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Efficient use of Jacobi rotations for orbital optimization and localization*

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Summary. Quantum chemical orbital optimizations can be accomplished by Newton-type iterations, where *all* orbitals are improved at *each* step; or by a succession of Jacobi rotations, where only *two* orbitals are improved at any one step. In both schemes, the iterative updating of the four-index two-electron integrals requires a large computational effort. We show that the four-index transformation due to a Jacobi rotation can be simplified to such a degree that the successive execution of the four-index transformations of $N(N-1)/2$ different Jacobi rotations requires no greater computational effort than that required by the *one* full orthogonal transformation which is the product of all $N(N-1)/2$ Jacobi rotations. The four-index updating has therefore no bearing on the relative merit of the Newton approach versus the Jacobi approach. The Jacobi approach has, however, an advantage if the optimization of each Jacobi rotation angle is simple and if the effectiveness of the individual Jacobi rotations can be assessed without the execution of four-index transformations. For, in that case, all ineffectual rotations are easily deleted from the iterative sequence. Whether convergence can be guaranteed for one or the other approach is also relevant. Our conclusions are illustrated by application to the problem of intrinsic orbital localization where the succession of Jacobi rotations is the more effective strategy.

Key words: Jacobi rotations – Four-index transformation – Orbital optimization – Orbital localization

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* Dedicated to Professor Per Olov Löwdin

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1 Introduction

Many quantum chemical problems call for the determination of a set of N orthonormal orbitals $\phi_1, \phi_2, \ldots, \phi_N$ which make some functional $L(\phi_1, \phi_2, \ldots, \phi_N)$ an extremum. If nonlinear, such problems can be attacked by many-parameter Newton–Raphson or Newton–Gauss procedures or, alternatively, by a factorization in terms of Jacobi rotations. In the former case, the functional is expanded to second order in terms of *all* $N(N-1)/2$ parameters of the orthogonal matrix $\boldsymbol{T}$ expressing the orbitals ϕ_j in terms of some orthonormal reference set and *all* of them are improved at each iteration. In the second case, the orthogonal matrix $\boldsymbol{T}$ is built up as the product of a sequence of Jacobi rotations $\boldsymbol{J}_\alpha$, i.e.:

$$\boldsymbol{T} = \boldsymbol{J}_{\text{final}} \cdots \boldsymbol{J}_4 \cdot \boldsymbol{J}_3 \cdot \boldsymbol{J}_2 \cdot \boldsymbol{J}_1 \tag{1.1}$$

each of which is defined as a $N \times N$ orthogonal transformation which mixes only *two* orbitals:

$$\boldsymbol{J}_\alpha = \boldsymbol{J}(ij) = \begin{array}{c|ccccc|} & & i & & j & \\ \hline & \begin{smallmatrix}1 & & \\ & \ddots & \\ & & 1\end{smallmatrix} & & & & \\ i & & \cos\gamma & & \sin\gamma & \\ & & & \begin{smallmatrix}1 & & \\ & \ddots & \\ & & 1\end{smallmatrix} & & \\ j & & -\sin\gamma & & \cos\gamma & \\ & & & & & \begin{smallmatrix}1 & & \\ & \ddots & \\ & & 1\end{smallmatrix} \end{array} \tag{1.2}$$

(all non-indicated elements vanish) whence:

$$\begin{aligned} \hat{\phi}_i &= \phi_i \cos\gamma + \phi_j \sin\gamma \\ \hat{\phi}_j &= -\phi_i \sin\gamma + \phi_j \cos\gamma \\ \hat{\phi}_\nu &= \phi_\nu \quad \text{for } \nu \neq i, j. \end{aligned} \tag{1.3}$$

In each iteration, the functional is then extremized only with respect to two orbitals at a time, i.e. with respect to one parameter γ. Such a sequence of optimizations of 2×2 orthogonal transformations was introduced by Jacobi in 1846 for the diagonalization of symmetric matrices and shown to be very efficient in that case [1].

Quantum chemical problems are more complicated because, in general, the relevant functionals L contain electron repulsion integrals which depend on products of *four* matrix elements of the orthogonal matrix $\boldsymbol{T}$, i.e. L depends on the fourth order direct product of $\boldsymbol{T}$ with itself whereas matrix diagonalizations depend only on the second order direct product of $\boldsymbol{T}$ with itself. In quantum chemical language: whereas matrix diagonalizations call for two-index transformations, electron repulsion integrals call for four-index transformations. The complication is non-trivial for the Jacobi approach as well as the Newton approach. Which of the two methods is more effective depends on the nature of the functional L. On the one hand, $N(N-1)/2$ Jacobi rotations are required to improve all parameters in $\boldsymbol{T}$, whereas each Newton iteration seeks to improve all parameters at once. On the other hand, the optimization can be done exactly for each Jacobi rotation since it depends only on one variable, whereas each Newton iteration is limited to a quadratic approximation.

The most serious bottleneck created by the two-electron character of L arises from the fact that the two-electron integrals between molecular orbitals must be continually updated by a four-index transformation during the iterative process. Such transformations are very operations-intensive and time-consuming and are often rate-determining. The operation count of a full four-index transformation, induced by a general orthogonal transformation $\boldsymbol{T}$, such as is needed in the Newton method, is known to be of order $O(N^5)$ [2]. Since one would assume that, typically, more Jacobi rotations than Newton iterations are needed for convergence, a crucial question is whether the four-index transformation induced by one Jacobi rotation requires significantly less computational effort. The extreme sparsity of the Jacobi rotations makes this likely.

In Sect. 2, we show that the four-index transformation induced by a Jacobi rotation is in fact of order $O(N^3)$ *and give explicit formulas for its most efficient evaluation.* It follows that *the construction of all four-index transformations generated by one sweep through all possible* $N(N-1)/2$ *Jacobi transformations embodied in a given orthogonal matrix* $\boldsymbol{T}$ *is of order* $O(N^3) \cdot O(N^2) = O(N^5)$, *i.e. it requires essentially the same computational effort as the one full four-index transformation generated by* $\boldsymbol{T}$.

In view of this result, the relative merit of the Newton approach versus the Jacobi-factorization approach for a particular problem is *not* determined by the integral update but by *other* algorithmic complexities of each iterative step as well as by the convergence properties of the iterative sequence. Certain advangages of the Jacobi rotation approach regarding the iterative sequencing will be discussed in Sect. 3.

An excellent example, illustrating the effectiveness of the Jacobi rotation approach, is the Edmiston–Ruedenberg algorithm for localizing molecular orbitals [3] which is briefly discussed in Sect. 4. Although the efficiencies derived in Sections 2 and 3 are straightforward and were actually implicit in the 1967 localization code of K.R.'s research group, authored by R.C.R. [4], they seem to have generally gone unnoticed and, because of the $O(N^5)$-presumed four-index updating, the E–R localization has been widely believed to be unwieldy. The quantitative application, reported in Section 4 for a system with about 50 occupied orbitals, illustrates that this inference is in fact unwarranted.

