Notes on Localised Orbitals

Annotated up to the Foster-Boys method

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1 Definition of Localised Orbitals

1.1 Transformation Invariance

Wave-Function description A determinantal wave-function of 2N electrons with N doubly occupied orthonormal real orbitals $\{\phi_i\}$, such that

$$\Phi = \mathcal{A}\{(\phi_1\alpha)^{(1)}(\phi_1\beta)^{(2)}\dots(\phi_N\alpha)^{(2N-1)}(\phi_N\beta)^{(2N)}\} \tag{1}$$

and defined by an SCF calculation is invariant to unitary transformation. Φ is therefore associated with the N-dimensional linear space subtended by $\{\phi_i\}$.

Electron Interaction Energy

$$\begin{aligned}
EI = C - X \ &= <\Phi|\sum_{i<j} r_{12}^{-1}|\Phi> \\
C &= \frac{1}{2}\int dV_1 \int \rho(1)\ r_{12}^{-1}\ \rho(2)\ dV_2 \\
&= \frac{1}{2}.2.2\sum_{mn}\int dV_1 \int \phi_m(1)^*\phi_m(1)\ r_{12}^{-1}\ \phi_n(2)^*\phi_n(2)\ dV_2 \\
&= 2\sum_{mn}[\phi_m^2|\phi_n^2] \qquad (2) \\
&= 2\sum_{pqrs}\{\sum_m T_{pm}^* T_{qm}\sum_n T_{rn}^* T_{sn}\}\ [\chi_p\chi_q|\chi_r\chi_s]; \quad \phi_m = \sum_i \chi_i T_{im} \\
&= 2\sum_{pqrs}\delta_{pq}\delta_{rs}\ [\chi_p\chi_q|\chi_r\chi_s] \\
C &= 2\sum_{pr}[\chi_p^2|\chi_r^2] \qquad (3)
\end{aligned}$$

As is evident, (2) $\equiv$ (3). The same principle demonstrates the invariance of the exchange integral to the orthogonal transformation of the basis associated with Φ.

1.2 Orbital Self-Repulsion Energy Maximisation

Diagonal Sum Basis Transformation The diagonal sum is defined by

$$\begin{aligned}
D(\phi) &= \sum_n [\phi_n^2|\phi_n^2] \qquad (4) \\
&= \sum_n \int dV_1 \int \phi_n(1)^*\phi_n(1)\ r_{12}^{-1}\ \phi_n(2)^*\phi_n(2)\ dV_2 \\
&= \sum_{pqrs}\{\sum_n T_{pn}^* T_{qn}\sum_n T_{rn}^* T_{sn}\}\ [\chi_p\chi_q|\chi_r\chi_s]; \quad \phi_n = \sum_i \chi_i T_{in} \\
&= \sum_{pqrs}\delta_{pq}\delta_{rs}\ [\chi_p\chi_q|\chi_r\chi_s] \\
&= \sum_{pr}[\chi_p^2|\chi_r^2] \qquad (5)
\end{aligned}$$

Clearly, while (4) = (5), (4) $\not\equiv$ (5). This sum occurs in both the coulomb and the exchange terms, and thus the objective here is to extremise its representation (maximise in the localised orbital basis) without altering the invariance of C and X to the same transformation. This defines certain characteristics of the energy-localised SCF orbitals [1].

2 Conditions for localised orbitals

2.1 Orthogonal Transformation of the infinitesimal variation

An orthogonal transformation changes the basis functions into

$$\phi_n(x) + \delta\phi_n(x) = \sum_i \phi_i(x) T_{in} \tag{6}$$

To delineate the off-diagonal terms, consider,

$$T_{ij} = \delta_{ij} + t_{ij}$$

$$\phi_n(x) + \delta\phi_n(x) = \sum_i \phi_i(x)(\delta_{in} + t_{in})$$

Therefore,

$$\delta\phi_n(x) = \sum_i \phi_i(x) t_{in}$$

With

$$\sum_n T_{in} T_{jn} = \delta_{ij},$$

$$\begin{aligned}\sum_n T_{in} T_{jn} &= \sum_n (\delta_{in} + t_{in})(\delta_{jn} + t_{jn}) \\ &= \delta_{ij} + t_{ij} + t_{ji} + \sum_n t_{in} t_{jn}\end{aligned}$$

