroup of $\mathscr{G}$, denoted $\mathscr{U}$, $\mathscr{V}$, $\mathscr{W}\ldots$ such that, e.g.

$$U\underline{r}_A=\underline{r}_A \forall U\in\mathscr{U} \tag{4}$$

where $\underline{r}_A$ is the position of A. Such a subgroup is termed the *stabilizer* of A [17], the order of the subgroup is denoted u.

The AO basis is assumed closed under $\mathscr{G}$ (this is invariably the case in practice) and each AO is then taken to be centered on a particular nucleus. The extension to AOs off the nuclear centers but "following" [8] (i.e. moving rigidly with) particular centers is straightforward. The AOs are assumed to be Cartesian or spherical harmonic Gaussian or Slater functions (that is, a product of a locally spherically symmetric radial function and some angular part). The ath AO on center A is denoted f_{aA}; the assumption of closure under $\mathscr{G}$ implies that f_{aA} transforms as

$$Uf_{aA}=\sum_U C_{\bar{a}aA}(U)f_{\bar{a}A},\ U\in\mathscr{U} \tag{5}$$

and

$$Gf_{aA}=\sum_G C_{\bar{a}aA}(G)f_{\bar{a}G(A)},\ G\in\mathscr{G} \tag{6}$$

where G transforms A into $G(A)$. Each $f_{\bar{a}A}$ is an AO with the same radial part as f_{aA} but possibly with different angular properties. For future reference we note that if $\mathscr{G}$ is D_{2h} or one of its subgroups $C_{\bar{a}aA}(G)$ becomes a parity factor which depends only on the angular type of the AO, not on its center, and can be denoted $p_a(U)$ $(=\pm 1)$. This differs from the notation used by Davidson [3], which appears to imply A dependence (not a dependence) of the parity factors.

SOs are generated from f_{aA} by applying projection (P^α_{ii}) and shift (P^α_{ir}) operators:

$$P^\alpha_{ii}=g^{-1}n_\alpha\sum_G D^\alpha_{ii}(G)^*G, \tag{7a}$$

$$P^\alpha_{ir}=g^{-1}n_\alpha\sum_G D^\alpha_{ir}(G)^*G. \tag{7b}$$

Here $\boldsymbol{D}^{\alpha}$ is one of a set of unitary irreducible representation (irrep) matrices for irrep α and n_{α} is the dimensionality of α. By operating with (7a, b) on f_{aA} we obtain

$$F_{aA\alpha ir} = P^{\alpha}_{ir} f_{aA} \tag{8}$$

where the SOs of species (α, i) are chosen as a linearly independent subset of the $F_{aA\alpha ir}$ (often by simply fixing on a particular r).

We introduce the double cosets $\mathcal{U}G\mathcal{V}$ for two subgroups $\mathcal{U}$ and $\mathcal{V}$ and $G \in \mathcal{G}$ [3, 18, 19]. Double cosets partition $\mathcal{G}$ into disjoint sets of elements - a *double coset decomposition* (DCD) [19] - in which each element occurs a fixed number of times (not necessarily only once, as in single cosets) for a particular G. This degeneracy is given by

$$\lambda_G = |\mathcal{U} \cap G\mathcal{V}G^{-1}| \tag{9}$$

which is the order of the subgroup $\mathcal{U} \cap G\mathcal{V}G^{-1}$, the stabilizer of the pair of nuclei A and $G(B)$. That is, any element of $\mathcal{U} \cap G\mathcal{V}G^{-1}$ leaves both A and $G(B)$ fixed. A set of *double coset representatives* (DCR) [19], denoted $\mathbb{R}$, consists of a set of operators R chosen one from each distinct double coset: with each $R \in \mathbb{R}$ there is a different degeneracy factor λ_R given by (9) with $G = R$. Sums over group elements G can be replaced by sums over elements of stabilizers and DCR, as in

$$P^{\alpha}_{ir} = g^{-1} n_{\alpha} \sum_{U} \sum_{V} \sum_{R} \lambda_R^{-1} D^{\alpha}_{ir}(URV)^* URV. \tag{10}$$

Here and in what follows a sum over R indicates a sum over elements of a particular set of DCR $\mathbb{R}$.

AO integral derivatives involve differentiation of AOs (or of operators) with respect to particular nuclear coordinates x_A, y_A, etc. Denoting the Cartesian direction by σ we use the symbol $\partial_{\sigma E}$, defined as

$$\partial_{\sigma E} = \partial / \partial \sigma_E, \tag{11}$$

as a convenient shorthand for the differentiation operator. Such operators are given in symmetry-adapted form as

$$\partial_{\sigma E \varepsilon m v} = g^{-1} n_{\varepsilon} \sum_{G} D^{\varepsilon}_{mv}(G)^* G \partial_{\sigma E} G^{-1}, \tag{12}$$

where $\partial_{\sigma E \varepsilon m v}$ behaves as an irreducible tensor operator of symmetry species (ε, m) [20]. A set of partner operators for this species is obtained by selecting a linearly independent subset of the $\partial_{\sigma E \varepsilon m v}$. Note that

$$G \partial_{\sigma E} G^{-1} = \sum_{\bar{\sigma}} C_{\bar{\sigma}\sigma E}(G) \partial_{\bar{\sigma} E}. \tag{13}$$

Now

$$\begin{aligned} \partial_{\sigma E} f_{aA} &= \delta_{AE} \partial_{\sigma A} f_{aA} \\ &= \delta_{AE} f^{\sigma}_{aA} \end{aligned} \tag{14}$$

using f^{σ}_{aA} for $\partial_{\sigma A} f_{aA}$. Hence

$$\begin{aligned}\partial_{\sigma E\varepsilon mv} G f_{aA} &= g^{-1} n_\varepsilon \sum_H D^{\varepsilon}_{mv}(H)^* H \partial_{\sigma E} H^{-1} G f_{aA} \\ &= g^{-1} n_\varepsilon \sum_H D^{\varepsilon}_{mv}(GH)^* GH \partial_{\sigma E} H^{-1} f_{aA} \\ &= g^{-1} n_\varepsilon \sum_H \sum_{\bar{m}} D^{\varepsilon}_{m\bar{m}}(G)^* D^{\varepsilon}_{\bar{m}v}(H)^* GH \partial_{\sigma E} H^{-1} f_{aA},\end{aligned} \tag{15}$$

using the rearrangement theorem [20] to replace H by GH in the sum over H. But

$$H \partial_{\sigma E} H^{-1} f_{aA} = 0, \text{ unless } E = A \text{ and } H \in \mathscr{U}, \tag{16}$$

hence

$$\partial_{\sigma E\varepsilon mv} G f_{aA} = \delta_{AE} g^{-1} n_\varepsilon \sum_U \sum_{\bar{\sigma}} \sum_{\bar{m}} D^{\varepsilon}_{m\bar{m}}(G)^* D^{\varepsilon}_{\bar{m}v}(U)^* C_{\bar{\sigma}\sigma A}(U) G f^{\bar{\sigma}}_{aA}. \tag{17}$$

