SCF methods, basis sets, and integrals

Lecture IV: Integrals

Wim Klopper

Abteilung für Theoretische Chemie, Institut für Physikalische Chemie
Karlsruher Institut für Technologie (KIT)

ESQC 2019, 8–21 September 2019
The Gaussian-product theorem

- The great success of GTOs is based on the fact that all necessary integrals are easily evaluated analytically.

- The most important reason for this efficiency is the Gaussian-product theorem (GPT).

- The figure shows the product of the (unnormalised) \( s \)-type GTOs \( \chi_a \) with exponent \( \alpha = 0.25 \) at \( A = (1, 0, 0) \) and \( \chi_b \) with exponent \( \beta = 0.50 \) at \( B = (-1, 0, 0) \),

\[
\chi_a(\mathbf{r}) = e^{-\alpha(\mathbf{r}-\mathbf{A})^2}, \quad \chi_b(\mathbf{r}) = e^{-\beta(\mathbf{r}-\mathbf{B})^2}
\]

- The two-centre product \( \chi_a(\mathbf{r})\chi_b(\mathbf{r}) \) is again a Gaussian \( \chi_p \) centred at the “centre of gravity” \( \mathbf{P} \).
The Gaussian-product theorem

- The product of the GTOs $\chi_a$ and $\chi_b$ can be written as
  \[
  \chi_a(r)\chi_b(r) = e^{-\frac{\alpha\beta}{\alpha+\beta}(A-B)^2} e^{-(\alpha+\beta)(r-P)^2}
  \]
  with
  \[
  P = \frac{\alpha A + \beta B}{\alpha + \beta}
  \]

- The factor $\exp(-\frac{\alpha\beta}{\alpha+\beta}(A-B)^2)$ is known as pre-exponential factor. Obviously, this factor vanishes for large distances between $A$ and $B$.

- Note that for two like exponents of the order of $10^{-3} a_0^{-2}$, the distance $|A - B|$ must be $\gg 100 a_0$ to make the pre-exponential factor smaller than $10^{-6}$. 
The overlap integral

- Using the GPT, we can easily compute the overlap integral $S_{ab}$ between two (real, unnormalised) $s$-type Gaussians,

\[
\int \chi_a(r) \chi_b(r) \, dr = e^{-\frac{\alpha \beta}{\alpha + \beta} (A - B)^2} \int e^{-(\alpha + \beta)(r - P)^2} \, dr
\]

\[
= e^{-\frac{\alpha \beta}{\alpha + \beta} (A - B)^2} \int e^{-(\alpha + \beta)r^2} \, dr
\]

\[
= e^{-\frac{\alpha \beta}{\alpha + \beta} (A - B)^2} \int e^{-(\alpha + \beta)x^2} \, dx \int e^{-(\alpha + \beta)y^2} \, dy \int e^{-(\alpha + \beta)z^2} \, dz
\]

\[
= e^{-\frac{\alpha \beta}{\alpha + \beta} (A - B)^2} \left( \frac{\pi}{\alpha + \beta} \right)^\frac{3}{2}
\]

- This equation reveals another important property of integrals over Gaussians: the 3D integral factorises into a product of three 1D integrals.

- Normalisation constant: $N_a = \left( \frac{2\alpha}{\pi} \right)^\frac{3}{4}$. 

The overlap integral

- The figure shows the overlap integral $S_{ab}$ for two $s$-type Gaussians with exponent $\alpha = \beta = 1$ $a_0^{-2}$ as a function of the distance $|A - B|$ (solid line).
- The dashed lines are overlap integrals with exponents 10 times larger and 10 times smaller.
- For the integral over contracted Gaussians (CGTOs), the overlap integral becomes

$$S_{\mu\nu} = \sum_{a=1}^{n_\mu} \sum_{b=1}^{n_\nu} c_{a\mu} S_{ab} c_{b\nu}$$

- In general, a large number of integrals over primitive functions contribute to a smaller number of integrals over CGTOs.
Primitive Cartesian GTOs