This results in

$$t_{ij} + t_{ji} + \sum_n t_{in} t_{jn} = 0 \tag{7}$$

Since t is an infinitesimal matrix, it is a reasonable approximation to consider only the first order terms:

$$\tau_{ij} + \tau_{ji} \approx 0$$

Accuracy losses are in the order of t_{ij}^2, therefore,

$$\delta\phi_n \approx \sum_i \phi_i(x)\tau_{in} \tag{8}$$

The variation in $D(\phi)$, then is:

$$\begin{aligned}\delta D(\phi) &= \sum_n [2\phi_n \delta\phi_n | \phi_n^2] + [\phi_n^2 | 2\phi_n \delta\phi_n] \\ &= 2\sum_n \{[\phi_n^2 | \phi_n \delta\phi_n]^* + [\phi_n^2 | \phi_n \delta\phi_n]\}; \quad \{\phi_i\} \in R \; \forall \; i \in Z^+ \\ &= 4\sum_n [\phi_n^2 | \phi_n \delta\phi_n]\end{aligned} \tag{9}$$

2.2 Basis transformation of extremised $D(\phi)$

$$\delta D = 4\sum_n [\phi_n^2 | \phi_n \delta\phi_n] = 4\sum_n [\phi_n^2 | \phi_n \phi_i] \tau_{in}; \quad \delta D(\phi) \equiv \delta D$$

Choosing from the independent elements of the infinitesimal matrix, split the sum into three cases:

$$\delta D = 4\{\sum_{m>n} [\phi_n^2 | \phi_m \phi_n] \tau_{mn} + \sum_{m<n} [\phi_n^2 | \phi_m \phi_n] \tau_{mn}\}$$

As $\tau_{nn} = 0$ and $\tau_{mn} = -\tau_{nm}$,

$$\delta D = 4\{\sum_{m>n} [\phi_n^2 | \phi_m \phi_n] \tau_{mn} - \sum_{m<n} [\phi_n^2 | \phi_m \phi_n] \tau_{nm}\}$$

By switching the indices of the second summation and reducing,

$$\delta D = 4 \sum_{m>n} \{[\phi_n^2|\phi_m\phi_n] - [\phi_m^2|\phi_m\phi_n]\}\tau_{mn} \tag{10}$$

To determine the basis $\{\lambda_i\}$ where $\lambda_\nu = \sum_i \phi_i T_{i\nu}$ such that $D(\lambda)$ is maximum, ie, of maximum localisation, $\delta D(\lambda) = 0$.

$$(10) \implies [\lambda_n^2|\lambda_m\lambda_n] = [\lambda_m^2|\lambda_m\lambda_n]$$

Due to the geometrical symmetry of these orbitals, this condition was expected to be true, and it clearly is. However, this is also true of when the localisation is minimum. Application of the method of steepest ascent suggests itself for finding the maximally localised orbitals $\{\lambda_\nu\}$ [1].

3 Determination of Localised Orbitals

3.1 Two-Dimensional Space

Consider an orthogonal transformation from the (ϕ_1, ϕ_2) space to (u_1, u_2) as defined by

$$T = \begin{bmatrix} \cos\gamma & \sin\gamma \\ -\sin\gamma & \cos\gamma \end{bmatrix}$$

Resulting in

$$\begin{aligned} u_1 &= \phi_1 \cos\gamma + \phi_2 \sin\gamma \\ u_2 &= -\phi_1 \sin\gamma + \phi_2 \cos\gamma \end{aligned}$$