Within the context of the variation principle, the method of Jacobi rotations has been used for the optimization of orbitals in Miller and Ruedenberg's [5] determination of pair wavefunctions for four-electron atomic systems, probably the earliest MCSCF calculations made. Raffenetti, Ruedenberg and Hoffman [6] have established the formulas for the construction of a general orthogonal transformation from Jacobi rotations and they were used by Mehler, Silver and Ruedenberg [7] for the variational determination of orbitals in molecular pair wavefunctions. The use of Jacobi rotations in general MCSCF calculations has recently been discussed by Carbo, Domingo Novoa and Peris [8].

2 Transformation of four-index integrals

2.1 General analysis

A general unitary rotation from an orbital set $\boldsymbol{\phi}$ into a new orbital set $\hat{\boldsymbol{\phi}}$ can be written as:

$$\hat{\phi}_p = \sum_{\mu}^{N} T_{p\mu}\phi_\mu. \tag{2.1}$$

If the two-electron integrals in terms of $\boldsymbol{\phi}$, namely $[\phi_p\phi_q \mid \phi_r\phi_s] = [pq \mid rs]$, are known, then the two-electron integrals in terms of $\hat{\boldsymbol{\phi}}$ are determined by:

$$[\hat{\phi}_p\hat{\phi}_q \mid \hat{\phi}_r\hat{\phi}_s] = \sum_{\mu\nu\varrho\sigma}^{N} T_{p\mu}T_{q\nu}T_{r\varrho}T_{s\sigma}[\mu\nu \mid \varrho\sigma]. \tag{2.2}$$

A Jacobi rotation of the orbital set $\boldsymbol{\phi}$ into the set $\hat{\boldsymbol{\phi}}$, say:

$$\hat{\phi}_p = \sum_{\mu}^{N} J_{p\mu}\phi_\mu, \tag{2.3}$$

can be written as:

$$J_{p\mu} = \delta_{p\mu} + \Delta_{p\mu}, \tag{2.4}$$

with Δ being a matrix giving the correction to the unit matrix and containing only four non-zero elements. If the Jacobi rotation is performed between the orbitals ϕ_i and ϕ_j, then the nonzero part of Δ takes the form of the 2×2 matrix:

$$\Delta = \begin{pmatrix} \Delta_{ii} & \Delta_{ij} \\ \Delta_{ji} & \Delta_{jj} \end{pmatrix} = \begin{pmatrix} \cos\gamma - 1 & \sin\gamma \\ -\sin\gamma & \cos\gamma - 1 \end{pmatrix}. \tag{2.5}$$

The Jacobi transformation of the two-electron integrals from the ϕ orbitals to the $\hat{\phi}$ orbitals can then be written in the form:

$$\begin{aligned}
[\hat{\phi}_p\hat{\phi}_q \mid \hat{\phi}_r\hat{\phi}_s] &= \sum_{\mu\nu\varrho\sigma}^{N} (\delta_{p\mu} + \Delta_{p\mu})(\delta_{q\nu} + \Delta_{q\nu})(\delta_{r\varrho} + \Delta_{r\varrho})(\delta_{s\sigma} + \Delta_{s\sigma})[\mu\nu \mid \varrho\sigma] \\
&= [pq \mid rs] \\
&\quad + \sum_{\sigma}^{N} \Delta_{s\sigma}[pq \mid r\sigma] + \sum_{\varrho}^{N} \Delta_{r\varrho}[pq \mid \varrho s] \\
&\quad + \sum_{\nu}^{N} \Delta_{q\nu}[p\nu \mid rs] + \sum_{\mu}^{N} \Delta_{p\mu}[\mu q \mid rs] \\
&\quad + \sum_{\varrho\sigma}^{N} \Delta_{r\varrho}\Delta_{s\sigma}[pq \mid \varrho\sigma] + \sum_{\nu\sigma}^{N} \Delta_{q\nu}\Delta_{s\sigma}[p\nu \mid r\sigma] \\
&\quad + \sum_{\nu\varrho}^{N} \Delta_{q\nu}\Delta_{rp}[p\nu \mid \varrho s] + \sum_{\mu\sigma}^{N} \Delta_{p\mu}\Delta_{s\sigma}[\mu q \mid r\sigma] \\
&\quad + \sum_{\mu\varrho}^{N} \Delta_{p\mu}\Delta_{rp}[\mu q \mid \varrho s] + \sum_{\mu\nu}^{N} \Delta_{p\mu}\Delta_{q\nu}[\mu\nu \mid rs] \\
&\quad + \sum_{\nu\varrho\sigma}^{N} \Delta_{q\nu}\Delta_{rp}\Delta_{s\sigma}[p\nu \mid \varrho\sigma] + \sum_{\mu\varrho\sigma}^{N} \Delta_{p\mu}\Delta_{r\varrho}\Delta_{s\sigma}[\mu q \mid \varrho\sigma]
\end{aligned}$$

$$+\sum_{\mu\nu\sigma}^{N} \Delta_{p\mu}\Delta_{q\nu}\Delta_{s\sigma}[\mu\nu \mid r\sigma] + \sum_{\mu\nu\varrho}^{N} \Delta_{p\mu}\Delta_{q\nu}\Delta_{r\varrho}[\mu\nu \mid \varrho s]$$

$$+\sum_{\mu\nu\varrho\sigma}^{N} \Delta_{p\mu}\Delta_{q\nu}\Delta_{r\varrho}\Delta_{s\sigma}[\mu\nu \mid \varrho\sigma]. \tag{2.6}$$

Since only those elements of Δ which give nonzero contributions are to be summed over, only two values, i and j, are assumed by the summation variables which index Δ. The only variables which contribute to the N-dependence of the computational complexity are, therefore, those which index *both* sets of two-electron integrals: those in terms of $\hat{\phi}$ and those in terms of ϕ. Equivalently, the exponent of N in the computational complexity of each term in Eq. (2.6) is equal to the number of indices which do *not* subscript Δ. At first glance, this gives an overall complexity of $O(N^4)$ due to the $[pq \mid rs]$ term. However, this is just a copy of the original set of integrals which can be avoided by first computing all of the corrections to the original set of integrals and then summing the corrections into these integrals. The remaining terms have at most three indices not occurring as an index to Δ, and thus the computational complexity of these terms is $O(N^3)$. The memory overhead of first storing the corrections to the $[pq \mid rs]$ before constructing the $[\hat{\phi}_p\hat{\phi}_q \mid \hat{\phi}_r \hat{\phi}_s]$ is also $O(N^3)$. However, by using the explicit formulas of Sect. 2.2 for the integrals that are transformed, intermediate storage of corrections is in fact not necessary.

