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Molecular symmetry. II. Gradient of electronic energy with respect to nuclear coordinates

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Symmetry methods employed in the HONDO *ab initio* polyatomic SCF program are extended to the analytic computation of energy gradients. Validity of the Hellmann–Feynman theorem is not assumed, i.e., all two-electron contributions to the gradient are included explicitly. The method is geared to the efficient computation of entire blocks of two-electron integrals. Just one of a set of symmetrically related blocks must be computed. The gradient contribution from each unique block is multiplied by q_4, the number of equivalent blocks, and added into a "skeleton gradient vector," all other blocks are simply omitted. After processing molecular integrals, the true gradient vector is generated by projecting the symmetric component out of the skeleton vector. The analysis is based on Eqs. (26) and (33) which are valid for many variational wavefunctions including restricted closed shell and unrestricted open shell self-consistent field functions. We also extend the use of translational symmetry proposed previously by Morokuma *et al*. To illustrate the method, the gradient of the restricted SCF energy is computed for eclipsed ethane using a Pople-type 631G** basis and D_{3h} symmetry. The same calculation is repeated using various subgroups of D_{3h}. Computation times for SCF and for the gradient are each roughly inversely proportional to the order of the group, and for a given symmetry, the gradient computation takes about two and a half times as long as SCF.

I. INTRODUCTION

Pulay's work[1,2] in the early 1970's marked a revival of interest in the force method in quantum chemistry, i.e., in the direct computation of derivatives of molecular energy with respect to nuclear displacement. Formulas for second derivatives of the energy appear in the literature,[3] but only first derivatives (gradients) have received much attention. Gradients are currently being employed within the *ab initio* SCF formalism to optimize geometries of small molecules[4,5] and, by taking numerical derivatives of the analytically computed components of the gradient, to determine vibrational force constants.[1,2,6] McIver and Komornicki have developed powerful methods for locating saddle points on potential energy surfaces by minimizing the norm of the gradient.[4,7] This method, originally developed within a semiempirical formalism, has now been implemented at the *ab initio* level.[8] Other applications of gradient computations include the calculation of transition probabilities in Raman and infrared spectroscopy based on a mathematical identity (first brought to our attention by Professor J. W. McIver[9]) which relates the electric field dependence of the gradient to the dipole moment derivative. Closely related gradient calculations arise in correcting the Born–Oppenheimer approximation, i.e., in the evaluation of integrals over vibronic kinetic energy operators.[10]

All these applications are beyond the scope of this paper. Our purpose here is to develop methods for using point group symmetry to make gradient computations more efficient. Symmetry considerations are useful whenever the molecular system has two or more symmetrically equivalent atoms. This is quite common. In geometry optimization studies it is often advantageous to first seek the most stable structure with an assumed symmetry, after which one can investigate the effect of symmetry-breaking distortions. It is also possible to retain some elements of symmetry when computing vibrational force constants. For example, to compute the triply degenerate bending and stretching frequencies of a tetrahedral AB_4 molecule one need only reduce the symmetry from T_d to C_{3v}. Similarly, the doubly degenerate bending mode and the symmetric stretch can retain symmetries D_{2d} and T_d, respectively.[11]

In a previous paper,[12,13] hereafter referred to as paper I, we discussed symmetry methods used in the Gaussian SCF program HONDO,[5] and established the nomenclature and organization for the present analysis. Following Pople and co-workers,[14] we group orbital basis functions into shells, and two-electron integrals into blocks so that a block contains all integrals associated with a given set of four shells. This seemingly trivial organizational decision is actually very important for two reasons. It permits one to take advantage of the Rys polynomial method for efficiently computing an entire block of integrals,[15,16] and provides a natural indexing scheme for the direct product representation of the symmetry transformation matrices. To elaborate upon this last point consider the Hilbert subspace spanned by the basis functions of a given shell. The subspaces have higher symmetry than do the individual basis functions themselves. A subspace is invariant under rotation about an axis passing through the shell center, and a general point group operation simply permutes subspaces among themselves. It follows that a symmetry transformation matrix for the entire molecular basis set is a direct product of an intershell permutation matrix and an intrashell transformation ma-

trix. In 1970 Dacre[17] presented a simple algorithm for eliminating nonunique integrals when basis functions are simply permuted by point group operations. Although individual basis functions do not generally satisfy the Dacre permutation criterion, the shells do. Thus, the generalized Dacre method[12,18] provides a simple and general approach to the permutation symmetry.