- The primitive Cartesian GTO is
  \[ \chi_a(r) = x_A^i y_A^j z_A^k \exp(-\alpha r_A^2), \quad r_A = r - A \]

- Integrals over real-valued spherical-harmonic GTOs
  \[ \chi'_a(r) = S_{lm}(x_A, y_A, z_A) \exp(-\alpha r_A^2) \]
  (where \( S_{lm}(x_A, y_A, z_A) \) is a real solid harmonic), can be obtained by transforming the integrals over primitive Cartesian GTOs with a corresponding transformation matrix.
  \[ S' = C^T S C \]

- Usually, this transformation is done after the contraction:
  primitive Cartesian GTOs \( \Rightarrow \) contracted Cartesian GTOs
  \( \Rightarrow \) contracted spherical-harmonic GTOs
Primitive Cartesian GTOs

- As already mentioned, the factorisation of the Cartesian GTOs is an important property,
  \[ \chi_a = \{ x^i_A \exp(-\alpha x^2_A) \} \{ y^i_A \exp(-\alpha y^2_A) \} \{ z^i_A \exp(-\alpha z^2_A) \} \]

- We can thus focus our attention on only one Cartesian component, say \( x \),
  \[ G_i(x, \alpha, A_x) = x^i_A \exp(-\alpha x^2_A) \]

- The self overlap of the \( x \) component is
  \[ \langle G_i|G_i \rangle = \frac{(2i - 1)!!}{(4\alpha)^i} \sqrt{\frac{\pi}{2\alpha}}, \quad \langle G_0|G_0 \rangle = \sqrt{\frac{\pi}{2\alpha}} \]

- All we have used thus far is the definite integral
  \[ \int_{-\infty}^{\infty} x^{2n} e^{-ax^2} \, dx = \frac{1 \cdot 3 \cdot 5 \ldots (2n - 1)}{(2a)^n} \sqrt{\frac{\pi}{a}} \]
Recurrence relations for Cartesian GTOs

- The differentiation property of Cartesian GTOs is needed on several occasions,
  \[
  \frac{\partial G_i}{\partial A_x} = - \frac{\partial G_i}{\partial x} = 2\alpha G_{i+1} - i G_{i-1}
  \]

- In words, differentiation of a $d_{xy}$-type GTO with respect to $x$ gives a linear combination of $p_y$ and $f_{x^2y}$, etc.

- For higher derivatives, we obtain
  \[
  \frac{\partial^{n+1} G_i}{\partial A_x^{n+1}} = \left( \frac{\partial}{\partial A_x} \right)^n (2\alpha G_{i+1} - i G_{i-1}) = 2\alpha \frac{\partial^n G_{i+1}}{\partial A_x^n} - i \frac{\partial^n G_{i-1}}{\partial A_x^n}
  \]

- We thus find (besides $G_{i+1} = x_A G_i$):
  \[
  G_i^{m+1} = 2\alpha G_i^m + i G_{i-1}^m, \quad \text{with} \quad G_i^m = \frac{\partial^m G_i}{\partial A_x^m}
  \]
Gaussian overlap distributions

• We define the Gaussian overlap distribution

\[ \Omega_{ab}(r) = \chi_a(r) \chi_b(r) \]

which factorises as

\[ \Omega_{ab}(r) = G_i(x, \alpha, A_x) G_j(x, \beta, B_x) \cdots = \Omega_{i,j}^x(x, \alpha, \beta, A_x, B_x) \cdots \]

• Due to the GPT, \( \Omega_{i,j}^x \) may be written as

\[ \Omega_{i,j}^x = K_{ab}^x x_A^i x_B^j \exp(-\eta x_P^2), \quad \text{with} \quad \eta = \alpha + \beta \]

\( K_{ab}^x \) is the \( x \) component of the pre-exponential factor.