2.2 Explicit formulas: Irreducible linear combinations of orbital products with respect to the group of Jacobi rotations between two orbitals

There exist six different cases for the two-electron integral updating, namely in any one integral: (*1*) *All four orbitals are rotated*; (*2*) *three orbitals are rotated*; (*3*) *two orbitals, occupied by the same electron, are rotated*; (*4*) *two orbitals, occupied by different electrons, are rotated*; (*5*) *one orbital is rotated*; (*6*) *none of the four orbitals is rotated.* As before, we denote the two orbitals between which the Jacobi rotation takes place as $(\phi_i, \phi_j) \rightarrow (\hat{\phi}_i, \hat{\phi}_j)$. In order to obtain the four-index transformation formulas in their simplest forms, it is expedient to begin by establishing those linear combinations of orbital products which transform according to the irreducible representations of the group of Jacobi rotations between two given orbitals.

First consider the two-orbital products. The appropriate linear combinations are:

$$f_1(1,2) = [\phi_i(1)\phi_i(2) + \phi_j(1)\phi_j(2)]/2, \tag{2.7a}$$

$$f_2(1,2) = [\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)]/2, \tag{2.7b}$$

$$g_1(1,2) = [\phi_i(1)\phi_i(2) - \phi_j(1)\phi_j(2)]/2, \tag{2.7c}$$

$$g_2(1,2) = [\phi_i(1)\phi_j(2) + \phi_j(1)\phi_i(2)]/2. \tag{2.7d}$$

Under the Jacobi rotation of Eq. (1.3), they are readily seen to transform as follows:

$$\hat{f}_1 = f_1, \tag{2.8a}$$

$$\hat{f}_2 = f_2, \tag{2.8b}$$

$$\hat{g}_1 = g_1 \cos 2\gamma + g_2 \sin 2\gamma, \tag{2.8c}$$

$$\hat{g}_2 = -g_1 \sin 2\gamma + g_2 \cos 2\gamma. \tag{2.8d}$$

Next consider the three-orbital products. The appropriate linear combinations are (note that $f_2(2,2)$ vanishes):

$$u_1(1,2)=\phi_i(1)f_1(2,2), \tag{2.9a}$$

$$u_2(1,2)=\phi_j(1)f_1(2,2), \tag{2.9b}$$

$$v_1(1,2)=[\phi_i(1)g_1(2,2)+\phi_j(1)g_2(2,2)]/2, \tag{2.9c}$$

$$v_2(1,2)=[\phi_i(1)g_2(2,2)-\phi_j(1)g_1(2,2)]/2, \tag{2.9d}$$

$$w_1(1,2)=[\phi_i(1)g_1(2,2)-\phi_j(1)g_2(2,2)]/2, \tag{2.9e}$$

$$w_2(1,2)=[\phi_i(1)g_2(2,2)+\phi_j(1)g_1(2,2)]/2. \tag{2.9f}$$

By virtue of Eqs. (1.3) and (2.8), these are seen to transform as follows:

$$\hat{u}_1=u_1\cos\gamma+u_2\sin\gamma, \tag{2.10a}$$

$$\hat{u}_2=-u_1\sin\gamma+u_2\cos\gamma \tag{2.10b}$$

$$\hat{v}_1=v_1\cos\gamma+v_2\sin\gamma, \tag{2.10c}$$

$$\hat{v}_2=-v_1\sin\gamma+v_2\cos\gamma, \tag{2.10d}$$

$$\hat{w}_1=w_1\cos 3\gamma+w_2\sin 3\gamma, \tag{2.10e}$$

$$\hat{w}_2=-w_1\sin 3\gamma+w_2\cos 3\gamma. \tag{2.10f}$$

Finally consider the four-orbital products. The relevant linear combinations are:

$$p_1(1,2)=f_1(1,1)f_1(2,2) \tag{2.11a}$$

$$p_2(1,2)=[g_1(1,1)g_1(2,2)+g_2(1,1)g_2(2,2)]/2 \tag{2.11b}$$

$$q_1(1,2)=f_1(1,1)g_1(2,2) \tag{2.11c}$$

$$q_2(1,2)=f_1(1,1)g_2(2,2) \tag{2.11d}$$

$$r_1(1,2)=[g_1(1,1)g_1(2,2)-g_2(1,1)g_2 2,2)]/2 \tag{2.11e}$$

$$r_2(1,2)=[g_1(1,1)g_2(2,2)+g_2(1,1)g_1(2,2)]/2. \tag{2.11f}$$

By virtue of the transformation Eqs. (2.8), one obtains for them the transformations:

$$\hat{p}_1=p_1 \tag{2.12a}$$

$$\hat{p}_2=p_2 \tag{2.12b}$$

$$\hat{q}_1=q_1\cos 2\gamma+q_2\sin 2\gamma \tag{2.12c}$$

$$\hat{q}_2=-q_1\sin 2\gamma+q_2\cos 2\gamma \tag{2.12d}$$

$$\hat{r}_1=r_1\cos 4\gamma+r_2\sin 4\gamma \tag{2.12e}$$

$$\hat{r}_2=-r_1\sin 4\gamma+r_2\cos 4\gamma. \tag{2.12f}$$

2.3 Explicit formulas: Integral transformations

With the help of the definitions (2.7), (2.9), (2.11) and the transformation formulas (2.8), (2.10), (2.12), compact and efficient two-electron integral-transformations are easily formulated. In agreement with the preceding conventions, the indices i, j, k, l denote orbitals which are rotated, whereas the indices p, q, r, s denote orbitals which are unaffected by the Jacobi rotation.

Case 1. All four orbitals are rotated. In analogy to Eqs. (2.11), define the following linear combinations of integrals:

$$\begin{aligned} P_1 &= [f_1 \,|\, f_1] \\ &= \{[i^2 \,|\, i^2] + [j^2 \,|\, j^2] + 2[i^2 \,|\, j^2]\}/4 \end{aligned} \tag{2.13a}$$

$$\begin{aligned} P_2 &= \{[g_1 \,|\, g_1] + [g_2 \,|\, g_2]\}/2 \\ &= \{[i^2 \,|\, i^2] + [j^2 \,|\, j^2] - 2[i^2 \,|\, j^2] + 4[ij \,|\, ij]\}/8 \end{aligned} \tag{2.13b}$$

$$\begin{aligned} Q_1 &= [f_1 \,|\, g_1] \\ &= \{[i^2 \,|\, i^2] - [j^2 \,|\, j^2]\}/4 \end{aligned} \tag{2.13c}$$

$$\begin{aligned} Q_2 &= [f_1 \,|\, g_2] \\ &= \{[i^2 \,|\, ij] + [j^2 \,|\, ij]\}/2 \end{aligned} \tag{2.13d}$$

$$\begin{aligned} R_1 &= \{[g_1 \,|\, g_1] + [g_2 \,|\, g_2]\}/2 \\ &= \{[i^2 \,|\, i^2] + [j^2 \,|\, j^2] - 2[i^2 \,|\, j^2] - 4[ij \,|\, ij]\}/8 \end{aligned} \tag{2.13e}$$

$$\begin{aligned} R_2 &= \{[g_1 \,|\, g_2] + [g_2 \,|\, g_1]\}/2 = [g_1 \,|\, g_2] \\ &= \{[i^2 \,|\, ij] - [j^2 \,|\, ij]\}/2. \end{aligned} \tag{2.13f}$$

It is evident that these integral combinations transform in exactly the same way as the corresponding two-electron functions. The integral transformation for this case is therefore accomplished as follows

(i) Calculate the quantities P_1 through R_2 from the integrals $[ij \,|\, kl]$ by Eqs. (2.13).