For future use we define

$$\Lambda^{A\varepsilon}_{\bar{\sigma}\sigma\bar{m}v} = g^{-1} n_\varepsilon \sum_U D^{\varepsilon}_{\bar{m}v}(U)^* C_{\bar{\sigma}\sigma A}(U), \tag{18}$$

using which

$$\partial_{\sigma E\varepsilon mv} G f_{aA} = \delta_{AE} \sum_{\bar{\sigma}} \sum_{\bar{m}} D^{\varepsilon}_{m\bar{m}}(G)^* \Lambda^{A\varepsilon}_{\bar{\sigma}\sigma\bar{m}v} G f^{\bar{\sigma}}_{aA}. \tag{19}$$

Equation (19) and the use of the rearrangement theorem will play a key role in the elaboration of formulas for SO integral derivatives. The differentiation of one-electron operators which depend explicitly on the nuclear coordinates is considered below.

Finally, by analogy with (18), we define for future use

$$\Lambda^{A\alpha}_{\bar{a}a\bar{\imath}r}(G) = g^{-1} n_\alpha \sum_U D^{\alpha}_{\bar{\imath}r}(GU)^* C_{\bar{a}aA}(GU) \tag{20}$$

and

$$\Lambda^{R(B)\beta}_{\bar{b}b\bar{\jmath}s}(G) = g^{-1} n_\beta \sum_V D^{\beta}_{\bar{\jmath}s}(GRVR^{-1})^* C_{\bar{b}bR(B)}(GRVR^{-1}). \tag{21}$$

In (21) the sum over V in RVR^{-1} generates elements of $R\mathscr{V}R^{-1}$, the stabilizer of $R(B)$.

3. Derivatives of SO integrals

We first consider the simplest case of integrals over a one-electron operator which does not depend on the nuclear coordinates. Without loss of generality we can restrict treatment to symmetry-adapted operators $O_{\gamma kt}$ which transform as irreducible tensor operators of species (γ, k). Differentiation of the SO integral

$$\langle F_{aA\alpha ir} | O_{\gamma kt} | F_{bB\beta js} \rangle \tag{22}$$

gives

$$\langle \partial_{\sigma E\varepsilon mv} F_{aA\alpha ir} | O_{\gamma kt} | F_{bB\beta js} \rangle \tag{23a}$$

$$+ \langle F_{aA\alpha ir} | O_{\gamma kt} | \partial_{\sigma E\varepsilon mv} F_{bB\beta js} \rangle \tag{23b}$$

We shall proceed by expanding the SOs in (23) in terms of distinct AOs and then differentiating. The same results could be obtained by differentiating the SOs and then expanding, of course, but then the algebra becomes somewhat more complicated. Following Davidson's treatment [3] for integrals over 'non-symmetric operators' this gives for (23a)

$$\begin{aligned} &g^{-1}n_\alpha \sum_G D^\alpha_{ir}(G)\langle \partial_{\sigma E\varepsilon mv} Gf_{aA}|O_{\gamma kt}|GG^{-1}F_{bB\beta js}\rangle \\ &\quad = g^{-1}n_\alpha \sum_G \sum_{\bar{j}} D^\alpha_{ir}(G)D^\beta_{j\bar{j}}(G^{-1})\langle \partial_{\sigma E\varepsilon mv} Gf_{aA}|O_{\gamma kt}|GF_{bB\beta\bar{j}s}\rangle \end{aligned} \tag{24}$$

Using a DCD we have

$$F_{bB\beta\bar{j}s} = g^{-1}n_\beta \sum_U \sum_V \sum_R \lambda_R^{-1} D^\beta_{\bar{j}s}(U^{-1}RV)^* U^{-1}RVf_{bB}, \tag{25}$$

where we have replaced U with U^{-1} in (10). Substituting (25) in (24) gives

$$\begin{aligned} &g^{-2}n_\alpha n_\beta \sum_G \sum_U \sum_V \sum_R \sum_{\bar{j}} D^\alpha_{ir}(G)D^\beta_{j\bar{j}}(G)^*\lambda_R^{-1}D^\beta_{\bar{j}s}(U^{-1}RV)^* \\ &\quad \times \langle \partial_{\sigma E\varepsilon mv} Gf_{aA}|O_{\gamma kt}|GU^{-1}RVf_{bB}\rangle \end{aligned} \tag{26}$$

Using the rearrangement theorem [20] to replace the sum over G everywhere in (26) by GU gives

$$\begin{aligned} &g^{-2}n_\alpha n_\beta \sum_G \sum_U \sum_V \sum_R \sum_{\bar{j}} D^\alpha_{ir}(GU)D^\beta_{j\bar{j}}(GU)^* \\ &\quad \times \lambda_R^{-1}D^\beta_{\bar{j}s}(U^{-1}RV)^*\langle \partial_{\sigma E\varepsilon mv} GUf_{aA}|O_{\gamma kt}|GRVf_{bB}\rangle \\ &= g^{-2}n_\alpha n_\beta \sum_G \sum_U \sum_V \sum_R \sum_{\bar{\imath}} \sum_{\bar{j}} \lambda_R^{-1} D^\alpha_{i\bar{\imath}}(G)D^\alpha_{\bar{\imath}r}(U)D^\beta_{j\bar{j}}(G)^*D^\beta_{\bar{j}s}(RV)^* \\ &\quad \times C_{\bar{a}aA}(U)C_{\bar{b}bB}(RV)\langle \partial_{\sigma E\varepsilon mv} Gf_{\bar{a}A}|O_{\gamma kt}|Gf_{\bar{b}R(B)}\rangle \\ &= \sum_R \sum_a \sum_b \sum_i \sum_j \lambda_R^{-1}(\Lambda^{A\alpha}_{\bar{a}a\bar{\imath}r})^*\Lambda^{B\beta}_{\bar{b}b\bar{j}s}(R) \sum_G D^\alpha_{i\bar{\imath}}(G)D^\beta_{j\bar{j}}(G)^* \\ &\quad \times \langle \partial_{\sigma E\varepsilon mv} Gf_{\bar{a}A}|O_{\gamma kt}|Gf_{\bar{b}R(B)}\rangle, \end{aligned} \tag{27}$$