Where

$$u_i(x) \equiv u_i; \quad \phi_i(x) \equiv \phi_i$$

$$\begin{aligned} u_1^2 &= \phi_1^2 + \sin^2\gamma(\phi_2^2 - \phi_1^2) + \sin 2\gamma(\phi_1\phi_2) \\ u_2^2 &= \phi_2^2 + \sin^2\gamma(\phi_1^2 - \phi_2^2) - \sin 2\gamma(\phi_1\phi_2) \end{aligned}$$

$$D(u) = \sum_{i=1}^{2} [u_i^2|u_i^2] = [u_1^2|u_1^2] + [u_2^2|u_2^2] \tag{11}$$

$$\begin{aligned} = D(\phi) &- 2\sin^2\gamma[\phi_1^2|\phi_1^2 - \phi_2^2] + 2\sin 2\gamma[\phi_1^2|\phi_1\phi_2] + \sin^4\gamma[\phi_1^2 - \phi_2^2|\phi_1^2 - \phi_2^2] - 2\sin^2\gamma\sin 2\gamma[\phi_1^2 - \phi_2^2|\phi_1\phi_2] + \sin^2 2\gamma[\phi_1\phi_2|\phi_1\phi_2] \\ &+2\sin^2\gamma[\phi_2^2|\phi_1^2 - \phi_2^2] - 2\sin 2\gamma[\phi_2^2|\phi_1\phi_2] + \sin^4\gamma[\phi_1^2 - \phi_2^2|\phi_1^2 - \phi_2^2] - 2\sin^2\gamma\sin 2\gamma[\phi_1^2 - \phi_2^2|\phi_1\phi_2] + \sin^2 2\gamma[\phi_1\phi_2|\phi_1\phi_2] \end{aligned}$$

$$\begin{aligned} = D(\phi) &- 2\sin^2\gamma[\phi_1^2 - \phi_2^2|\phi_1^2 - \phi_2^2] + 2\sin 2\gamma[\phi_1^2 - \phi_2^2|\phi_1\phi_2] + 2\sin^4\gamma[\phi_1^2 - \phi_2^2|\phi_1^2 - \phi_2^2] - 4\sin^2\gamma\sin 2\gamma[\phi_1^2 - \phi_2^2|\phi_1\phi_2] \\ &+2\sin^2 2\gamma[\phi_1\phi_2|\phi_1\phi_2] \end{aligned}$$

$$= D(\phi) + (2\sin^2 2\gamma - 1 + 1)([\phi_1\phi_2|\phi_1\phi_2] - \frac{1}{4}[\phi_1^2 - \phi_2^2|\phi_1^2 - \phi_2^2]) + 2\sin 2\gamma(1 - 2\sin^2\gamma)[\phi_1^2 - \phi_2^2|\phi_1\phi_2]$$

$$= D(\phi) + A_{12} + (A_{12}^2 + B_{12}^2)^{1/2}\left\{\cos 4\gamma \frac{-A_{12}}{(A_{12}^2 + B_{12}^2)^{1/2}} + \sin 4\gamma \frac{B_{12}}{(A_{12}^2 + B_{12}^2)^{1/2}}\right\}$$

Where

$$A_{12} = [\phi_1\phi_2|\phi_1\phi_2] - \frac{1}{4}[\phi_1^2 - \phi_2^2|\phi_1^2 - \phi_2^2]; \qquad B_{12} = [\phi_1^2 - \phi_2^2|\phi_1\phi_2]$$

Since

$$|A_{12}| \leq |(A_{12}^2 + B_{12}^2)^{1/2}| \quad and \quad |B_{12}| \leq |(A_{12}^2 + B_{12}^2)^{1/2}|,$$

It is valid to set

$$4\alpha = \arccos \frac{-A_{12}}{(A_{12}^2 + B_{12}^2)^{1/2}} = \arcsin \frac{B_{12}}{(A_{12}^2 + B_{12}^2)^{1/2}}$$

Subject to the condition that

$$4\alpha = \arctan \frac{-B_{12}}{A_{12}}$$

Therefore,

$$D(u) = D(\phi) + A_{12} + (A_{12}^2 + B_{12}^2)^{1/2} \cos 4(\gamma - \alpha) \tag{12}$$