(ii) Calculate the quantities $\hat{P}_1, \hat{P}_2, \hat{Q}_1, \hat{Q}_2, \hat{R}_1, \hat{R}_2$ from Eqs. (2.12) with the lower case symbols p, q, r replaced by the capital symbols P, Q, R.

(iii) Calculate the transformed integrals $[\widehat{ij} \,|\, \widehat{kl}]$ from the quantities $\hat{P}_1, \hat{P}_2, \hat{Q}_1, \hat{Q}_2, \hat{R}_1, \hat{R}_2$ by inverting the equation system (2.13), which yields:

$$[\hat{i}^2 \,|\, \hat{i}^2] = \hat{P}_1 + \hat{P}_2 + \hat{R}_1 + 2\hat{Q}_1, \tag{2.14a}$$

$$[\hat{j}^2 \,|\, \hat{j}^2] = \hat{P}_1 + \hat{P}_2 + \hat{R}_1 - 2\hat{Q}_1, \tag{2.14b}$$

$$[\hat{i}^2 \,|\, \hat{j}^2] = \hat{P}_1 - \hat{P}_2 - \hat{R}_1, \tag{2.14c}$$

$$[\widehat{ij} \,|\, \widehat{ij}] = \hat{P}_2 - \hat{R}_1, \tag{2.14d}$$

$$[\hat{i}^2 \,|\, \widehat{ij}] = \hat{Q}_2 + \hat{R}_2, \tag{2.14e}$$

$$[\hat{j}^2 \,|\, \widehat{ij}] = \hat{Q}_2 - \hat{R}_2. \tag{2.14f}$$

Case 2. Three orbitals are rotated. In analogy to Eqs. (2.9), we now define the integral combinations:

$$\begin{aligned} U_{1p} &= [\phi_p \phi_i \,|\, f_1] \\ &= \{[pi \,|\, i^2] + [pi \,|\, j^2]\}/2 \end{aligned} \tag{2.15a}$$

$$\begin{aligned} U_{2p} &= [\phi_p \phi_j \,|\, f_1] \\ &= \{[pj \,|\, i^2] + [pj \,|\, j^2]\}/2 \end{aligned} \tag{2.15b}$$

$$V_{1p} = \{[\phi_p\phi_i \,|\, g_1] + [\phi_p\phi_j \,|\, g_2]/2$$

$$= \{[pi \,|\, i^2] - [pi \,|\, j^2] + 2[pj \,|\, ij]\}/4 \tag{2.15c}$$

$$V_{2p} = \{[\phi_p\phi_i \,|\, g_2] - [\phi_p\phi_j \,|\, g_1]\}/2$$

$$= \{2[pi \,|\, ij] - [pj \,|\, i^2] + [pj \,|\, j^2]\}/4 \tag{2.15d}$$

$$W_{1p} = \{[\phi_p\phi_i \,|\, g_1] - [\phi_p\phi_j \,|\, g_2]\}/2$$

$$= \{[pi \,|\, i^2] - [pi \,|\, j^2] - 2[pj \,|\, ij]\}/4 \tag{2.15e}$$

$$W_{2p} = \{[\phi_p\phi_i \,|\, g_2] + [\phi_p\phi_j \,|\, g_1]\}/2$$

$$= \{2[pi \,|\, ij] + [pj \,|\, i^2] - [pj \,|\, j^2]\}/4. \tag{2.15f}$$

The transformation of the integrals $[pi \,|\, jk]$ is then accomplished as follows:

(i) Calculate the quantities U_{1p} through W_{2p} from the integrals $[pi \,|\, jk]$ by Eqs. (2.15).

(ii) Calculate the quantities $\hat{U}_{1p}$ to $\hat{W}_{2p}$ from the quantities U_{1p} to W_{2p} according to Eqs. (2.10) with u, v, w replaced by U, V, W.

(iii) Calculate the integrals $[p\hat{i} \,|\, \hat{j}\hat{k}]$ by inverting Eqs. (2.15), which yields:

$$[p\hat{i} \,|\, \hat{i}^2] = \hat{U}_{1p} + \hat{V}_{1p} + \hat{W}_{1p} \tag{2.16a}$$

$$[p\hat{i} \,|\, \hat{j}^2] = \hat{U}_{1p} - \hat{V}_{1p} - \hat{W}_{1p} \tag{2.16b}$$

$$[p\hat{j} \,|\, \hat{i}^2] = \hat{U}_{2p} - \hat{V}_{2p} + \hat{W}_{2p} \tag{2.16c}$$

$$[p\hat{j} \,|\, \hat{j}^2] = \hat{U}_{2p} + \hat{V}_{2p} - \hat{W}_{2p} \tag{2.16d}$$

$$[p\hat{i} \,|\, \hat{i}\hat{j}] = \hat{V}_{2p} + \hat{W}_{2p} \tag{2.16e}$$

$$[p\hat{j} \,|\, \hat{i}\hat{j}] = \hat{V}_{1p} - \hat{W}_{1p}. \tag{2.16f}$$

Case 3. Two orbitals are rotated. If the electron coordinates "1" and "2" are identical, i.e. "1" = "2", in Eqs (2.7), then f_2 vanishes. We define therefore the following three integral combinations:

$$F_{1pq} = [\phi_p\phi_q \,|\, f_1]$$

$$= \{[pq \,|\, i^2] + [pq \,|\, j^2]\}/2 \tag{2.17a}$$

$$G_{1pq} = [\phi_p\phi_q \,|\, g_1]$$

$$= \{[pq \,|\, i^2] - [pq \,|\, j^2]\}/2 \tag{2.17b}$$

$$G_{2pq} = [\phi_p\phi_q \,|\, g_2]$$

$$= [pq \,|\, ij]. \tag{2.17c}$$

The transformation of the integrals $[pq \,|\, ij]$ is now accomplished by:

(i) Calculating the quantities F_{1pq}, G_{1pq}, G_{2pq} from the integrals $[pq \,|\, ij]$ by Eqs. (2.17).