using (18) and (20). But from (19)

$$\langle \partial_{\sigma E\varepsilon mv} Gf_{\bar{a}A}|O_{\gamma kt}|Gf_{\bar{b}R(B)}\rangle = \delta_{AE} \sum_{\bar{m}} \sum_{\bar{\sigma}} D^\varepsilon_{m\bar{m}}(G)(\Lambda^{A\varepsilon}_{\bar{\sigma}\sigma\bar{m}v})^*\langle Gf^{\bar{\sigma}}_{\bar{a}A}|O_{\gamma kt}|Gf_{\bar{b}R(B)}\rangle, \tag{28}$$

giving for (23a)

$$\begin{aligned} &\delta_{AE} \sum_R \sum_{\bar{\imath}} \sum_{\bar{j}} \sum_{\bar{m}} \sum_{\bar{a}} \sum_{\bar{b}} \sum_{\bar{\sigma}} \lambda_R^{-1}(\Lambda^{A\alpha}_{\bar{a}a\bar{\imath}r})^*\Lambda^{B\beta}_{\bar{b}b\bar{j}s}(R)(\Lambda^{A\varepsilon}_{\bar{\sigma}\sigma\bar{m}v})^* \\ &\quad \times \sum_G D^\alpha_{i\bar{\imath}}(G)D^\beta_{j\bar{j}}(G)^*D^\varepsilon_{m\bar{m}}(G)\langle Gf^{\bar{\sigma}}_{\bar{a}A}|O_{\gamma kt}|Gf_{\bar{b}R(B)}\rangle. \end{aligned} \tag{29}$$

Now

$$\langle Gf^{\bar{\sigma}}_{\bar{a}A}|O_{\gamma kt}|Gf_{\bar{b}R(B)}\rangle = \langle f^{\bar{\sigma}}_{\bar{a}A}|G^{-1}O_{\gamma kt}G|f_{\bar{b}R(B)}\rangle, \tag{30}$$

and

$$G^{-1}O_{\gamma kt}G=\sum_{k} D_{k\bar{k}}(G^{-1})^{*}O_{\gamma\bar{k}t} \tag{31}$$

by definition [20], so by substituting (30) and (31) into (29) we obtain

$$\delta_{AE}\sum_{R}\sum_{\bar{\imath}}\sum_{\bar{\jmath}}\sum_{\bar{k}}\sum_{\bar{m}}\sum_{\bar{a}}\sum_{\bar{b}}\sum_{\bar{\sigma}}\lambda_{R}^{-1}(\Lambda_{\bar{a}a\bar{\imath}r}^{A\alpha})^{*}\Lambda_{\bar{b}b\bar{\jmath}s}^{B\beta}(R)(\Lambda_{\bar{\sigma}\sigma\bar{m}v}^{A\varepsilon})^{*}$$
$$\times\sum_{G} D_{i\bar{\imath}}^{\alpha}(G)D_{j\bar{\jmath}}^{\beta}(G)^{*}D_{m\bar{m}}^{\gamma}(G)D_{\bar{k}k}^{\varepsilon}(G)\langle f_{\bar{a}A}^{\bar{\sigma}}|O_{\gamma\bar{k}t}|f_{\bar{b}R(B)}\rangle. \tag{32}$$

Following a similar procedure for (23b) gives finally

$$\partial_{\sigma E\varepsilon mv}\langle F_{aA\alpha ir}|O_{\gamma kt}|F_{bB\beta js}\rangle$$
$$=\sum_{R}\sum_{\bar{\imath}}\sum_{\bar{\jmath}}\sum_{\bar{k}}\sum_{\bar{m}}\sum_{\bar{a}}\sum_{\bar{b}}\sum_{\bar{\sigma}}\lambda_{R}^{-1}(\Lambda_{\bar{a}a\bar{\imath}r}^{A\alpha})^{*}\Lambda_{\bar{b}b\bar{\jmath}s}^{B\beta}(R)$$
$$\times\sum_{G} D_{i\bar{\imath}}^{\alpha}(G)D_{j\bar{\jmath}}^{\beta}(G)^{*}D_{\bar{k}k}^{\gamma}(G)$$
$$\times\{\delta_{AE}D_{m\bar{m}}^{\varepsilon}(G)(\Lambda_{\bar{\sigma}\sigma\bar{m}v}^{A\varepsilon})^{*}\langle f_{\bar{a}A}^{\bar{\sigma}}|O_{\gamma\bar{k}t}|f_{\bar{b}R(B)}\rangle$$
$$+\delta_{R(B),E}D_{m\bar{m}}^{\varepsilon}(G)^{*}\Lambda_{\bar{\sigma}\sigma\bar{m}v}^{R(B)\varepsilon}\langle f_{aA}|O_{\gamma\bar{k}t}|f_{bR(B)}^{\bar{\sigma}}\rangle \tag{33}$$

for the derivative of an SO integral over an operator independent of the nuclear coordinates. Evidently, the sum over G of the product of representation matrix elements in (33) gives "selection rules" on the SO integral derivatives. For example, in the common case of γ the totally symmetric irrep $\alpha\otimes\varepsilon$ must contain β (whereupon $\beta\otimes\varepsilon$ contains α) for (33) to be non-vanishing.

In practice, the "translational invariance" of AO integrals (and their derivatives) [12, 13, 21-24] is used to reduce the number of integral derivatives that must be calculated. For (33) this means exploiting the relationship

$$\langle f_{\bar{a}A}^{\bar{\sigma}}|O_{\gamma\bar{k}t}|f_{\bar{b}R(B)}\rangle+\langle f_{\bar{a}A}|O_{\gamma\bar{k}t}|f_{\bar{b}R(B)}^{\bar{\sigma}}\rangle=0. \tag{34}$$

involving the two AO integral derivatives.