• In the above equation, we give \( x \) relative to \( A_x, x_B \) and \( x_P \). We therefore rewrite the equation using

\[
x_A = x - A_x = x - P_x + (P_x - A_x) = x - P_x + X_{PA} = x_P + X_{PA} \\
x_B = x - B_x = x - P_x + (P_x - B_x) = x_P + X_{PB}
\]
Properties of overlap distributions

- We have the obvious relationships
  \[ x_A \Omega^x_{i,j} = \Omega^x_{i+1,j}, \quad x_B \Omega^x_{i,j} = \Omega^x_{i,j+1}, \quad X_{AB} \Omega^x_{i,j} = \Omega^x_{i,j+1} - \Omega^x_{i+1,j} \]

- Differentiating the overlap distributions yields
  \[ \frac{\partial \Omega^x_{i,j}}{\partial A_x} = 2\alpha \Omega^x_{i+1,j} - i \Omega^x_{i-1,j}, \quad \frac{\partial \Omega^x_{i,j}}{\partial B_x} = 2\beta \Omega^x_{i,j+1} - j \Omega^x_{i,j-1} \]

- We furthermore note that
  \[ X_{PA} = P_x - A_x = \frac{\alpha A_x + \beta B_x}{\eta} - \frac{\alpha + \beta}{\eta} A_x = \frac{\beta}{\eta} (B_x - A_x) = -\frac{\beta}{\eta} X_{AB} \]

  \[ X_{PB} = P_x - B_x = \frac{\alpha A_x + \beta B_x}{\eta} - \frac{\alpha + \beta}{\eta} B_x = \frac{\alpha}{\eta} (A_x - B_x) = \frac{\alpha}{\eta} X_{AB} \]

- It is sometimes convenient to work with \( P_x \) and \( X_{AB} \) in the place of \( A_x \) and \( B_x \).
The Obara–Saika scheme for $S_{ij}$

- We consider the integral

$$S_{ij} = \int_{-\infty}^{\infty} \Omega_{ij}^{x} dx$$

- This integral is invariant to a translation of the coordinate system along the $x$-axis,

$$\frac{\partial S_{ij}}{\partial A_{x}} + \frac{\partial S_{ij}}{\partial B_{x}} = 0$$

- This yields the *translational recurrence relation*

$$2\alpha S_{i+1,j} - i S_{i-1,j} + 2\beta S_{i,j+1} - j S_{i,j-1} = 0$$

- This recurrence relation alone is not useful, because there are two terms with "quantum number" $i + j + 1$.

- The idea is to first compute $S_{00}$ and then to obtain all other integrals from the recurrence relation.
The Obara–Saika scheme for $S_{ij}$

- In order to be useful, the translational recurrence relation

$$2\alpha S_{i+1,j} - i S_{i-1,j} + 2\beta S_{i,j+1} - j S_{i,j-1} = 0$$

must be combined with the horizontal recurrence relation,

$$S_{i,j+1} - S_{i+1,j} = X_{AB} S_{ij}$$

- By doing this, we obtain the Obara–Saika (OS) recurrence relations for the Cartesian overlap integrals,

$$S_{i+1,j} = X_{PA} S_{ij} + \frac{1}{2\eta} (i S_{i-1,j} + j S_{i,j-1})$$

$$S_{i,j+1} = X_{PB} S_{ij} + \frac{1}{2\eta} (i S_{i-1,j} + j S_{i,j-1})$$

- We start with $S_{00} = K_{ab}^x \sqrt{\frac{\pi}{\eta}}$ and then compute

$$S_{10} = X_{PA} S_{00}$$

$$S_{20} = X_{PA} S_{10} + \frac{1}{2\eta} S_{00}, \ etc.$$
The Obara–Saika scheme for $S_{ij}$

- The fundamental ideas are:
  1. Translational invariance:
     \[ \frac{\partial S_{ij}}{\partial A_x} + \frac{\partial S_{ij}}{\partial B_x} = 0 \]
  2. Horizontal recurrence:
     \[ x_B - x_A = X_{AB} \]

- Each $S_{ij}$ in the triangle is computed from one of the two above it and from the two above that one.
- The target integral $S_{ij}$ may be generated in many different ways.
- Note that horizontal recurrence relation can be applied to transfer “quantum numbers” from $i$ to $j$ and vice versa for all kinds of basis functions, also contracted Gaussians.