(ii) Calculating the transformed quantities $\hat{F}_{1pq}\hat{G}_{1pq}\hat{G}_{2pq}$ using Eqs. (2.8) with f and g replaced by F and G.

(iii) Calculating the integrals $[pq\,|\,\hat{i}\hat{j}]$ by inverting Eqs. (2.17) which yields

$$[pq\,|\,\hat{i}^2] = \hat{F}_{1pq} + \hat{G}_{1pq}, \tag{2.18a}$$

$$[pq\,|\,\hat{j}^2] = \hat{F}_{1pq} - \hat{G}_{1pq}, \tag{2.18b}$$

$$[pq\,|\,\hat{i}\hat{j}] = \hat{G}_{2pq}. \tag{2.18c}$$

Case 4. Two orbitals are rotated. In addition to the integral notation of Eq. (2.2), we use here also the alternative notation

$$\langle ij|\,|kl\rangle = \int dV_1 \int dV_2\, \phi_i(1)\phi_j(2) r_{12}^{-1} \phi_k(1)\phi_l(2) = [ik\,|\,jl]$$

for convenience. In analogy to Eqs. (2.7), we define the integral combinations:

$$\begin{aligned} D_{1pq} &= \langle \phi_p\phi_q|\,|f_1\rangle \\ &= \{[pi\,|\,qi] + [pj\,|\,qj]\}/2 \end{aligned} \tag{2.19a}$$

$$\begin{aligned} D_{2pq} &= \langle \phi_p\phi_q|\,|f_2\rangle \\ &= \{[pi\,|\,qj] - [pj\,|\,qi]\}/2 \end{aligned} \tag{2.19b}$$

$$\begin{aligned} H_{1pq} &= \langle \phi_p\phi_q|\,|g_1\rangle \\ &= \{[pi\,|\,qi] - [pj\,|\,qj]\}/2 \end{aligned} \tag{2.19c}$$

$$\begin{aligned} H_{2pq} &= \langle \phi_p\phi_q|\,|g_2\rangle \\ &= \{[pi\,|\,qj] + [pj\,|\,qi]\}/2. \end{aligned} \tag{2.19d}$$

The transformation of the integrals $[pi\,|\,qj]$ is accomplished by:

(i) Calculating the quantities D_{1pq} to H_{2pq} from the integrals $[pi\,|\,qj]$ by Eqs. (2.19).

(ii) Calculating the quantities $\hat{D}_{1pq}$ to $\hat{H}_{2pq}$ using Eqs. (2.8) with the letters f and g replaced by D and H respectively.

(iii) Calculating the transformed integrals $[p\hat{i}\,|\,q\hat{j}]$ by inverting the equation system (2.19) which yields:

$$[p\hat{i}\,|\,q\hat{i}] = \hat{D}_{1pq} + \hat{H}_{1pq}, \tag{2.20a}$$

$$[p\hat{j}\,|\,q\hat{j}] = \hat{D}_{1pq} - \hat{H}_{1pq}, \tag{2.20b}$$

$$[p\hat{i}\,|\,q\hat{j}] = \hat{D}_{2pq} + \hat{H}_{2pq}, \tag{2.20c}$$

$$[p\hat{j}\,|\,q\hat{i}] = -\hat{D}_{2pq} + \hat{H}_{2pq}, \tag{2.20d}$$

Note that, when $p = q$, $= D_{2pp}$ and $\hat{D}_{2pp}$ both vanish, reducing the four equations (2.19) as well as those of (2.20) to three, which are similar to Case 3.

Case 5. One orbital is rotated. In this case, the Jacobi rotation formulas of Eq. (1.3) can be directly inserted in the two-electron integrals, yielding:

$$[pq\,|\,r\hat{i}] = [pq\,|\,ri]\cos\gamma + [pq\,|\,rj]\sin\gamma, \tag{2.21a}$$

$$[pq\,|\,r\hat{j}] = -[pq\,|\,ri]\sin\gamma + [pq\,|\,rj]\cos\gamma. \tag{2.21b}$$

This set of transformations is the only one of order $O(N^3)$.

Case 6. No orbital is rotated. These integrals $[pq \mid rs]$ are unaffected by the Jacobi rotation between orbitals i and j and require no updating.

2.4. Transformation algorithm

We have implemented a program based on the explicit formulas of the preceding section. Efficiency and minimization of temporary storage can be accomplished because *no one integral requires more than six integrals as input and each member of such an integral input set involves only the other members of the same set in the updating process.* The challenge is to construct the program in such a way that, for any Jacobi rotation between two arbitrary orbitals, the code will cycle through all update sets in an efficient manner. Computer memory, either real or virutal, is assumed to be large enough to hold the entire integral set so that it is straightforward to locate any integral by standard indexing procedures.

The following strategy is followed to ensure that all required updates are made and indexing is done economically:

(i) Arrange for input acceptance of the dimension N of the orbital set and of the original integral array.

(ii) Arrange for input acceptance of the index pair (i, j) indentifying the two orbitals to be rotated and of the rotation angle γ or an appropriate function of γ. This matter will be discussed in further detail below. Calculate the factors $\sin\gamma$, $\cos\gamma$, $\sin 2\gamma$, $\cos 2\gamma$, $\sin 4\gamma$, $\cos 4\gamma$.

(iii) Calculate pair indices and index offsets such as $i(i-1)/2$, $i(i+1)/2$, and

$$\langle ij\rangle = j + i(i-1)/2 \quad \text{if } i \geqslant j, \qquad \langle ij\rangle = i + j(j-1)/2 \quad \text{if } i < j, \tag{2.22}$$

as well as the analogous quantities between the numbers $\langle ii\rangle$, $\langle ij\rangle$, $\langle jj\rangle$. In all calling routines the convention $i > j$ is strictly observed.

(iv) Update the six integrals $[i^2 \mid i^2]$, $[j^2 \mid j^2]$, $[i^2 \mid j^2]$, $[i^2 \mid ij]$, $[j^2 \mid ij]$, $[ij \mid ij]$, by the formulas of Sect. 2.3, Case 1.

(v) Update the integrals $[pq \mid i^2]$, $[pq \mid j^2]$, $[pq \mid ij]$ in groups of three according to the formulas of Sect. 2.3, Case 3, and within a pair of loops over p and q, with p running from 1 to N and q, running from 1 to p. Omitted are the (p, q) pairs for which $\langle pq\rangle = \langle ii\rangle$ or $\langle jj\rangle$ or $\langle ij\rangle$, where the definition of Eq. (2.22) has been used.