It then follows that

$$\gamma_{max} \equiv \alpha + \frac{n\pi}{2} \qquad \text{and} \qquad \gamma_{min} \equiv \alpha + \frac{(2n+1)\pi}{4}, \quad \gamma \in [2(m-1)\pi,\ 2m\pi]; \quad m,\ n \in Z$$

$$D_{max}(u) = D(\phi) + A_{12} + (A_{12}^2 + B_{12}^2)^{1/2} \tag{13}$$

$$D_{min}(u) = D(\phi) + A_{12} - (A_{12}^2 + B_{12}^2)^{1/2} \tag{14}$$

The localised orbitals $\{\lambda_i\}$ are

$$\lambda_1 = \cos\alpha_0\phi_1 + \sin\alpha_0\phi_2$$
$$\lambda_2 = -\sin\alpha_0\phi_1 + \cos\alpha_0\phi_2$$

The value of α_0 is one of λ_{max}. As T is a rotational orthogonal matrix, the other values of α_0 correspond to equivalent sign altering rotations of the same magnitude about the (orthonormal and real) basis vectors. The values of the energy integrals may be computed numerically, however, a complete analytical method is also described [1].

4 Extending the Jacobi Rotations for the general n-dimensional case

4.1 General Principle

Now that the 2x2 Givens rotation is determined for the optimisation of a subproblem,

$$T = \begin{bmatrix} \cos\gamma & \sin\gamma \\ -\sin\gamma & \cos\gamma \end{bmatrix}$$

This lends itself immediately to a series of 2x2 rotations that are independent of each other. The rotations are repeated for every unique pair of orbitals present in the canonical input:

$$J_1 = T^{(1)}_{\frac{(n)(n-1)}{2}} * T^{(1)}_{\frac{(n)(n-1)}{2}-1} ... * T^{(1)}_2 * T^{(1)}_1$$

Therefore, at the end of each set of rotations, which shall henceforth be referred to as a pass, v passes of $m = \frac{(n)(n-1)}{2}$ rotations are repeated to arrive at:

$$J = \prod_{k=1}^{v} \prod_{i=0}^{m-1} T^{(k)}_{m-i} \ = \ \prod_{k=1}^{v} J_k \tag{15}$$

v is defined by the point of convergence. There are multiple ways to achieve convergence, the easiest of which is readily applicable to the Jacobi method.

$$L = [i^2|i^2]; \qquad [u_i^2|u_i^2] \equiv [i^2|i^2]$$

In theory, any localisation/delocalisation problem can use the determination of the ER functional above to determine if further iteration is required. However, the Jacobi method is incremental, and therefore does not encounter some of the problems that other procedures may when using this criterion to judge convergence.

4.2 Implementing the Jacobi method

It is essential to determine the result of a rotation on the value of the 2-electron energy integral, specifically, the values of A_{ij} and B_{ij}. This is described in detail in [2]. To simplify the expressions:

$$R_1 = \{[i^2|i^2] + [j^2|j^2] - 2[i^2|j^2] - 4[ij|ij]\}/8 \tag{16}$$
$$R_2 = \{[i^2|ij] - [j^2|ij]\}/2 \tag{17}$$

$$A_{ij} = -2R_1$$
$$B_{ij} = 2R_2$$

In these terms,

$$\Delta L = (R_1 \cos 4\gamma + R_2 \sin 4\gamma - R_1) \tag{18}$$

As there are no more integrals to compute for the localisation problem, the result of R_1, R_2 when transformed will suffice, derived from [2]. To denote this transformation, $\hat{R}_i$ is used:

$$\hat{R}_1 = R_1 \cos 4\gamma + R_2 \sin 4\gamma$$
$$\hat{R}_2 = -R_1 \cos 4\gamma + R_2 \sin 4\gamma$$