The case of an operator which depends on the nuclear coordinates is somewhat more complicated. Instead of $O_{\gamma kt}$ we consider an operator $O_{C\gamma kt}$ which is of symmetry species (γ, k) and is constructed from operators on nucleus C (and its transforms $G(C)$) according to

$$O_{C\gamma kt}=g^{-1}n_{\gamma}\sum_{G} D_{kt}^{\gamma}(G)^{*}GO_{C}G^{-1}. \tag{35}$$

$\mathscr{W}$ is the stabilizer of C. In

$$\partial_{\sigma E\varepsilon mv}\langle F_{aA\alpha ir}|O_{C\gamma kt}|F_{bB\beta js}\rangle$$
$$=\langle\partial_{\sigma E\varepsilon mv}F_{aA\alpha ir}|O_{C\gamma kt}|F_{bB\beta js}\rangle+\langle F_{aA\alpha ir}|O_{C\gamma kt}|\partial_{\sigma E\varepsilon mv}F_{bB\beta js}\rangle$$
$$+\langle F_{aA\alpha ir}|\partial_{\sigma E\varepsilon mv}O_{C\gamma kt}|F_{bB\beta js}\rangle, \tag{36}$$

the first two terms on the RHS may be handled by the technique used above for the operator $O_{\gamma kt}$. The third term is expanded by noting that

$$\begin{aligned}\partial_{\sigma E\varepsilon mv}O_{C\gamma kt} &= g^{-2}n_\gamma n_\varepsilon \sum_H \sum_J D^\gamma_{kt}(H)^* D^\varepsilon_{mv}(J)^* J\partial_{\sigma E}J^{-1}HO_CH^{-1} \\ &= g^{-2}n_\gamma n_\varepsilon \sum_H \sum_J \sum_n D^\gamma_{kt}(H)^* D^\varepsilon_{mn}(H)^* D^\varepsilon_{nv}(J)^* HJ\partial_{\sigma E}J^{-1}O_CH^{-1}.\end{aligned} \tag{37}$$

Clearly, the operator product $J\partial_{\sigma E}J^{-1}O_C$ vanishes unless $C = E$ and $J \in \mathscr{W}$, so that (37) may be rewritten as

$$\begin{aligned}&\delta_{CE}g^{-2}n_\gamma n_\varepsilon \sum_H \sum_W \sum_n \sum_{\bar\sigma} D^\gamma_{kt}(H)^* D^\varepsilon_{mn}(H)^* D^\varepsilon_{nv}(W)^* \times C_{\bar\sigma\sigma C}(W)HO^{\bar\sigma}_CH^{-1} \\ &= \delta_{CE}g^{-1}n_\gamma \sum_H \sum_n \sum_{\bar\sigma} D^\gamma_{kt}(H)^* D^\varepsilon_{mn}(H)^* \Lambda^{C\varepsilon}_{\bar\sigma\sigma nv}HO^{\bar\sigma}_CH^{-1},\end{aligned} \tag{38}$$

using the notation $O^{\bar\sigma}_C$ for $\partial O/\partial\bar\sigma_C$. If (38) is inserted in the third term of (36) and the SOs are expanded as above we find

$$\begin{aligned}&\langle F_{aA\alpha ir}|\partial_{\sigma E\varepsilon mv}O_{C\gamma kt}|F_{bB\beta js}\rangle \\ &\quad = \delta_{CE}g^{-1}n_\gamma \sum_R \sum_{\bar\imath} \sum_{\bar\jmath} \sum_n \sum_{\bar a} \sum_{\bar b} \sum_{\bar\sigma} \lambda^{-1}_R (\Lambda^{A\alpha}_{\bar a a\bar\imath r})^* \Lambda^{B\beta}_{\bar b b\bar\jmath s}(R)\Lambda^{C\varepsilon}_{\bar\sigma\sigma nv} \times \sum_G D^\alpha_{i\bar\imath}(G)D^\beta_{j\bar\jmath}(G)^* \\ &\quad \times \sum_H D^\gamma_{kt}(H)^* D^\varepsilon_{mn}(H)^* \langle Gf_{\bar aA}|HO^{\bar\sigma}_CH^{-1}|Gf_{\bar bR(B)}\rangle.\end{aligned} \tag{39}$$

This expression may be simplified further by replacing H with GH giving

$$\begin{aligned}&\delta_{CE}g^{-1}n_\gamma \sum_R \sum_{\bar\imath} \sum_{\bar\jmath} \sum_{\bar k} \sum_{\bar m} \sum_n \sum_{\bar a} \sum_{\bar b} \sum_{\bar\sigma} \lambda^{-1}_R (\Lambda^{A\alpha}_{\bar a a\bar\imath r})^* \Lambda^{B\beta}_{\bar b b\bar\jmath s}(R)\Lambda^{C\varepsilon}_{\bar\sigma\sigma nv} \\ &\quad \times \sum_G D^\alpha_{i\bar\imath}(G)D^\beta_{j\bar\jmath}(G)^* D^\gamma_{k\bar k}(G)^* D^\varepsilon_{m\bar m}(G)^* \\ &\quad \times \sum_H D^\gamma_{kt}(H)^* D^\varepsilon_{\bar mn}(H)^* \langle f_{\bar aA}|HO^{\bar\sigma}_CH^{-1}|f_{\bar bR(B)}\rangle.\end{aligned} \tag{40}$$

Note that if desired this form could be rewritten in terms of a symmetry-adapted differentiated operator transforming according to row $\bar k\bar m$ of the direct product representation $\gamma \otimes \varepsilon$.

If (40) is combined with the appropriate form of (33) to give the result of differentiating the SO, we finally obtain

$$\begin{aligned}&\partial_{\sigma E\varepsilon mv}\langle F_{aA\alpha ir}|O_{C\gamma kt}|F_{bB\beta js}\rangle \\ &\quad = g^{-1}n_\gamma \sum_R \sum_{\bar\imath} \sum_{\bar\jmath} \sum_{\bar k} \sum_{\bar m} \sum_{\bar a} \sum_{\bar b} \sum_{\bar\sigma} \lambda^{-1}_R (\Lambda^{A\alpha}_{\bar a a\bar\imath r})^* \Lambda^{B\beta}_{\bar b b\bar\jmath s}(R) \\ &\qquad \times \sum D^\alpha_{i\bar\imath}(G)D^\beta_{j\bar\jmath}(G)^* \\ &\qquad \times \{\delta_{AE}D^\gamma_{\bar kk}(G)^* D^\varepsilon_{m\bar m}(G)(\Lambda^{A\varepsilon}_{\bar\sigma\sigma\bar mv})^* \sum_H D^\gamma_{kt}(H)^* \langle f^{\bar\sigma}_{\bar aA}|HO_CH^{-1}|f_{\bar bR(B)}\rangle \\ &\qquad + \delta_{R(B),E}D^\gamma_{\bar kk}(G)^* D^\varepsilon_{m\bar m}(G)^* \Lambda^{R(B)\varepsilon}_{\bar\sigma\sigma\bar mv} \sum_H D^\gamma_{kt}(H)^* \langle f_{\bar aA}|HO_CH^{-1}|f^{\bar\sigma}_{\bar bR(B)}\rangle \\ &\qquad + \delta_{CE}D^\gamma_{k\bar k}(G)^* D^\varepsilon_{m\bar m}(G)^* \sum_n \Lambda^{C\varepsilon}_{\bar\sigma\sigma nv} \sum_H D^\gamma_{kt}(H)^* D^\varepsilon_{\bar mn}(H)^* \\ &\qquad \times \langle f_{\bar aA}|HO^{\bar\sigma}_CH^{-1}|f_{\bar bR(B)}\rangle.\end{aligned} \tag{41}$$