(vi) Update the integrals $[pi \mid pi]$, $[pj \mid pj]$, $[pi \mid pj]$ in groups of three within a single loop over p according to the formulas of Sec. 2.3, Case 4. Note that the four-integral update for Case 4 degenerates into a three-integral update when $p = q$. The loop runs over p from 1 to N, omitting the cases $p = i$ and $p = j$.

(vii) Update the integrals $[pq \mid ri]$, $[pq \mid rj]$ according to the formulas of Sect. 2.3, Case 5 in groups of two within a triple loop over p, q, r with $1 \leqslant r \leqslant N$, $1 \leqslant q \leqslant N$, $1 \leqslant p \leqslant q$. Omitted are all cases for which $r = i$ or j. *This relatively simple case is the only one with an operation count of* $O(N^3)$.

(viii) In the program, the integrals $[pi \mid qi]$, $[pj \mid qj]$, $[pi \mid qj]$, $[pj \mid qi]$ for $p \neq q$ are not obtained by using the formulas of Sec. 2.3, Case 4, but by two consecutive single orbital updates of the type of Case 5 [see item (vii)].

(ix) In the program, the integrals $[pi\,|\,jk]$ are not obtained by the formulas of Sect. 2.3, Case 2, but by following the Case 3 update, discussed above under item (v), with a single orbital update of the type of Case 5 [see item (vii)].

As regards the calculation of γ (see item (ii) above), it is to be noted that many quantum mechanical functionals are *invariant with respect ot sign changes in all orbitals* and, hence, the addition of $\pm\pi$ to γ. In such cases, L turns out to be a function of $\cos 2\gamma$ and $\sin 2\gamma$, and γ can be limited to a range of extent π. In the interest of continuity in the successive orbital changes during the iterative process, in particular when γ is close to convergence, this range should be chosen as:

$$-\pi/2 \leqslant \gamma < \pi/2. \tag{2.23}$$

This will prevent uncontrolled orbital sign changes.

If L depends only on $\cos 2\gamma$ and $\sin 2\gamma$, each orbital improvement calculation determines only (2γ). Most likely it will determine $\cos 2\gamma$ and $\sin 2\gamma$. From there, one can obtain $\cos\gamma$ and $\sin\gamma$ through:

$$\cos\gamma = [(1+\cos 2\gamma)/2]^{1/2}, \qquad \sin\gamma = [(1-\cos 2\gamma)/2]^{1/2}. \tag{2.24}$$

To insure the domain limitation of Eq. (2.23), the signs must be chosen as follows: If $\cos\gamma$ is non-zero, then it is positive; if $\sin\gamma$ is non-zero, then one has $\sin\gamma > 0$ when $\sin 2\gamma > 0$, and $\sin\gamma < 0$ when $\sin 2\gamma \leqslant 0$. From $\cos\gamma$, $\sin\gamma$, $\cos 2\gamma$, $\sin 2\gamma$, one can then calculate $\cos 3\gamma$, $\sin 3\gamma$, $\cos 4\gamma$, $\sin 4\gamma$, so that it is never necessary to calculate trigonometric functions or their inverses.

Some functionals such as the one pertaining to orbital localization are *also invariant with respect to orbital interchanges.* It is readily seen that, in such cases, the functional L will depend only upon $\cos 4\gamma$ and $\sin 4\gamma$. We shall discuss this case in Sect. 4.

While the current program is written in a sequential mode, it should be noted that the algorithms described under items (v), (vi), (vii) each describe loops over *independent* update sets. By virtue of this independence, *the total procedure is readily amenable to implementation for parallel or distributed programming environments.*

3 Sequencing of the Jacobi rotations

The efficiency of any iterative scheme depends critically on the *number* of iterations required for convergence. Economy in this respect is particularly important in quantum chemical problems because of the high cost of the concomitant four-index transformations. In the context of the Jacobi rotation approach, this number can be reduced by deciding whether or not to execute each individual 2 × 2 transformation at any given stage of the calculation. Manifestly, such a decision must be based on an assessment of the efficacy of any particular Jacobi rotation and, to be useful, such an assessment must be possible without prior execution of the four-index transformation. In a general context, a perturbation estimate for the extremization functional L may be appropriate to obtain such an assessment. In the case of the E–R orbital localization algorithm [3], it turns out that an *exact* prediction of the localization gain due to a Jacobi rotation is available at practically no cost, as we shall see in the next section.

One can think of various ways of removing ineffectual Jacobi rotations. In all of them, the calculation is arranged in terms of a sequence of *sweeps* each of which goes through all $N(N-1)/2$ possible different Jacobi rotations in some systematic order. The most straightforward procedure is to execute, during each sweep, only the one Jacobi rotation with the maximal extremization gain, as suggested by E-R [3]. A slight modification consists of executing, during each sweep, all those Jacobi rotations whose extremization gain is greater than a certain fraction (say 50%) of the maximal extremization gain. A third algorithm is similar to that in general use for the Jacobi diagonalization method [9]. Here, only those Jacobi rotations are executed during any given sweep for which the pretested localization gain exceeds a certain threshold (*th*). The latter starts out loose and is progressively tightened in the course of the iterative process. Since the total increase in the localization functional L typically is of the order of a fraction of a hartree per orbital, the following sequence of thresholds is used for the case of localization: $(th) = 1, \tau, \tau^2, \tau^3, \ldots, \tau^k$ hartree, where $0 < \tau < 1$ (typically between 0.3 and 0.6) and $\tau^k \leqslant$ the absolute convergence criterion demanded for L, e.g. 10^{-12} hartree. Each intermediate threshold (*th*) is lowered whenever a sweep through all $N(N-1)/2$ Jacobi rotations turns up no more than one rotation with a localization gain larger than the current (*th*). If the increment from one value of (*th*) to the next is chosen extremely small, i.e. τ is close to unity, then this strategy approaches the first mentioned procedure of always choosing the next Jacobi rotation as that with the largest predicted gain. We shall discuss the performance of these approaches for the case of the localization functional in Sect. 4.3.

The procedures are obviously applicable to general quantum chemical optimization problems by replacing the test of the localization gain with a test of the predicted increment ΔL in the relevant function L. The Jacobi rotation method offers thus the advantage of being able *to omit those four-index transformations which are associated with ineffectual orbital rotations without loss of orthogonality in a manner not possible for the Newton procedure.* It is of course also a simple matter to exclude the mixing of certain orbitals from the optimization process entirely, based on physical or chemical a priori considerations. This is accomplished by never allowing *any* Jacobi rotations between such orbitals.