Section V of this paper treats some additional considerations which further reduce computational labor. Among other things, we extend the use of translational symmetry of individual integrals discussed previously by Morokuma and co-workers.[8] This aspect of our analysis is applicable even to molecular systems possessing no point group symmetry at all. In Sec. VI we discuss the implementation of these ideas and report computation times for the gradient of an ethane RHF–SCF energy using the full D_{3h} symmetry and, alternatively, various subgroups. We also present some results concerning application of the generalized translational symmetry discussed in Sec. V.

II. FUNCTIONAL NOTATION

Let χ be a real Cartesian basis function

$$\chi(\mathbf{Q}, q, nx, ny, nz; \mathbf{r})$$
$$= (x - Q_x)^{nx}(y - Q_y)^{ny}(z - Q_z)^{nz} g_q(|\mathbf{r} - \mathbf{Q}|) \quad (1)$$

where nx, ny, and nz are nonnegative integers, $\mathbf{Q}$ is the center of the function (located on a nucleus), and $\mathbf{r}$ the argument of the function. The radial factor, g_q, is usually a linear combination of Gaussians

$$g_q(u) = \sum_p c_p \exp(-a_p u^2) , \quad (2)$$

where contraction coefficients, c_p, exponential parameters, a_p, and number of terms are all specified by the q index. We introduce the "rotational quantum number"

$$\lambda = nx + ny + nz , \quad (3)$$

and refer to a function as being of type s, p, d, etc. when λ equals $0, 1, 2$, respectively. The nomenclature in (1) is admittedly cumbersome, but sometimes we wish to focus attention on the location of the center, sometimes on the angular dependence, etc. so we may drop unimportant indices when it is felt that the meaning is obvious from context.

Let χ^h denote the first derivative of χ with respect to Q_x, Q_y, or Q_z when h equals 1, 2, or 3, respectively. Thus

$$\chi^2(\mathbf{Q}, q, nx, ny, nz; \mathbf{r}) = -ny\chi(\mathbf{Q}, q, nx, ny - 1, nz; \mathbf{r})$$
$$+ \chi(\mathbf{Q}, q', nx, ny + 1, nz; \mathbf{r}), \quad (4)$$

where

$$g_{q'}(u) = u^{-1} dg_q/du . \quad (5)$$

If (2) applies then $g_{q'}$ has that same form but with each c_p multiplied by $2a_p$. Basis functions are grouped into shells.[12,14] Functions in the same shell have the same $\mathbf{Q}$, q, and λ, so an alternative notation is

$$\chi(I, m) \equiv \chi(\mathbf{Q}_I, q_I, nx, ny, nz; \mathbf{r}) , \quad (6)$$

where I is the shell index and (λ_I, m) replaces (nx, ny, nz) according to any convention of choice. When $\gamma = 1$, let $m = 1$ denote $(1, 0, 0)$, and $m = 2$ denote $(0, 1, 0)$, etc. We insist that a shell be closed under any rotation about its own center, thus it includes all combinations (nx, ny, nz) consistent with the given λ_I. It follows that m takes on values $m = 1, 2, \ldots, M(\lambda_I)$, where

$$M(\lambda) = (\lambda + 1)(\lambda + 2)/2 . \quad (7)$$

(The analysis would not be seriously altered if one employed conventional angular momentum functions with $m = 1, 2, \ldots, 2l + 1$.) A simple alternative notation is

$$\chi_i = \chi(I, m) , \quad (8)$$

where all basis functions for the molecule are numbered from 1 to n and i is the mth index assigned to shell I.

III. SYMMETRY TRANSFORMATIONS

Let G be the point group of the molecule, and R an element of G. Operator $\hat{R}$ maps point $\mathbf{r}$ into $\mathbf{r}'$, function $f(\mathbf{r})$ into $f'(\mathbf{r})$, and shell I into I'. Shells I and I' have the same q and λ and their centers are related by

$$\mathbf{Q}_{I'} = \hat{R}\mathbf{Q}_I . \quad (9)$$

Basis function $\chi(I, m)$ maps into a linear combination of functions in shell I' given by

$$\hat{R}\chi(I, m) = \sum_{m'=1}^{M(\lambda)} \chi(I', m') R(\lambda_I; m', m) . \quad (10)$$