Transformed operators HOH^{-1} feature in (41) and (implicitly) in (33). In general, some AO integral derivatives generated by the sum over H will be redundant. Such redundancies can be eliminated, following Taylor [6], by replacing the sum over H with a DCD involving $\mathcal{W}$ (the stabilizer of C), $\mathcal{M}_R$, the stabilizer of the pair $(A, R(B))$, and a DCR set T. This is straightforward and will be omitted here, although it is of interest to point out that for O independent of the nuclear coordinate $\mathcal{W} = \mathcal{G}$ and the sum over elements of DCR $\mathbb{T}$ reduces to a single term, which is conveniently taken to be the identity operator.

The use of translational invariance is somewhat more complicated for integral derivatives involving $O_{C\gamma kt}$. The appropriate relationship is most easily obtained by considering the translational invariance of the AO integral $\langle H^{-1}f_{\bar{a}A}|O_C|H^{-1}f_{\bar{b}R(B)}\rangle$, giving

$$\sum_{\bar{\sigma}} C_{\bar{\sigma}\sigma C}(H)^*\langle f^{\bar{\sigma}}_{\bar{a}A}|HO_CH^{-1}|f_{\bar{b}R(B)}\rangle+\sum_{\bar{\sigma}} C_{\bar{\sigma}\sigma C}(H)\langle f_{\bar{a}A}|HO_CH^{-1}|f^{\bar{\sigma}}_{\bar{b}R(B)}\rangle$$
$$+\langle f_{\bar{a}A}|HO^{\sigma}_CH^{-1}|f_{\bar{b}R(B)}\rangle=0. \tag{42}$$

By using (42) it is possible to avoid explicit calculation of matrix elements of the differentiated operator O^{σ}_C. This is especially convenient when O_C is of complicated algebraic form (such as certain pseudopotential operators). Note that in any computationally efficient procedure for generating AO integral derivatives all three Cartesian directions σ would be handled together, so all contributions that might arise in the first two terms of (42) would be available simultaneously.

A two electron integral (over the totally symmetric operator r_{12}^{-1}) over SOs is

$$[F_{aA\alpha ir}F_{bB\beta js}|F_{cC\gamma kt}F_{dD\delta lu}], \tag{43}$$

using charge density notation. Differentiation gives four terms:

$$[\partial_{\sigma E\varepsilon mv}F_{aA\alpha ir}F_{bB\beta js}|F_{cC\gamma kt}F_{dD\delta lu}]$$
$$+[F_{aA\alpha ir}\partial_{\sigma E\varepsilon mv}F_{bB\beta js}|F_{cC\gamma kt}F_{dD\delta lu}]$$
$$+[F_{aA\alpha ir}F_{bB\beta js}|\partial_{\sigma E\varepsilon mv}F_{cC\gamma kt}F_{dD\delta lu}]$$
$$+[F_{aA\alpha ir}F_{bB\beta js}|F_{cC\gamma kt}\partial_{\sigma E\varepsilon mv}F_{dD\delta lu}]. \tag{44}$$

If we expand the SOs in terms of distinct AOs [3] we obtain

$$\sum_R\sum_S\sum_T\sum_{\bar{a}}\sum_{\bar{b}}\sum_{\bar{c}}\sum_{\bar{d}}\sum_{\bar{\imath}}\sum_{\bar{\jmath}}\sum_{\bar{k}}\sum_{\bar{l}}\lambda_T^{-1}(\Lambda^{A\alpha}_{\bar{a}a\bar{\imath}r})^*\Lambda^{B\beta}_{\bar{b}b\bar{\jmath}s}(R)(\Lambda^{C\gamma}_{\bar{c}c\bar{k}t}(T))^*\Lambda^{D\delta}_{\bar{d}d\bar{l}u}(TS)$$
$$\times\sum_G D^{\alpha}_{i\bar{\imath}}(G)D^{\beta}_{j\bar{\jmath}}(G)^*D^{\gamma}_{k\bar{k}}(G)D^{\delta}_{l\bar{l}}(G)^*$$
$$\times\{[\partial_{\sigma E\varepsilon mv}Gf_{\bar{a}A}Gf_{\bar{b}R(B)}|Gf_{\bar{c}T(C)}Gf_{\bar{d}TS(D)}]$$
$$+[Gf_{\bar{a}A}\partial_{\sigma E\varepsilon mv}Gf_{\bar{b}R(B)}|Gf_{\bar{c}T(C)}Gf_{\bar{d}TS(D)}]$$
$$+[Gf_{\bar{a}A}Gf_{\bar{b}R(B)}|\partial_{\sigma E\varepsilon mv}Gf_{\bar{c}T(C)}Gf_{\bar{d}TS(D)}]$$
$$+[Gf_{\bar{a}A}Gf_{\bar{b}R(B)}|Gf_{\bar{c}T(C)}\partial_{\sigma E\varepsilon mv}Gf_{\bar{d}TS(D)}]\}. \tag{45}$$