It has been suggested [10] to save on four-index transformation time by accumulating all $N(N-1)/2$ Jacobi transformations for one sweep and, then, performing the four-index integral transformation only after each sweep. However, as was pointed out in Sect. 1, the total number of operations for the accumulated four-index transformation depends on N in exactly the same manner as when the two-electron integrals are updated after each individual Jacobi rotation by the algorithm of Sect. 2 *with no Jacobi rotation omitted.* It is therefore apparent that the "accumulation approach" involves *more* computational effort than the "individual approach" when many Jacobi rotations can be skipped because of their ineffectiveness. In addition, it is to be expected that the delay in updating the two-electron integrals will slow down the convergence. It has not even been proven that convergence is guaranteed for the accumulation approach although, in our experience, this approach has always converged satisfactorily.

4 Intrinsic localization of orthonormal orbitals

4.1. Localization formalism

Perhaps the best known instance of using a sequence of Jacobi rotations in quantum chemistry (outside the classical matrix diagonalization routines) is the intrinsic orbital localization procedure introduced by Edmiston and Ruedenberg [3]. The effectiveness of this approach derives from the facts that, for the relevant functional, (i) optimization of the 2×2 problem is extremely simple, (ii) convergence is guaranteed when all integrals are updated after each Jacobi iteration and (iii) the localization gain of each Jacobi step can be simply predicted. For reasons which will become apparent in Sect. 4.3, the application of Newton-type procedures to orbital localization [3, 11] has proven less successful.

The E-R localization of N orthonormal molecular orbitals ϕ_i, $\phi_1, \ldots, \phi_N$ is based on the maximization of the functional:

$$L = \sum_{p=1}^{N} [pp \mid pp], \tag{4.1}$$

where

$$[ij \mid kl] = \int dV_1 \int dV_2 \, \phi_i(1)\phi_j(1) r_{12}^{-1} \phi_k(2)\phi_l(2). \tag{4.2}$$

The functional of Eq. (4.1) is invariant with respect sign changes in any one orbital and to any exchange of the orbital indices. In that case, L depends only on (4γ), as will be seen below, and the rotation angle in the Jacobi matrix of Eq. (1.3) can be limited to the range:

$$-\pi/4 \leqslant \gamma < \pi/4. \tag{4.3}$$

This choice guarantees continuity in successive orbital changes during the iterative process, in particular when γ is close to convergence.

The change in L due to the Jacobi rotations of Eqs. (1.2), (1.3) is given by:

$$\begin{aligned} \Delta L(ij) &= L(\hat{1}, \hat{2}, \ldots, \hat{N}) - L(1, 2, \ldots, N) \\ &= [\hat{i}^2 \mid \hat{i}^2] + [\hat{j}^2 \mid \hat{j}^2] - [i^2 \mid i^2] - [j^2 \mid j^2]. \end{aligned} \tag{4.4}$$

By virtue of Eqs. (2.14a) and (2.14b), it can be written as:

$$\Delta L(ij) = 2[\hat{P}_1 + \hat{P}_2 + \hat{R}_1 - P_1 - P_2 - R_1] \tag{4.5}$$

and, by virtue of the transformation of Eqs. (2.12a), (2.12b), (2.12e), this expression simplifies to:

$$\Delta L(ij) = 2[R_1 \cos 4\gamma + R_2 \sin 4\gamma - R_1]. \tag{4.6}$$

Define now:

$$A_{ij} = -2R_1 = I(ij, ij) - [I(ii, ii) + I(jj, jj) - 2I(ii, jj)/4, \tag{4.7}$$

$$B_{ij} = 2R_2 = I(ij, ii) - I(ij, jj), \tag{4.8}$$

$$\begin{aligned} \cos 4\alpha &= A_{ij}/(A_{ij}^2 + B_{ij}^2)^{1/2}, \\ \sin 4\alpha &= B_{ij}/(A_{ij}^2 + B_{ij}^2)^{1/2}, \end{aligned} \tag{4.9}$$

and use these equations to replace R_1 and R_2 by $\cos 4\gamma$, $\sin 4\gamma$ and $(A_{ij}^2 + B_{ij}^2)^{1/2}$ in the first two terms within the brackets on the RHS of Eq. (4.6). Application of the cosine addition theorem then yields the E-R expression for the γ dependence of ΔL:

$$\Delta L(ij) = A_{ij} + (A_{ij}^2 + B_{ij}^2)^{1/2} \cos 4(\gamma - \alpha). \tag{4.10}$$

Equations (4.9) determine the angle (4α) within a range of 2π. We choose this range as:

$$-\pi \leqslant 4\alpha < \pi. \tag{4.11}$$

The Jacobi rotation which maximizes the RHS of Eq. (4.10) is manifestly obtained in closed form by setting γ equal to one of the values $(\alpha + n\pi/2)$. Because of the choice of Eq. (4.11), the value of γ lying in the range defined by Eq. (4.3) is then given by:

$$\gamma(\max) = \alpha = 4\alpha/4. \tag{4.12}$$

This type of 2 × 2 orbital optimization is iterated for all possible orbital pairings until L cannot be increased anymore. By virtue of the additive form of the total localization functional of Eq. (4.1), the latter will increase monotonically during this process and convergence to a maximum is guaranteed.

Analogously, the *most delocalized orbitals* are obtained by replacing Eq. (4.11) with the range choice:

$$0 \leqslant 4\alpha < 2\pi \tag{4.13}$$

and consistently choosing γ as

$$\gamma(\min) = \alpha - \pi/4 = (4\alpha - \pi)/4. \tag{4.14}$$

The Jacobi-rotation approach is particularly advantageous in the present context because the *localization or delocalization gain* resulting from any one Jacobi rotation is available from Eq. (4.10) *before* the actual execution of the rotation. It is

$$\Delta L_{\max}(i,j) = A_{ij} \pm (A_{ij}^2 + B_{ij}^2)^{1/2} \tag{4.15}$$

so that only five multiplications and a square root are required. The sequencing algorithm discussed in Sect. 3 can therefore be used very effectively.

4.2 Integral transformation

For the calculation of the critical quantities A_{ij}, B_{ij}, the integrals on the RHS of Eqs. (4.7), (4.8) must be available. Their generation requires all integrals $[ij, kl]$ of the preceding iteration if all possible Jacobi rotations are to be pretested for the next iteration. It is therefore necessary to update all integrals $[ij, kl]$ for each Jacobi rotation that is carried out, and the efficiency provided by the algorithm described in Sect. 2 is essential.