If $\lambda = 2$, for example, then $R(\lambda; m', m)$ is an element of a 6 by 6 matrix, $\mathbf{R}(2)$. Note that all D shells in the molecule transform according to the same $\mathbf{R}(2)$ matrix. Examples of $\mathbf{R}(\lambda)$ matrices are given in Eqs. (58)–(59) in paper I. Let a position vector in three-dimensional space be represented by a 3 by 1 column vector and let $\chi(I)$ be a 1 by $M(\lambda_I)$ row vector. Then (9) and (10) can be expressed as matrix products

$$\hat{R}\mathbf{Q} = \mathbf{R}(1)\mathbf{Q} \quad (11)$$

and

$$\hat{R}\chi(I) = \chi(I') \mathbf{R}(\lambda_I) . \quad (12)$$

Note that the $\mathbf{R}(1)$ matrix describes the rotation of either a point in space or of a P shell.

Consider the effect of a symmetry operation on a basis function derivative χ^h. First note that rotation and differentiation with respect to Q_x are noncommutative operations. To understand the rotational properties of χ^h let us express the derivative as a limit using the notation

$$\chi(\mathbf{Q}_I, m) \equiv \chi(I, m) . \quad (13)$$

Let $\mathbf{h}$ be a unit vector along the hth Cartesian axis, and

$$\chi^h(\mathbf{Q}, m) = \lim_{\epsilon \to 0} \epsilon^{-1}[\chi(\mathbf{Q} + \epsilon\mathbf{h}, m) - \chi(\mathbf{Q}, m)] . \quad (14)$$

To describe the effect of a symmetry operation on this function use (10) and recall that $\hat{R}$ is a linear operator.

$$\hat{R}\chi^h(\mathbf{Q}, m) = \lim_{\epsilon \to 0} \epsilon^{-1}\sum_{m'} [\chi(\hat{R}\mathbf{Q} + \epsilon\hat{R}\mathbf{h}, m')$$
$$- \chi(R\mathbf{Q}, m')]R(\lambda, m', m) . \quad (15)$$

According to (11) $\hat{R}h$ is a vector represented by the hth column of $\mathbf{R}(1)$, i.e.

$$\hat{R}h = \sum_{h'} h' R(1, h', h) , \tag{16}$$

where h is a unit vector along a Cartesian axis. Let I' be the image of shell I under this R so

$$\mathbf{Q} = \mathbf{Q}_I \text{ and } \hat{R}\mathbf{Q} = \mathbf{Q}_{I'} . \tag{17}$$

The quantity in square brackets in (15) can be expanded in terms of derivatives with respect to the new center

$$\chi(\mathbf{Q}_{I'} + \epsilon \hat{R}h, m') - \chi(\mathbf{Q}_{I'}, m')$$

$$= \epsilon \sum_{h'} \chi^{h'}(I', m') R(1, h', h) + O(\epsilon^2) . \tag{18}$$

Substituting (18) into (15) yields the desired derivative transformation formula

$$\hat{R}\chi^h(I, m) = \sum_{m'} \sum_{h'} \chi^{h'}(I', m') R(1, h', h) R(\lambda, m', m) . \tag{19}$$

IV. GRADIENT OF ELECTRON-REPULSION ENERGY

Hartree–Fock wavefunctions belong to the class of approximate solutions to the Schrödinger equation which satisfy the Hellmann–Feynman theorem. The theorem states that the gradient of the energy is a one-electron property.[19,20] Experience shows, however, that typical basis sets for SCF calculations lack the flexibility to remove the contribution from two-electron terms, and it is these terms that dominate the computational labor in computing gradients.[1,6] To simplify the analysis, we consider the gradient of just the electron-electron repulsion energy, E.

$$E = \sum_{ijkl} (ij \mid \mid kl) P_{ijkl} . \tag{20}$$

Each index in (20) runs independently from 1 to n in the notation of (8). Indices ij refer to the same particle.

$$(ij \mid \mid kl) = \langle \chi_i(1)\chi_j(1) \mid r_{12}^{-1} \mid \chi_k(2)\chi_l(2) \rangle . \tag{21}$$