Here $R \in \mathbb{R}$, a set of DCR for subgroups $\mathscr{U}$ and $\mathscr{V}$, $S \in \mathbb{S}$, a set of DCR for $\mathscr{W}$ and $\mathscr{X}$ (stabilizers of C and D respectively), and $T \in \mathbb{T}$, a set of DCR for subgroups $\mathscr{M}_R$ and $\mathscr{N}_S$, stabilizers of the pairs $(A, R(B))$ and $(C, S(D))$ respectively. Using (19) the four terms in braces in (45) can be written as

$$\begin{aligned}
\sum_{\bar{m}} \sum_{\bar{\sigma}} \{ & \delta_{AE} D^{\varepsilon}_{m\bar{m}}(G)(\Lambda^{A\varepsilon}_{\bar{\sigma}\sigma\bar{m}v})^{*}[Gf^{\bar{\sigma}}_{\bar{a}A} Gf_{\bar{b}R(B)} | Gf_{\bar{c}T(C)} Gf_{\bar{d}TS(D)}] \\
& + \delta_{R(B),E} D^{\varepsilon}_{m\bar{m}}(G)^{*} \Lambda^{R(B)\varepsilon}_{\bar{\sigma}\sigma\bar{m}v}[Gf_{\bar{a}A} Gf^{\bar{\sigma}}_{\bar{b}R(B)} | Gf_{\bar{c}T(C)} Gf_{\bar{d}TS(D)}] \\
& + \delta_{T(C),E} D^{\varepsilon}_{m\bar{m}}(G)(\Lambda^{T(C)\varepsilon}_{\bar{\sigma}\sigma\bar{m}v})^{*}[Gf_{\bar{a}A} Gf_{\bar{b}R(B)} | Gf^{\bar{\sigma}}_{\bar{c}T(C)} Gf_{\bar{d}TS(D)}] \\
& + \delta_{TS(D),E} D^{\varepsilon}_{m\bar{m}}(G)^{*} \Lambda^{TS(D)\varepsilon}_{\bar{\sigma}\sigma\bar{m}v}[Gf_{\bar{a}A} Gf_{\bar{b}R(B)} | Gf_{\bar{c}T(C)} Gf^{\bar{\sigma}}_{\bar{d}TS(D)}]\}
\end{aligned} \tag{46}$$

The operation of G in the integral derivatives is simply to transform all four functions appearing in the integral simultaneously, and thus leaves the value of the integral unaffected. Eliminating these operators and substituting (46) into (45) gives

$$\begin{aligned}
& \partial_{\sigma E\varepsilon m}[F_{aA\alpha ir} F_{bB\beta js} | F_{cC\gamma kt} F_{dD\delta lu}] \\
& \quad = \sum_{R} \sum_{S} \sum_{T} \lambda^{-1}_{T} \sum_{\bar{a}} \sum_{\bar{b}} \sum_{\bar{c}} \sum_{\bar{d}} \sum_{\bar{\sigma}} \sum_{\bar{\imath}} \sum_{\bar{\jmath}} \sum_{\bar{k}} \sum_{\bar{l}} \sum_{\bar{m}} (\Lambda^{A\alpha}_{\bar{a}a\bar{\imath}r})^{*} \\
& \quad \times \Lambda^{B\beta}_{\bar{b}b\bar{\jmath}s}(R)(\Lambda^{C\gamma}_{\bar{c}ck t}(T))^{*} \Lambda^{D\delta}_{\bar{d}d\bar{l}u}(TS) \\
& \quad \times \sum_{G} D^{\alpha}_{i\bar{\imath}}(G) D^{\beta}_{j\bar{\jmath}}(G)^{*} D^{\gamma}_{k\bar{k}}(G) D^{\delta}_{l\bar{l}}(G)^{*} \\
& \quad \times \{\delta_{AE} D^{\varepsilon}_{m\bar{m}}(G)(\Lambda^{A\varepsilon}_{\bar{\sigma}\sigma\bar{m}v})^{*}[f^{\bar{\sigma}}_{\bar{a}A} f_{\bar{b}R(B)} | f_{\bar{c}T(C)} f_{\bar{d}TS(D)}] \\
& \quad + \delta_{R(B),E} D^{\varepsilon}_{m\bar{m}}(G)^{*} \Lambda^{R(B)\varepsilon}_{\bar{\sigma}\sigma\bar{m}v}[f_{\bar{a}A} f^{\bar{\sigma}}_{\bar{b}R(B)} | f_{\bar{c}T(C)} f_{\bar{d}TS(D)}] \\
& \quad + \delta_{T(C),E} D^{\varepsilon}_{m\bar{m}}(G)(\Lambda^{T(C)\varepsilon}_{\bar{\sigma}\sigma\bar{m}v})^{*}[f_{\bar{a}A} f_{\bar{b}R(B)} | f^{\bar{\sigma}}_{\bar{c}T(C)} f_{\bar{d}TS(D)}] \\
& \quad + \delta_{TS(D)} D^{\varepsilon}_{m\bar{m}}(G)^{*} \Lambda^{TS(D)\varepsilon}_{\bar{\sigma}\sigma\bar{m}v}[f_{\bar{a}A} f_{\bar{b}R(B)} | f_{\bar{c}T(C)} f^{\bar{\sigma}}_{\bar{d}TS(D)}]\}.
\end{aligned} \tag{47}$$

Alternatively, (47) can be obtained by applying G^{-1} to the four integral derivatives in braces in (45), followed by expanding as in (46).

In both the one- and two-electron integral derivatives we have tacitly ignored the possibility that $\{f_{aA}\} = \{f_{bB}\}$, etc. In such cases the stabilizers can be expanded and the set of DCR required in a given case can be decreased. Full details are given by Davidson [3]. In addition, the number of independent integral derivatives is reduced by translational invariance [12, 13, 21-24]: the sum of the four AO integral derivatives appearing in the expression in braces in (47) is zero. Of course, the number of independent terms is reduced even further when nuclear centers coincide [21]. Clearly, the use of translational invariance to reduce the number of independent terms to be computed fits very simply into the symmetry treatment, just as for the one-electron cases discussed above. We have not considered additional savings arising from exploitation of rotational invariance [22-24], as this would introduce considerable complications - it should be noted, however, that in practice rotational invariance is usually invoked *after* derivatives have been contracted with reduced density matrices [23].

The final derivative expressions, (33), (41) and (47), may appear somewhat forbidding - this is hardly surprising given that the expressions for the SO integrals themselves are quite complicated [3]. A simple overview of the various terms in, say, (47) can be given: the Λ factors represent coefficients of the *linearly independent* $Gf_{\bar{a}A}$, etc, in the SOs $F_{aA\alpha i r}, \ldots$ [3], and of linearly independent *derivatives* $Gf_{\bar{a}A}^{\bar{\sigma}}$ in the differentiated SOs. The sum over G in the product of representation matrix elements gives selection rules for the SO integral derivatives. It is important to realize that (47) is very little more complicated than the formula for SO *integrals* [3]. In particular, the same sets of DCR, $\mathbb{R}$, $\mathbb{S}$ and $\mathbb{T}$, appear in the integrals and their derivatives, and consequently the program loop structure required to generate distinct AO integral derivatives and to combine them into SO integral derivatives will differ only trivially (in the inclusion of the extra Λ factors and the accounting for different selection rules) from that required for distinct AO integrals and their combination to give SO integrals. This is discussed further in the next section.