The formulas given in Sect. 2.3 depend upon γ only through the functions $\cos \nu\gamma$, and $\sin \nu\gamma$ with $\nu = 1, 2, 3, 4$. In the present case, these functions can be calculated directly from the quantities A_{ij}, B_{ij} of Eqs. (4.7), (4.8), without recourse to trigonometric function evaluations. First, calculate $\cos 4\gamma, \sin 4\gamma$. From Eqs. (4.12) and (4.14), it is seen that $\cos 4\gamma = \cos 4\alpha$, $\sin 4\gamma = \sin 4\alpha$ in the case of *localization* and $\cos 4\gamma = -\cos 4\alpha$, $\sin 4\gamma = -\sin 4\alpha$ in the case of *delocalization*. The values of $\cos 4\alpha$ and $\sin 4\alpha$ are however directly given by Eqs. (4.9). Having $\cos 4\gamma$ and $\sin 4\gamma$, one obtains:

$$\cos 2\gamma = [(1 + \cos 4\gamma)/2]^{1/2}, \qquad \sin 2\gamma = [(1 - \cos 4\gamma)/2]^{1/2}. \tag{4.16}$$

Since, according to construction, the angle (4γ) lies in the range $-\pi \leqslant 4\gamma < \pi$, the signs of $\cos 2\gamma$ and $\sin 2\gamma$, *if they do not vanish*, must be chosen as follows:

If $\cos 2\gamma \neq 0$, then: $\cos 2\gamma > 0$ always

If $\sin 2\gamma \neq 0$, then: $\sin 2\gamma > 0$ if $\sin 4\gamma > 0$; $\sin 2\gamma < 0$ if $\sin 4\gamma \leqslant 0$.

From $\cos 2\gamma$, $\sin 2\gamma$ one obtains:

$$\cos\gamma = [(1+\cos 2\gamma)/2]^{1/2}, \qquad \sin\gamma = [(1-\cos 2\gamma)/2]^{1/2}, \tag{4.17}$$

where $\cos\gamma$ is always positive and $\sin\gamma \geqslant 0$ if $\sin 2\gamma \geqslant 0$; $\sin\gamma \leqslant 0$ if $\sin 2\gamma \leqslant 0$. From the calculated functions one finally obtains:

$$\cos 3\gamma = \cos\gamma\cos 2\gamma - \sin\gamma\sin 2\gamma, \quad \sin 3\gamma = \cos\gamma\sin 2\gamma + \sin\gamma\cos 2\gamma. \tag{4.18}$$

The functions of Eq. (4.17) are, of course, also needed for the orbital transformation.

4.3 *Quantitative results*

As a test we applied the described localization program to the anthracene molecule, $C_{14}H_{10}$. All CC distances were assumed to be 1.4 Å, all CH distances 1.1 Å. A minimal basis set (8*s*, 4*p* on carbon, 3*s* on hydrogen, eventempered) was used. All 47D_{2h}-symmetry-adapted occupied molecular orbitals were determined by an SCF calculation. Starting with these MO's, the 47 localized orbitals were determined until the localization sum changed by less than 10^{-12} hartree.

Quantitative data about the iterative process pertaining to the third procedure discussed in Sect. 3 are listed in Table 1 for various choices of the threshold factor τ. (The sequential thresholds are $1, \tau, \tau^2, \tau^3, \ldots,$ the last one being the first $\leqslant 10^{-12}$.) From this table, we can draw the following conclusions.

Table 1. Quantitative documentation of the localization of all 47 molecular orbitals of anthracene, starting with D_{2h} symmetry-adapted SCF orbitals. Convergence criterion of localization sum = 10^{-12} hartree

Threshold factor (τ)	.99	.95	.9	.6	.3	.1	.01	.001	.0001
Number of thresholds (T)	2750	539	263	55	23	12	6	4	3
Number of actual sweeps (S)	3776	1114	605	182	83	58	41	36	33
Average number of sweeps/threshold (S/T)	1.37	2.07	2.30	3.31	3.61	4.83	6.83	9.00	11.00
Total no. of Jacobi rotations (J)	3712	3794	3813	4068	3587	4253	4338	4681	5050
Equivalent number of full sweeps[a] ($J/1081$)[b]	3.43	3.51	3.53	3.76	3.32	3.93	4.01	4.33	4.67
Average number of Jacobi rotations/sweep (J/S)	0.98	3.41	6	22	43	73	106	130	153
Averagte number of Jacobi rotations/threshold (J/T)	1.35	7.04	14	74	156	354	723	1170	1683
Relative RMSQ deviation of *actual* no. of (Jacobi rot./threshold) from *average* no. of (Jacobi rot./threshold)	119%	60%	49%	37%	32%	31%	33%	35%	30%

[a] This would be the number of iterations in which a quasi-Newton procedure would have to converge in order to be competitive with the Jacobi rotation approach

[b] 1081 = 47 × 46/2 = Number of independent Jacobi rotations in a full orthogonal transformation of 47 orbitals

(i) There is not too much difference in efficiency, as measured by the total number of Jacobi rotations required (J), for threshold factors between 0.3 and 0.9. Further calculations in this range revealed no smooth dependence of J on τ; the actual number seems to depend on numerical accidents. However, the total number of Jacobi rotations increases markedly for very small τ. A choice of τ between 0.3 and 0.6 is likely to give good results.

(ii) For such choices of τ, about three to four sweeps are executed for each threshold value and, in each sweep, about 30% of the Jacobi rotations are executed.

(iii) The number of Jacobi rotations per threshold oscillates considerably from one threshold value to another in any one localization calculation, as indicated by the 30% to 40% deviation from its average value.

(iv) Since a full transformation of all 47 orbitals would require $47 \times 46/2 = 1081$ Jacobi rotations, it is apparent that *the present procedure requires less computational effort than what would be required for the integral transformations of* 4 *quasi-Newton iterations. It seems highly unlikely that a quasi-Newton procedure would converge to* 10^{-12} *hartree in three iterations.*

Table 1 also suggests, however, that at least as effective would be the first method discussed in Sect. 3, namely to execute only the Jacobi rotation with the largest localization gain in each sweep. Indeed, this algorithm required 3723 Jacobi rotations in as many sweeps in close agreement with the results for $\tau = 0.99$ in Table 1.

The computation times required for the localization are compared with those of the other parts of the SCF calculation in Table 2. The time required for the localization process is seen to be about equal to that required for the transformation from the two-electron integrals between AO's to those between the occupied MO's. Both processes take about twice as long as the SCF calculation itself but only 20% of the time needed for the initial calculation of the AO integrals. It should be noted that the times required for the AO integrals, the SCF calculation and the transformation from AO to MO integrals, all will increase substantially when extended basis sets are used instead of the minimal basis sets. *The localization calculation itself (including the four-index updating) will, however, take no longer than for the minimal basis.* It will therefore account for an even smaller fraction of the total computation time. Thus, the E–R localization does not require as great a computation effort as is often believed. Most likely, the misconception is due to unawareness of the efficiencies discussed in Sections 2 and 3.

Table 2. Comparison of computation times for anthracene

Generation and sorting of AO integrals[a]	10
SCF calculation[a]	1
Transformation of two-electron integrals from the full AO basis to the basis of occupied MO's	1.7
Localization calculation (depends on choice of τ)	1.7–2

[a] Calculated without use of D_{2h} symmetry. This seems appropriate for comparison with the localization procedure molecule, in principle, must mix orbitals of different irreps

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