To determine the rotation vectors, it is sufficient to calculate the nonzero components of the Givens rotation matrix[2]:

$$\cos 4\gamma = \cos 4\alpha = \frac{-R_1}{(R_1^2 + R_2^2)^{1/2}} \tag{19}$$
$$\sin 4\gamma = \sin 4\alpha = \frac{R_2}{(R_1^2 + R_2^2)^{1/2}} \tag{20}$$

As such, it is trivial to determine:

$$\cos\gamma = \{\frac{1 + (\frac{1+\cos^2 4\gamma}{2})^{1/2}}{2}\}^{1/2}$$
$$\sin\gamma = \sqrt{1 - \cos^2\gamma}$$

Naturally, this imposes some constraints on the rotation, as there are multiple possible values in the defined range of $[-\pi, \pi]$, even if $\cos\gamma$ is determinate. It is of paramount importance, then, to ensure that $\arctan(\frac{R_2}{-R_1}) = 4\gamma$.

Alternatively, it may serve the purpose of clarity without sacrificing any rigour, to perform:

$$cos\gamma = cos(\frac{1}{4}arccos(cos4\gamma))$$
$$sin\gamma = sin(\frac{1}{4}arcsin(sin4\gamma))$$

This fully detrmines the value of $tan\gamma$. Following, this approach however, poses some additional constraints on the bounds, detailed in [3]

5 Direct Inversion in Iterative Subspace

5.1 Nature of inversion, subspace definition and saddle points

The premise of the DIIS method is the optimisation of already mostly localised MOs, which is achieved by identifying the saddle point at the maximum of the ER functional. This is described in detail in [3], and proved in the appendix.

The ER functional to be maximised is homogenous and of the fourth order, described in terms of a single transformation for step a and transformation i:

$$\xi(U) = \sum_{ijklr} U_{ji}U_{ki}U_{li}U_{ri}(\chi_j^{(a)}\chi_k^{(a)}|\chi_l^{(a)}\chi_r^{(a)})$$

The subspace defined by the transformation generated by U is chosen such that $U \epsilon SO(m)$, with SO(m) defined such that $\det(U) = 1$ and the orthogonal group defined by this transformation is such that $UU^T = Id$ at the limit. Further requirements for generation are present in [4]

Given a set of m orthonormal occupied MOs, the determination of the maximally self-interacting orbitals is defined by the canonical ER functional in (5)

A single step in this transformation is defined by:

$$\eta(U) = \sum_i (\chi_i\chi_i^{(0)}|\chi_i^{(0)}\chi_i^{(0)})$$

Where χ_i is the transformed orbital towards a localised basis. In terms of its transformation, the integral may be represented as:

$$\eta(U) = \sum_{ji} U_{ji}(\chi_j^{(0)}\chi_i^{(0)}|\chi_i^{(0)}\chi_i^{(0)})$$

Inferring from (10), the saddle point should be at $[\chi_n^2|\chi_m\chi_n] = [\chi_m^2|\chi_m\chi_n]$

If SO(m) is parametrised according the exponential map that generates U such that $U = e^{\Delta}$, Δ being the antisymmetric generator matrix, described in [1] and [4], the saddle point is at:

$$R_{ji}^{(k)} = R_{ij}^{(k)}; \qquad R_{ji}^{(k)} = (\chi_j^{(k)}\chi_i^{(k)}|\chi_i^{(k)}\chi_i^{(k)}) \tag{21}$$

This is proved in the appendix of [4], however, it is also evident, given that (10) was true primarily due to the geometry of the localised orbitals, and therefore (21) must be too.

Constructing U for $U \epsilon SO(m)$, it is shown in [4] that $\eta(U)$ has a unique maxima at $U = R(R^TR)^{-1/2}$.