4. Integral derivatives for D_{2h} and its subgroups

The special case of D_{2h} and its subgroups not only brings great simplifications, but is of considerable practical importance, as few program systems explicitly use higher symmetries in beyond-SCF calculations. This case is therefore explored in some detail here.

Firstly, it should be observed that D_{2h} and all its subgroups are Abelian and all elements are of order two. As noted in Sect. 2 above the transformation matrix elements $C_{\bar{a}aA}(U)$ become $p_a(U) = \pm 1$. The presence of only one-dimensional irreps means that any irrep α of $\mathcal{G} \subseteq D_{2h}$ is subduced by a single irrep α_A of $\mathcal{U}$. The factor $\Lambda_a^{A\alpha}$ (obtained from (20)) is then zero unless f_{aA} is of the species α_A, when $\Lambda_a^{A\alpha} = ug^{-1}$ [3]. Secondly,

$$\begin{aligned} \lambda_R &= |\mathcal{U} \cap R\mathcal{V}R^{-1}| \\ &= |\mathcal{U} \cap \mathcal{V}| \end{aligned} \tag{48}$$

which is independent of which R is used. λ_R will therefore be written $\lambda_{\mathbb{R}}$. Also, it follows that the stabilizer of $R(B)$, $R\mathcal{V}R^{-1}$, is simply $\mathcal{V}$. Finally, it is convenient to introduce the symbol $I_{\alpha\beta\gamma\ldots}$ which is unity if $\alpha \otimes \beta \otimes \gamma \cdots$ is the totally symmetric irrep and zero otherwise. Note that

$$\sum_G \chi^\alpha(G) \times \chi^\beta(G) \times \chi^\gamma(G) \cdots = gI_{\alpha\beta\gamma\cdots} \tag{49}$$

We then obtain

$$\begin{aligned} \partial_{\sigma E\varepsilon}\langle F_{aA\alpha}|O_\gamma|F_{bB\beta}\rangle = \lambda_{\mathbb{R}}^{-1} uvg^{-2} I_{\alpha\beta\gamma\varepsilon} \sum_R p_b(R)\chi^\beta(R) \\ \times \{\delta_{AE} u\langle f_{aA}^\sigma|O_\gamma|f_{bB}\rangle + \delta_{R(B),E} v\langle f_{aA}|O_\gamma|f_{bB}^\sigma\rangle\} \end{aligned} \tag{50}$$

or the equivalent form

$$\begin{aligned} &\lambda_{\mathbb{R}}^{-1} uvg^{-3} I_{\alpha\beta\gamma\varepsilon} \sum_R p_b(R)\chi^\beta(R) \\ &\quad \times \sum_G \chi^\gamma(G)\{\delta_{AE} u\langle f_{aA}^\sigma|GOG^{-1}|f_{bR(B)}\rangle \\ &\quad + \delta_{R(B),E} v\langle f_{aA}|GOG^{-1}|f_{bR(B)}^\sigma\rangle\}. \end{aligned} \tag{51}$$

These integrals are non-vanishing only if f_{aA} is of symmetry α_A, etc. The form (51) is especially convenient for the use of translational invariance, as the sum of the two integrals in braces in (51) is zero for each G. The reduction from a sum over G using a DCD based on the subgroups $\mathcal{M} = \mathcal{U} \cap \mathcal{V}$ and $\mathcal{W}(= \mathcal{G})$ (stabilizer of O) is straightforward [6].

For an operator which depends on the nuclear coordinates

$$\begin{aligned}\partial_{\sigma E\varepsilon}\langle F_{aA\alpha}|O_{C\gamma}|F_{bB\beta}\rangle = \lambda_{\mathbb{R}}^{-1}uvg^{-3}I_{\alpha\beta\gamma\varepsilon}\sum_R p_b(R)\chi^\beta(R)\\ \times\sum_G \chi^\gamma(G)\{\delta_{AE}u\langle f_{aA}^\sigma|GO_CG^{-1}|f_{bR(B)}\rangle\\ +\delta_{R(B),E}v\langle f_{aA}|GO_CG^{-1}|f_{bR(B)}^\sigma\rangle\\ +\delta_{CE}w\chi^\varepsilon(G)\langle f_{aA}|GO_C^\sigma G^{-1}|f_{bR(B)}\rangle\}.\end{aligned} \tag{52}$$

Again, this could be rewritten in terms of matrix elements of $O_{C\gamma}$ and of $O_{C\delta}^\sigma$, where $\delta = \gamma \otimes \varepsilon$, but (52) makes the use of translational invariance more obvious, as

$$\langle f_{aA}^\sigma|GO_CG^{-1}|f_{bR(B)}\rangle + \langle f_{aA}|GO_CG^{-1}|f_{bR(B)}^\sigma\rangle + p_\sigma(G)\langle f_{aA}|GO_C^\sigma G^{-1}|f_{bR(B)}\rangle = 0. \tag{53}$$

A DCD can again be used to eliminate redundant terms generated in the sum over G.

For the two-electron case

$$\begin{aligned}&\partial_{\sigma E\varepsilon}[F_{aA\alpha}F_{bB\beta}|F_{cC\gamma}F_{dD\delta}]\\ &\quad= \lambda_{\mathbb{T}}^{-1}uvwxg^{-4}I_{\alpha\beta\gamma\delta\varepsilon}\sum_R\sum_S\sum_T \chi^\beta(R)\chi^\gamma(T)\chi^\delta(TS)\\ &\qquad\times p_b(R)p_c(T)p_d(TS)\\ &\qquad\times\{\delta_{AE}u[f_{aA}^\sigma f_{bR(B)}|f_{cT(C)}f_{dTS(D)}]\\ &\qquad+\delta_{R(B),E}v[f_{aA}f_{bR(B)}^\sigma|f_{cT(C)}f_{dTS(D)}]\\ &\qquad+\delta_{T(C),E}w[f_{aA}f_{bR(B)}|f_{cT(C)}^\sigma f_{dTS(D)}]\\ &\qquad+\delta_{TS(D),E}x[f_{aA}f_{bR(B)}|f_{cT(C)}f_{dTS(D)}^\sigma]\}.\end{aligned} \tag{54}$$