For an unrestricted SCF wavefunction[21] the P_{ijkl} coefficients are obtained from the coefficients C_{ip}^α and C_{ip}^β of the pth alpha and beta-type occupied spinorbitals according to

$$P_{ijkl} = 8^{-1}(4D_{ij}^+ D_{kl}^+ - D_{ik}^+ D_{jl}^+ - D_{il}^+ D_{jk}^+ - D_{ik}^- D_{jl}^- - D_{il}^- D_{jk}^-) , \tag{22}$$

where $\mathbf{D}^\pm$ are the density matrices

$$D_{ij}^\pm = \sum_p (C_{ip}^\alpha C_{jp}^\alpha \pm C_{ip}^\beta C_{jp}^\beta) . \tag{23}$$

Note that D^- vanishes for RHF-SCF. Equation (22) implies that

$$P_{ijkl} = P_{jikl} = P_{ijlk} = P_{lkij} . \tag{24}$$

In the case of, say, an MCSCF wavefunction (20) still applies but (22) becomes more complicated. In any case (24) is valid when using real basis functions. Let x_α^h denote the hth coordinate of nucleus α. An element of the gradient vector is

$$E_\alpha^h \equiv \partial E / \partial x_\alpha^h . \tag{25}$$

It is well known[1] that derivatives of P_{ijkl} in (20) make no contribution to (25) for an SCF wavefunction. Epstein[20] points out that this result applies to a wide class of variational wavefunctions, namely, those for which the variation of P_{ijkl} due to a nuclear displacement is contained in the class of all "allowed variations" for which the wavefunction was optimized. In all such cases

$$E_\alpha^h = \sum_{ijkl} [(i^h j \mid \mid kl)\delta(\alpha, \alpha_i) + (ij^h \mid \mid kl)\delta(\alpha, \alpha_j)$$
$$+ (ij \mid \mid k^h l)\delta(\alpha, \alpha_k) + (ij \mid \mid kl^h)\delta(\alpha, \alpha_l)] P_{ijkl} , \tag{26}$$

where $(i^h j \mid \mid kl)$ is obtained by substituting χ_i^h for χ_i in (21). The Kronecker delta in (26) expresses the obvious fact that χ_i on nucleus α_i is unaffected by displacement of another center α.

In shell notation, (26) becomes a sum over eight indices: $I, J, K, L, m_i, m_j, m_k,$ and m_l. Let $\Delta E_\alpha^h(IJKL)$ denote the partial sum given by (26) but with i running over only the basis functions in shell I, j in J, etc. It is natural, therefore, to define $\Delta E_\alpha^h(IJKL)$ to be a sum over $m_i, m_j, m_k,$ and m_l and to use an appropriate notation for the P_{ijkl} coefficient:

$$\Delta E_\alpha^h(IJKL) = \sum_{m_i, m_j, m_k, m_l} [4 \text{ terms}] P(IJKL, m_i, m_j, m_k, m_l) . \tag{27}$$

In the language of paper I, (26) becomes a sum over G4, the grande list of four-labels.

$$E_\alpha^h = \sum_{G4} \Delta E_\alpha^h(IJKL) \tag{28}$$

For each four-label one computes twelve blocks of integrals, i.e., four for each h value. The number of integrals in a block is

$$M_{\text{block}} = M(\lambda_I) M(\lambda_J) M(\lambda_K) M(\lambda_L) . \tag{29}$$

Each block contributes to one and only one element of the gradient vector.

We now discuss how summation over G4 in (28) can be replaced by a sum over P4, the petite list of four-labels, just as was done[12] in the computation of the Fock matrix. Let $IJKL$ and $I''J''K''L''$ be equivalent four-labels under the direct product group $T_4 \times G$. As in paper I, T_4 is a group (of order eight) of index permutations corresponding to Dacre's[17] "trivial symmetries."

$$
\begin{array}{ccccc}
I & \xrightarrow{\hat{R}} & I' & \xrightarrow{\hat{T}} & I'' \\
J & \longrightarrow & J' & \longrightarrow & J'' \\
K & & K' & & K'' \\
L & & L' & & L''
\end{array} \tag{30}
$$

Let us compare contributions made to the gradient by equivalent four-labels. Inspection of (24) and (26)–(27) reveals that

$$\Delta E_\alpha^h(I'J'K'L') = \Delta E_\alpha^h(I''J''K''L'') , \tag{31}$$

so we need only compare $IJKL$ with $I'J'K'L'$. The unitary property of $\hat{R}$ leads immediately to

$$(i^h j \mid \mid kl) = \langle (\hat{R}\chi_i^h)(\hat{R}\chi_j) \mid r_{12}^{-1} \mid (\hat{R}\chi_k)(\hat{R}\chi_l) \rangle . \tag{32}$$