5.2 Construction of DIIS transformation

Before proceeding, it is important to note that traversing the space $SO(m)$ defined above, one arrives at the ER orbitals at a point such that $R^{(k)}$ is symmetric, however, it is not necessary that the saddle point represents this maxima. In particular,

$$\lim_{k\to\infty} U^{(k)} = \lim_{k\to\infty} R^{(k)}((R^{(k)})^T R^{(k)})^{-1/2}) = Id$$

As there are no conditions on the second derivative, all that can be said for the orthonormal and localised $\{\chi^{(k)}\}$ generated is that it is an extremum for $\frac{\delta\xi}{\delta\Delta_{ij}}$. This is dealt with in depth in [4].

The algorithm is described in [4] under section III. It is relatively straightforward for when $((R^{(k)})^T R^{(k)})$ is positive definite, ([4], Appendix subsection 3 on maxima) however, due to the numerical accuracy threshold of most decomposition algorithms, it is sufficient for it to satisfy positive semi-definiteness.

There are two ways to generate $((R^{(k)})^T R^{(k)})^{-1/2}$, the first is using Cholesky decomposition: [5]

$$((R^{(k)})^T R^{(k)}) = LL^T$$

By virtue of the nature of the decomposition,

$$((R^{(k)})^T R^{(k)})^{1/2} = L$$

Since L is a lower triangular matrix, the inverse is easily determined. As $U^{(k)} \epsilon SO(m)$ and $((R^{(k)})^T R^{(k)})$ is symmetric, it is invertible and symmetric.

$$((R^{(k)})^T R^{(k)})^{-1/2} = L^{-1}$$

The second way is to determine the inverse first, and then perform and eigendecomposition to determine the square-root. The most efficient way to do this is to use the Bunch-Kaufman factorisation, which has the added benefit of working for symmetric indefinite matrices. [5]

Once the inverse $((R^{(k)})^T R^{(k)})^{(-1)}$ is determined, eigendecomposition is possible.

$$((R^{(k)})^T R^{(k)})^{-1} = VSV^T$$

The eigenvalues are contained in the diagonal of the matrix S. It is then a simple matter to determine:

$$((R^{(k)})^T R^{(k)})^{-1/2} = VS^{1/2}V^{-1}$$

It is fairly straightforward to prove that the eigenvectors of S are also eigenvectors of $S^{1/2}$:

$$(VS^{1/2}V^{-1})^2 = VS^{1/2}V^{-1}VS^{1/2}V^{-1} = VSV^{-1} = ((R^{(k)})^T R^{(k)})^{(-1)}$$

Therefore, we have a means of constructing the transformation. Once it is ascertained for one iteration,

$$R^{(k)}_{ji} = \sum_{pqrs} D_{pj}D_{qi}D_{ri}D_{si}R^{(0)}_{ji}$$

The remainder of the algorithm for performing DIIS is present in [4], and may be implemented ad pedem litterae.

6 The Foster-Boys method

6.1 Attempting a simpler approach

In spite of the theoretical advantages of the Edmiston-Ruedenberg (ER) procedure, the computational complexity of each iterative step increases N^5 with the number of electrons N, while Boys' algorithm behaves like N^3. Because of this fact Boys

localization is used almost exclusively in contemporary applications. Boys and Foster also laid the basis of localisation using one-electron moment integrals, which are inherently easier to calculate.

The Boys localization procedure chooses a transformation that minimises the orbital self-extension:

$$I(\phi) = \sum_{i=1}^{n} \int \phi_i(1)\phi_i(1)\ r_{12}^2\ \phi_i(2)\phi_i(2)\ dv_1 dv_2$$

An equivalent formulation maximises the sum of squares of distances of the orbital centroids from the arbitrarily defined origin of the molecular coordinate system:

$$D(\phi) = \sum_{i=1}^{n} < \phi_i |\ \vec{r}\ | \phi_i >^2 \tag{22}$$

Each of these procedures leads to the same set of LMO's. Following Boys' suggestion to utilise (22), which is referred to hereafter as the SOS (Sum of Squares) criterion, maximization of D is especially easy to implement and requires manipulation of far fewer molecular integrals than would direct minimization of I.