\[
\langle x_A \chi_\mu | \chi_\nu \rangle = \langle \chi_\mu | x_B \chi_\nu \rangle - X_{AB} \langle \chi_\mu | \chi_\nu \rangle
\]
Obara–Saika for multipole moments

- The Obara–Saika scheme may be applied to multipole-moment schemes in a slightly modified form,

\[ S_{ab}^{efg} = \langle \chi_a | x_C^e y_C^f z_C^g | \chi_b \rangle = S_{ij}^e S_{kl}^f S_{mn}^g \]

- The \( x \) component is

\[ S_{ij}^e = \langle G_i^e | x_C^e | G_j^e \rangle = \int_{-\infty}^{\infty} x_C^e \Omega_{ij}^x dx \]

- **Translational invariance** for this integral means that

\[ \frac{\partial S_{ij}^e}{\partial A_x} + \frac{\partial S_{ij}^e}{\partial B_x} + \frac{\partial S_{ij}^e}{\partial C_x} = 0 \]

- Furthermore, the **horizontal recurrence relation** for the order of the multipole operator is (\( x_C = x_A + X_{AC}, \) etc.)

\[ S_{ij}^{e+1} = S_{i+1,j}^e + X_{AC} S_{ij}^e = S_{i,j+1}^e + X_{BC} S_{ij}^e \]
Obara–Saika for multipole moments

• Putting it all together yields

\[
S_{i+1,j}^e = X_{PA}S_{ij}^e + \frac{1}{2\eta} \left( i S_{i-1,j}^e + j S_{i,j-1}^e + eS_{ij}^{e-1} \right)
\]

\[
S_{i,j+1}^e = X_{PB}S_{ij}^e + \frac{1}{2\eta} \left( i S_{i-1,j}^e + j S_{i,j-1}^e + eS_{ij}^{e-1} \right)
\]

\[
S_{ij}^{e+1} = X_{PC}S_{ij}^e + \frac{1}{2\eta} \left( i S_{i-1,j}^e + j S_{i,j-1}^e + eS_{ij}^{e-1} \right)
\]

• These recurrence relations may be used in conjunction with the horizontal recurrences

\[
S_{ij}^{e+1} = S_{i+1,j}^e + X_{AC}S_{ij}^e = S_{i,j+1}^e + X_{BC}S_{ij}^e
\]

and

\[
S_{i,j+1}^e = X_{AB}S_{ij}^e + S_{i+1,j}^e
\]

• The final integrals are obtained by multiplying the \(x\), \(y\) and \(z\) factors, followed by a transformation to contracted spherical-harmonic components.
Differential operators

- We now consider the integrals in a slightly modified form,

\[ D_{ab}^{efg} = \langle \chi_a | \frac{\partial e}{\partial x^e} \frac{\partial f}{\partial y^f} \frac{\partial g}{\partial z^g} | \chi_b \rangle = D_{ij}^e D_{kl}^f D_{mn}^g \]

- The \( x \) component is

\[ D_{ij}^e = \langle G_i | \frac{\partial e}{\partial x^e} | G_j \rangle = \int_{-\infty}^{\infty} G_i \frac{\partial e G_j}{\partial x^e} dx \]

- The trick we use here is that we can differentiate the Gaussian \( G_i(x, \alpha, A_x) \) with respect to the electron coordinate \( x \) or the basis-function centre \( A_x \), because the function depends on the difference \( (x - A_x) \)

\[ \frac{\partial G_i(x, \alpha, A_x)}{\partial x} = - \frac{\partial G_i(x, \alpha, A_x)}{\partial A_x} \]
Differential operators

• Since $\frac{\partial G_i}{\partial x} = -\frac{\partial G_i}{\partial A_x}$ and $\frac{\partial S_{ij}}{\partial A_x} = -\frac{\partial S_{ij}}{\partial B_x}$, we obtain

$$D_{ij}^e = \frac{\partial e}{\partial A_x} S_{ij} = (-1)^e \frac{\partial e}{\partial B_x} S_{ij}$$