The sum of the four integral derivatives in the braces in (54) is zero. To see how little extra complication in the symmetry processing is introduced as a result of differentiating, (54) may be compared with the corresponding SO integral formula [3]:

$$\begin{aligned}&[F_{aA\alpha}F_{bB\beta}|F_{cC\gamma}F_{dD\delta}]\\ &\quad= \lambda_{\mathbb{T}}^{-1}uvwxg^{-3}I_{\alpha\beta\gamma\delta}\sum_R\sum_S\sum_T \chi^\beta(R)\chi^\gamma(T)\chi^\delta(TS)\\ &\qquad\times p_b(R)p_c(T)p_d(TS)[f_{aA}f_{bR(B)}|f_{cT(C)}f_{dTS(D)}].\end{aligned} \tag{55}$$

Clearly, there is no difference between (54) and (55) in the loops over DCR elements R, S and T, and therefore there will be no difference in the loop structures of programs based on (54) and (55). Only the factors outside the loops and the weight factors which appear with each of the four different integral derivatives are different.

5. Higher derivatives

The techniques used in Sects. 3 and 4 can be extended readily to higher derivatives, although for arbitrary finite point groups the manipulations are tedious and the results lengthy. As a simple example we give the second derivative of an SO two-electron integral in D_{2h} symmetry:

$$\begin{aligned}
&\partial_{\tau F\zeta}\partial_{\sigma E\varepsilon}[F_{aA\alpha}F_{bB\beta}|F_{cC\gamma}F_{dD\delta}]\\
&\quad=\lambda_{\mathbb{T}}^{-1}uvwxg^{-5}I_{\alpha\beta\gamma\delta\varepsilon\zeta}\sum_R\sum_S\sum_T\chi^{\beta}(R)\chi^{\gamma}(T)\chi^{\delta}(TS)p_b(R)p_c(T)p_d(TS)\\
&\qquad\times\{u^2\delta_{AE}\delta_{AF}[f^{\sigma\tau}_{aA}f_{bR(B)}|f_{cT(C)}f_{dTS(D)}]\\
&\qquad+uv\delta_{AE}\delta_{R(B),F}[f^{\sigma}_{aA}f^{\tau}_{bR(B)}|f_{cT(C)}f_{dTS(D)}]\\
&\qquad+uw\delta_{AE}\delta_{T(C),F}[f^{\sigma}_{aA}f_{bR(B)}|f^{\tau}_{cT(C)}f_{dTS(D)}]\\
&\qquad+ux\delta_{AE}\delta_{TS(D),F}[f^{\sigma}_{aA}f_{bR(B)}|f_{cT(C)}f^{\tau}_{dTS(D)}]\\
&\qquad+uv\delta_{AF}\delta_{R(B),E}[f^{\tau}_{aA}f^{\sigma}_{bR(B)}|f_{cT(C)}f_{dTS(D)}]\\
&\qquad+v^2\delta_{R(B),E}\delta_{R(B),F}[f_{aA}f^{\sigma\tau}_{bR(B)}|f_{cT(C)}f_{dTS(D)}]\\
&\qquad+vw\delta_{R(B),E}\delta_{T(C),F}[f_{aA}f^{\sigma}_{bR(B)}|f^{\tau}_{cT(C)}f_{dTS(D)}]\\
&\qquad+vx\delta_{R(B),E}\delta_{TS(D),F}[f_{aA}f^{\sigma}_{bR(B)}|f_{cT(C)}f^{\tau}_{dTS(D)}]\\
&\qquad+uw\delta_{AF}\delta_{T(C),E}[f^{\tau}_{aA}f_{bR(B)}|f^{\sigma}_{cT(C)}f_{dTS(D)}]\\
&\qquad+vw\delta_{R(B),F}\delta_{T(C),E}[f_{aA}f^{\tau}_{bR(B)}|f^{\sigma}_{cT(C)}f_{dTS(D)}]\\
&\qquad+w^2\delta_{T(C),E}\delta_{T(C),F}[f_{aA}f_{bR(B)}|f^{\sigma\tau}_{cT(C)}f_{dTS(D)}]\\
&\qquad+wx\delta_{T(C),E}\delta_{TS(D),F}[f_{aA}f_{bR(B)}|f^{\sigma}_{cT(C)}f^{\tau}_{dTS(D)}]\\
&\qquad+ux\delta_{AF}\delta_{TS(D),E}[f^{\tau}_{aA}f_{bR(B)}|f_{cT(C)}f^{\sigma}_{dTS(D)}]\\
&\qquad+vx\delta_{R(B),F}\delta_{TS(D),E}[f_{aA}f^{\tau}_{bR(B)}|f_{cT(C)}f^{\sigma}_{dTS(D)}]\\
&\qquad+wx\delta_{T(C),F}\delta_{TS(D),E}[f_{aA}f_{bR(B)}|f^{\tau}_{cT(C)}f^{\sigma}_{dTS(D)}]\\
&\qquad+x^2\delta_{TS(D),E}\delta_{TS(D),F}[f_{aA}f_{bR(B)}|f_{cT(C)}f^{\sigma\tau}_{TS(D)}]\}.
\end{aligned}\tag{56}$$

For $\sigma=\tau$ there are only 10 independendent integral second derivatives out of the 16 terms in braces in (56). Further, translational invariance can be used to reduce the 16 terms to only 9 (or 10 to 7) [23, 24]. Again, it is clear from a comparison of (55) and (56) that the same program loop structure required for SO integrals can be used for second derivatives just as for first derivatives. This situation will hold in any order of differentiation, although the formulas become increasingly complicated, of course.

6. Conclusions

Formulas for derivatives of SO integrals with respect to symmetry-adapted nuclear coordinates have been derived in terms of symmetry-distinct AO integral derivatives. The procedure is applicable to any (finite) point group and to derivatives of any order: the same program structure used for symmetry processing in SO integral generation is used for derivatives. Full use of translational invariance can be made without any modification of the procedure. It is thus possible to obtain, straightforwardly, derivatives of SO integrals and then to transform these into the MO basis very efficiently. Indeed, the only modification required to a symmetry-blocked transformation program for handling integral derivatives is that needed to take account of different selection rules. Use of the results of this work to go directly from distinct AO integral derivatives to MO integral derivatives will be described elsewhere.

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7. References

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