First substitute (10) and (19) into (32) and then (32) into the first term of (27). Make similar substitutions for the other three terms. At this point $\Delta E_\alpha^h(IJKL)$ is a sum over nine indices: m_i, m_i', m_j, m_j', m_k, m_k', m_l, m_l', and h. Summation over the unprimed m indices can be eliminated using the following equation (discussed below):

$$\sum_{m_i, m_j, m_k, m_l} R(\lambda_I, m_i', m_i) R(\lambda_J, m_j', m_j) R(\lambda_K, m_k', m_k)$$

$$\times R(\lambda_L, m_l', m_l) P(IJKL, m_i, m_j, m_k, m_l)$$

$$= P(I'J'K'L', m_i', m_j', m_k', m_l') . \qquad (33)$$

After summing over unprimed m indices, the remaining sums over primed m indices give $\Delta E_\alpha^{h'}(I'J'K'L')$, where R maps nucleus α into α'. Thus, we arrive at the useful result

$$\Delta E_\alpha^h(IJKL) = \sum_{h'} \Delta E_\alpha^{h'}(I'J'K'L') R(1, h', h) . \qquad (34)$$

For RHF–SCF (33) follows from (22) using either (8) or (42) in paper I, which were derived assuming that the electronic charge density transforms according to the completely symmetric representation of the point group. For UHF a similar argument applies if the alpha and beta densities are individually symmetric. In general, (33) implies a symmetric two-particle density matrix. We believe that (33) is widely applicable but make no attempt here to define the most general class of wavefunctions satisfying this condition. It should be pointed out, however, that for spatially degenerate states (spin degeneracy excluded) the symmetry of the charge density is generally lower than that of the nuclear framework,[22] for example, equilateral H_3 has ground state symmetry $^2E'$ under D_{3h}. In this case the methods of this paper could be used with point point $G = C_{2v}$, which is the maximum symmetry of the charge density.[23]

The significance of (34) is that it allows us to eliminate most of the terms in the summation of (28). Let $q_4(IJKL)$ be the number of four-labels equivalent to $IJKL$ under $T_4 \times G$. Let $I'J'K'L'$ be a representative member of the set for which one calculates $\Delta E_\alpha^{h'}(I'J'K'L')$ for all h and all α'. The set of all representative four-labels is the petite list, P4. A systematic procedure for generating contributions from the other equivalent $IJKL$ is to apply (34) for all operations in $T_4 \times G$ and then divide by $n(IJKL)$, where $n(IJKL)$ is the number of repetitions, i.e., the number of operations in $T_4 \times G$ that map $IJKL$ into itself. Equation (15) in paper I gives

$$n(IJKL) = 8g/q_4(IJKL) , \qquad (35)$$

where g is the order of G. According to (31) the factor of eight in (35) is cancelled by summation over T_4. Summation over R and h' can be performed outside the sum over shell labels. Thus one first calculates a "skeleton gradient vector" with elements

$$E_\alpha^{*h} = \sum_{P4} q_4(IJKL) \Delta E_\alpha^h(IJKL) . \qquad (36)$$

From this the true gradient is obtained by a final "symmetrization."

$$E_\alpha^h = g^{-1} \sum_R \sum_{h'} E_\alpha^{*h'} R(1, h', h) . \qquad (37)$$

In other words, the true gradient vector is obtained by projecting the completely symmetric component out of the skeleton gradient vector.

When G consists simply of the identity operation then $E_\alpha^{*h} = E_\alpha^h$, but (28) and (36) still differ due to trivial symmetries, i.e., shell labels run from 1 to N_{shell} independently of one another in (28) but occur only in "standard order" ($I \geq J$, $K \geq L$, etc.) in (36).