6.2 The Boys orbitals transformation algorithm

The Boys LMOs are obtained by successive application of two-orbital transformations until a predetermined convergence criterion is satisfied. This approach is completely analogous to that outlined by Edmiston and Ruedenberg for obtaining the energy-localized orbitals:

$$T = \begin{bmatrix} \cos\gamma & \sin\gamma \\ -\sin\gamma & \cos\gamma \end{bmatrix}$$

However, the values determined are derived from [6] as:

$$A_{ij} = \vec{r_{ij}}^{\,2} - \frac{1}{4}(\vec{r_{ii}}^{\,2} - \vec{r_{jj}}^{\,2})$$
$$B_{ij} = (\vec{r_{ii}} - \vec{r_{jj}}).\vec{r_{ij}}; \qquad\qquad \vec{r_{ij}} \equiv < \phi_i |\ \vec{r}\ | \phi_j >$$

The rest of the transformation follows identically to the ER Jacobi transformation, and is detailed, along with the convergence criterion in [6]:

$$D_{max}(\mu) = D(\phi) + A_{ij} + (A_{ij}^2 + B_{ij}^2)^{1/2} \tag{23}$$

Drawing from [6], it follows that convergence, which may be determined from B_{ij}, as it is also derived from the removal of non-maximising transformations, is attained when:

$$\left|\nabla D\right| = 4\left\{\sum_{i<j}^{n} [(\vec{r_{ii}} - \vec{r_{jj}}).\vec{r_{ij}}]^2\right\}^{1/2} \longrightarrow 0 \tag{24}$$

As with any iterative transformation extremisation algorithm, there are difficulties in determining the course of maximisation/minimisation and the final saddle point. This is dealt with further in [3], and may warrant changes in each of the respective algorithms.

Here, (25) is not strictly required throughout the process of transformation as it imposes a signficant penalty on computational complexity, it is sufficient to use it when (23) appears to converge. However, it is entirely possible that may not occur, therefore, it is advisable to set an upper threshold for iterations after which (24) is always checked. Further research into this is required [6], [3].

Appendices

A Integral Transformation Bottleneck

In most scenarios, the performance of an algorithm is determined by the speed with which the interaction (2 electron)/moment (1 electron) integrals are transformed from one basis to the next. With any system, the NxN case for 2e integrals scales with N^8, which is a very substantial cost, especially for each increment in dimension. Fortunately, for the methods presented above and most systems, these integrals obey several useful symmetry properties. Combined with the fact that memory costs are usually much lower in complexity than computation costs, storing the transformation of an index before moving to the next allows for a considerable speedup, of the order of N^3, reducing overall complexity to N^5.

Algorithm 4 index, 2 electron Integral transformation

procedure INTGL2ETRANSPS(n, T, $< p\ q \mid r\ s >$)
  loop p *over* 1...n
    loop q *over* 1...n
      loop r *over* 1...n
        loop s *over* 1...n
          Over l, $< p\ q \mid r\ l > = < p\ q \mid r\ l > + \sum_{l=1}^{n} T(l,s) < p\ q \mid r\ s >$
        end loop
        Over kl, $< p\ q \mid k\ l > = < p\ q \mid k\ l > + \sum_{k=1}^{n} T(k,r) < p\ q \mid r\ l >$
      end loop
      Over jkl, $< p\ j \mid k\ l > = < p\ j \mid k\ l > + \sum_{j=1}^{n} T(j,q) < p\ q \mid k\ l >$
    end loop
    Over ijkl, $< i\ j \mid k\ l > = < i\ j \mid k\ l > + \sum_{i=1}^{n} T(i,p) < p\ j \mid k\ l >$
  end loop
end procedure

The same principle may be applied to the 1e integrals.

B Effective Parallelisation

The 2x2 Jacobi methods lend themselves very well to parllel execution of the localisation as well as the transformation algorithm described above. Due to improvements in the openmp spec, it is no longer necessary to manually define the stack size and allocate chunks, the directive for dynamic/static scheduling of do loops automatically achieves good performance[7].

References

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