• Furthermore, since $\frac{\partial X_{PA}}{\partial A_x} = -\frac{\beta}{\eta}$ and $\frac{\partial X_{PB}}{\partial A_x} = \frac{\alpha}{\eta}$, we obtain the Obara–Saika recurrence relations

\[
\begin{align*}
D_{i+1,j}^e &= X_{PA} D_{ij}^e + \frac{1}{2\eta} \left( i D_{i-1,j}^e + j D_{i,j-1}^e - 2\beta e D_{ij}^{e-1} \right) \\
D_{i,j+1}^e &= X_{PB} D_{ij}^e + \frac{1}{2\eta} \left( i D_{i-1,j}^e + j D_{i,j-1}^e + 2\alpha e D_{ij}^{e-1} \right) \\
D_{ij}^{e+1} &= 2\alpha D_{i+1,j}^e - i D_{i-1,j}^e
\end{align*}
\]

• The horizontal recurrence relation becomes

$$D_{i,j+1}^e - D_{i+1,j}^e = X_{AB} D_{ij}^e + e D_{ij}^{e-1}$$
Momentum and kinetic-energy integrals

- Consider the one-electron integrals
  
  \[ P_{ab} = -i \langle G_a | \nabla | G_b \rangle \] (linear momentum)
  
  \[ L_{ab} = -i \langle G_a | \mathbf{r} \times \nabla | G_b \rangle \] (angular momentum)
  
  \[ T_{ab} = -\frac{1}{2} \langle G_a | \Delta | G_b \rangle \] (kinetic energy)

- The \( z \) components of the momentum integrals, for example, may be easily computed from

  \[ P_{ab}^z = -i S_{ij} S_{kl} D_{mn}^1 \]
  
  \[ L_{ab}^z = -i \langle G_a | x \frac{\partial}{\partial y} - \frac{\partial}{\partial x} y | G_b \rangle = -i \left( S_{ij}^1 D_{kl}^1 S_{mn} - D_{ij}^1 S_{kl}^1 S_{mn} \right) \]

- For the kinetic-energy integral, we obtain

  \[ T_{ab} = -\frac{1}{2} \left( D_{ij}^2 S_{kl} S_{mn} + S_{ij} D_{kl}^2 S_{mn} + S_{ij} S_{kl} D_{mn}^2 \right) \]
Coulomb integrals over spherical Gaussians

• We consider the electrostatics of the (normalised) spherical Gaussian charge distributions

\[ \rho_p(r) = \left( \frac{\eta}{\pi} \right)^{3/2} \exp(-\eta r_p^2), \quad \rho_q(r) = \left( \frac{\zeta}{\pi} \right)^{3/2} \exp(-\zeta r_Q^2) \]

• The normalisation means that

\[ \int \rho_p(r) \, dr = \int \rho_q(r) \, dr = 1 \]

• The electrostatic potential at \( C \) due to \( \rho_p \) is

\[ V_p(C) = \int \frac{\rho_p(r)}{r_C} \, dr \]
Coulomb integrals over spherical Gaussians

- The energy of repulsion between the charge distributions $\rho_p$ and $\rho_q$ is

$$V_{pq} = \int \int \frac{\rho_p(r)\rho_q(r')}{|r - r'|} dr dr'$$

- The difficulty with this integral and $V_p(C)$ is that they do not factorise into products of $x$, $y$ and $z$ components due to the distances (square roots) $r_C$ and $|r - r'|$.

- Integrals over $r^k$ with $k$ even are easy, those with $k$ odd are difficult.

- However, the integrals factorise again after the integral transform

$$\frac{1}{r_C} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp(-r_C^2 t^2) dt$$

- This is the key step in treating Coulomb integrals.
Coulomb integrals over spherical Gaussians

- In the integral $V_p(C)$, we have a product of two Gaussians: $\rho_p(r)$ and $\exp(-r_C^2 t^2)$.