V. FURTHER SYMMETRY REDUCTION

In the preceding section it was shown that instead of summing over the entire G4 list of four-labels in (28) it is sufficient to sum over the much shorter P4 list using (36). According to (27), each term in (36) is itself a sum of $4M_{block}$ contributions. Let the four terms in square brackets in (26)–(27) be identified by an index t running from one to four. In this section we discuss additional relationships that allow us to eliminate certain t values. For example, for the water molecule it is never necessary to compute more than two of the four terms, and some four-labels in P4 require only one, and others none at all. There are two types of symmetry involved here. The first is completely general and derives from translational invariance of (21). The second depends upon the molecular point group and the particular four-label. We refer to this second kind as *subgroup symmetry*. A necessary but not sufficient condition for the presence of subgroup symmetry is that at least two of the $IJKL$ shell indices must be equivalent. For example, the second term in (27) is obviously equal to the first when $I = J$. (Equality of shell labels is a special case of equivalence.)

Consider a given four-label. For this $IJKL$ we define four vectors (in three-dimensional space). Let these vectors be $\Delta \mathbf{E}(t)$, $t = 1$ to 4. For example,

$$\Delta \mathbf{E}(1) = \sum_h \mathbf{h} \sum_{m_i, m_j, m_k, m_l} P(IJKL, m_i, m_j, m_k, m_l)$$

$$\times \langle \chi^h(I, m_i) \chi(J, m_j) | | \chi(K, m_k) \chi(L, m_l) \rangle . \qquad (38)$$

The given four-label makes a gradient contribution $\Delta \mathbf{E}(1)$ to nucleus α_I, $\Delta \mathbf{E}(2)$ to nucleus α_J, etc. Komornicki, Morokuma, and co-workers[8] have pointed out that translational invariance of an individual integral implies the relationship

$$(i^h j | | kl) + (ij^h | | kl) + (ij | | k^h l) + ij | | kl^h) = 0 . \qquad (39)$$

Substituting (39) into (38) leads to the conclusion that the following vectorial sum is zero:

$$\sum_{t=1}^{4} \Delta \mathbf{E}(t) = 0 . \qquad (40)$$

Any one of the centers associated with the given $IJKL$ can be eliminated using (40). For example, if all shells are on the same center then that four-label makes no contribution to the gradient. If shells I, J, and K share a common center, then we compute only the fourth term of (27) and make a contribution $\Delta \mathbf{E}(4)$ to nucleus α_L, and a contribution $-\Delta \mathbf{E}(4)$ to nucleus α_I. Note that both

contributions should be explicitly added into the skeleton vector, i.e., one contribution is not automatically generated from the other during symmetrization. Morokuma et al.[8] use (39) to eliminate the $t = 4$ term, but that is not the best tactic. In the above example that would eliminate only one term instead of three. There are yet other choices, for example, one could eliminate the t values on the center with the highest λ. In that way, one could compute a gradient for methane using a polarized basis set (p's on hydrogen and d's on carbon) without ever having to evaluate integrals over f functions since one would never differentiate the d-type basis functions on carbon. That does not impress us as recommending that tactic, however, since high angular momentum functions are easy to compute by the Rys polynomial method.[16] In fact, arguments can be advanced for eliminating the center with the smallest λ.

We comment in passing that the $\Delta \mathbf{E}(t)$ vectors also satisfy a relationship derived from rotational invariance of (21). In the special case of four S-type shells, the additional relation is

$$\sum_{t=1}^{4} \mathbf{Q}(t) \times \Delta \mathbf{E}(t) = 0 \ . \qquad (41)$$

Unlike (40), this equation by itself does not determine any one of the four vectors from knowledge of the other three, and we make no use of it.

Use of subgroup symmetry is a straightforward extension of the analysis leading from (28) to (36). Let S be the subgroup of $T_4 \times G$ which maps $IJKL$ into itself. The number of elements in S is given by (35). Each element is the product of an $R \in G$ and a $T \in T_4$. Let $G(IJKL)$ be the subgroup of G consisting of all R in S. Program HONDO[5] generates $G(IJKL)$ in the process of computing the q_4 factor. Note that a subgroup operation simply permutes the four shell indices. We say that $\Delta \mathbf{E}(1)$ is equivalent to $\Delta \mathbf{E}(2)$ if $I' = J$ for some $R \in G(IJKL)$. Similarly, we say that $\Delta \mathbf{E}(1)$ is equivalent to $\Delta \mathbf{E}(3)$ if $I' = K$, etc. It is necessary to compute only one member out of each set of equivalent vectors.[24]

Proof of these remarks concerning use of subgroup symmetry follows our earlier analysis. To be specific consider a molecule with symmetry T_d, and a four-label with subgroup C_2. An example is described in Fig. 1 where the pair of open circles refer to equivalent shells ($\lambda_J = \lambda_L$ and $q_J = q_L$), and the closed circles refer to another equivalent pair. Heavy lines connect shells occupied by the same particles. Two different two-fold axes of T_d are shown in the figure. Only the vertical axis belongs to the subgroup. The other two-fold axis rotates shell I into a closed circle on center J, which is not one of the shells in this four-label. Let R in (32) be the rotation about the vertical axis. Substitute (32) into (38), use (10), (19), (33), and (24). Note that $I'J'K'L' = KLIJ$. The result can be expressed in matrix form

$$\Delta \mathbf{E}(1) = \Delta \mathbf{E}(3)\mathbf{R}(1) \ , \qquad (42)$$

where $\Delta \mathbf{E}(t)$ is a 1 by 3 row vector. Similarly,

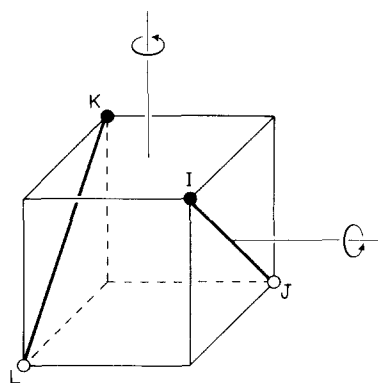$$\Delta \mathbf{E}(2) = \Delta \mathbf{E}(4)\mathbf{R}(1) \ . \qquad (43)$$

FIG. 1. Example of a four-label such that $I' = K$ and $J' = L$ under a subgroup operation.

Thus it is valid to omit terms $t = 1$ and 2 if one doubles the q_4 factor for the other two. Of course the skeleton vector then receives too large a contribution on center K and none on center I, but center I eventually recovers its proper share during symmetrization when the rotation in (42) is implicitly performed.

For any given four-label in P4 we can use either translational invariance or subgroup symmetry to eliminate certain t values, but it is not valid to use both for the same four-label. In the case discussed in the preceding paragraph, subgroup symmetry is more effective that translational symmetry in that it eliminates two terms instead of one.

VI. RESULTS

One of us (MD) has incorporated these ideas into a new version of HONDO that computes the gradient of a restricted or an unrestricted SCF energy.

Program organization

The SCF energy and density matrices are computed in an initial step using the methods of paper I, after which the gradient is computed as a separate (and optional) second step. The gradient computation does not use the SCF integral file, nor does it create another. Instead, each block of integrals is used as generated and then discarded thus eliminating a serious storage problem. The two-electron portion of the gradient program executes an outer loop over the petite list of four-labels in accordance with (36). For each unique $IJKL$ the appropriate block of P_{ijkl} coefficients is generated prior to looping over t labels. For each unique $\Delta \mathbf{E}(t)$ the program generates two intermediate blocks of integrals over shells of contracted Cartesian Gaussian functions and then performs an inner sum over the four m indices. For example, if $\lambda = 2$ for all four shells, and $t = 1$, then the program generates a $PDDD$ block and an $FDDD$ block where the P-shell employs the contraction coefficients of shell I but for the F-shell these are multiplied by factors of $2a_b$ in accordance with (5). Altogether there are $(3 + 10)6^3 = 2808$ integrals in these intermediate blocks. The $\Delta \mathbf{E}(1)$ vector is then obtained by summing over m indices using (38). Note that each term in this sum is a product of a P_{ijkl} factor and an

TABLE I. Computer time (in seconds) for SCF energy and gradient computations for eclipsed ethane.

Run No.	Point group	g	SCF 2-electron integrals	SCF 15 cycles	SCF total	2-electron gradient three t	2-electron gradient mini-mum t	Ratio grad SCF
1	D_{3h}	12	37	57	94	320	195	2.1
2	C_{3v}	6	70	82	152	586	365	2.4
3	C_{2v}	4	81	106	187	677	462	2.5
4	C_3	3	90	107	197	820	540	2.7
5	C_2	2	131	165	296	1158	786	2.7
6	$Cs(\sigma_h)$	2	135	169	304	1163	787	2.6
7	$Cs(\sigma_v)$	2	152	185	337	1306	893	2.6
8	C_1	1	251	302	553	2248	1540	2.8

$(i^h j \| kl)$ integral. The latter is obtained by picking the appropriate pair of integrals from the intermediate blocks and combining them as implied by (4). After looping over t, the $\Delta E(t)$ vectors are added into appropriate elements of the skeleton gradient vector. After looping over P4, one-electron contributions are added and symmetrization (37) is performed.

Computation times for ethane

Computations have been carried out for the C_2H_6 molecule in the eclipsed configuration with bond lengths CC = 1.54068 Å and CH = 1.08622 Å and angles HCH = 107.09° and CCH = 111.76°. We used a Pople-type 6-31G** split valence basis set with polarization functions. This is a $(10s, 4p, 1d/4s, 1p)$ primitive basis contracted to $[3s, 2p, 1d/2s, 1p]$ for a total of 20 shells and 60 spatial functions. Polarization function exponents were $\alpha_d = 0.8$ (on carbon) and $\alpha_p = 0.75$ (on hydrogen); other parameters were assigned standard values.[25] The RHF–SCF energy and its gradient were computed using the full D_{3h} symmetry, and the entire calculation was then repeated using seven different subgroups. Results of the eight calculations are in excellent agreement with one another, for example, each gives E_{SCF} = −79.2319981 Hartrees. Computation times are reported in Table I using an IBM 361/195 programmed in double precision. The program has been extensively tested for numerical precision, but some fine tuning of the code remains to be done for efficiency. Nonetheless, the effects of using point group symmetry are immediately evident upon inspection of the table.

The observed symmetry reductions for the SCF calculations are very much in line with results reported in paper I. SCF integral evaluation times (column four in the table) are roughly inversely proportional to the order of the group (column three). That this is not strictly true can be seen by comparing runs 5, 6, and 7 each of which involves just one element of symmetry. Four nuclei lie in the σ_v plane (run 7) so that this group element is not as effective as either the two-fold axis or the plane perpendicular to the C–C axis. Total SCF times corresponding to fifteen iterations are reported in column 6. Times reported in columns 7 and 8 include that for selecting the unique four-labels, evaluating two-electron integrals, forming the $\Delta E(t)$ vectors and adding them into the skeleton vector. This was carried out in

two different ways. Column 7 corresponds to using translational symmetry to eliminate the $t = 4$ term as discussed in Sec. V. Column 8 corresponds to eliminating the center with the largest number of shells. Subgroup symmetry was not used at all. Further programming improvements will probably reduce these gradient times somewhat. For example, a special subroutine is employed by the SCF program for SSSS-type integrals, whereas all integrals are evaluated by a single, general-purpose integral routine in the gradient program.

Column nine in Table I gives the ratio of times in columns eight and six, and indicates that it takes about two and half times as long to compute the gradient as to compute E_{SCF} itself. Efficiencies due to symmetry are somewhat greater for the gradient than for E_{SCF} so that this ratio is closer to two for high symmetry and closer to three for low symmetry. In either case it is clearly evident that direct computation of the gradient is far cheaper than a finite difference approximation using point-by-point evaluation of E_{SCF}. In the case of UHF this comparison is even more in favor of the analytic gradient due to the increased complexity of the SCF calculation and the tendency toward less rapid convergence of the self-consistent field process. For even more sophisticated variational methods it is anticipated that gradient calculations will be relatively inexpensive. In all cases, point group symmetry should prove worthwhile whenever there are two or more symmetrically equivalent atoms.

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[5] A few computer programs, including a recent version of HONDO, exist that employ gradients to automatically locate local minima on an SCF potential energy surface, but the authors are not aware of any such programs presently suitable for public distribution. Both IBM and CDC versions of HONDO using the symmetry methods of paper I, but without gradients, are available: M. Dupuis, J. Rys, and H. F. King, HONDO 76, Programs 338 and 336, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47401.

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[13] The reader is alerted to three misprints in Ref. 12. In Eq. (28) "$2q$" should read "$2g$". In the line following Eq. (52) the expression "$T_2 \times G$" should read "$T_4 \times G$." In Eq. (62), the upper limit of index L is J when K equals I, otherwise it is K.

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[23] In this case one could construct a complex wavefunction with symmetric charge density, but the analysis in this paper assumes a real wavefunction.

[24] Note that $I' = J$ implies $J' = I$ for any subgroup operation. This follows from the fact that $T = T^{-1}$ for any element of T_4, and that R and T give rise to identical permutations of the shell indices in the given four-label.

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