- This product yields a new Gaussian centred at
  $$S = (\eta P + t^2 C)/(\eta + t^2)$$
  according to the Gaussian-product theorem (GPT),

$$V_p(C) = \frac{\eta^{3/2}}{\pi^2} \int_{-\infty}^{\infty} \left\{ \int \exp[-(\eta + t^2) r_S^2] dr \right\} \exp \left( -\frac{\eta t^2}{\eta + t^2} R_{PC}^2 \right) dt$$

- The spatial integral can easily be computed and we obtain

$$V_p(C) = \frac{2\eta^{3/2}}{\sqrt{\pi}} \int_0^{\infty} (\eta + t^2)^{-3/2} \exp \left( -\eta R_{PC}^2 \frac{t^2}{\eta + t^2} \right) dt$$

which can be solved after substituting $u^2 = t^2/(\eta + t^2)$. 
The Boys function

- Since \( dt = \sqrt{\eta}(1 - u^2)^{-3/2}du \), we obtain

\[
V_p(C) = \sqrt{\frac{4\eta}{\pi}} \int_0^1 \exp(-\eta R_{PC}^2 u^2)du
\]

- The integration over all space \((x, y \text{ and } z \text{ from } -\infty \text{ to } \infty)\) has been replaced by a one-dimensional integration over a finite interval.

- This integral is the Boys function \( F_m(x) \) with \( m = 0 \),

\[
F_m(x) = \int_0^1 t^{2m} \exp(-xt^2)dt, \quad F_0(x) = \sqrt{\frac{\pi}{4x}} \text{erf} (\sqrt{x})
\]

(\text{erf} \text{ is the error function}).

- We can thus write

\[
V_p(C) = \sqrt{\frac{4\eta}{\pi}} F_0(\eta R_{PC}^2)
\]
Calculating the Boys function

- The Boys function can be computed efficiently by pretabulating $F_m(x_k)$ for a series of grid points $x_k$.

- For example, we can tabulate $F_m(x_k)$ for $m = 0, 1, 2, \ldots, m_{\text{max}} + 5$ at regular intervals $x_1 = 0.0, x_2 = 0.1, x_3 = 0.2, \ldots, x_n = 2m_{\text{max}} + 36$.

- The Boys functions $F_m(x)$ may then be computed with machine precision from a six-term Taylor expansion around $x_k$,

$$F_m(x) = F_m(x_k + \Delta x) = F_m(x_k) - F_{m+1}(x_k)\Delta x + \frac{1}{2} F_{m+2}(x_k)(\Delta x)^2$$
$$- \frac{1}{6} F_{m+3}(x_k)(\Delta x)^3 + \frac{1}{24} F_{m+4}(x_k)(\Delta x)^4 - \ldots$$

The figure shows the grid points involved in computing $F_2(x)$ with $x_7 < x < x_8$. 
Calculating the Boys function

- We note in passing that the exponential $\exp(-x)$ can be computed similarly by pretabulating $\exp(-x_k)$ at a number of grid points $x_k$.

- This number can be chosen such that a four-term Taylor expansion is enough to obtain machine precision.

- At the grid points $x_k$, the Boys functions are computed by downward recursion,

\[
F_m(x) = \frac{2xF_{m+1}(x) + \exp(-x)}{2m + 1}, \quad F_\infty(x) = 0
\]

- $F_m(x)$ can be set equal to zero for sufficiently large $m$.

- For large $x$, we have

\[
F_m(x) \approx \frac{(2m - 1)!!}{2^{m+1}} \sqrt{\frac{\pi}{x^{2m+1}}}, \quad (x \text{ large})
\]
The OS scheme for one-electron Coulomb integrals

- We write the Coulomb integral as

\[ \Theta_{ijklmn}^0 = \langle G_a \mid \frac{1}{r_C} \mid G_b \rangle = \int \frac{\Omega_{ab}(r)}{r_C} \, dr = \int \frac{\Omega_x \Omega_y \Omega_z}{r_C} \, dr \]

- We obtain \( \Theta_{ijklmn}^0 \) from \( \Theta_{000000}^N = \frac{2\pi}{\eta} K_{ab}^{xyz} F_N(\eta R_{PC}^2) \) and

\[
\Theta_{i+1,jklmn}^N = X_{PA} \Theta_{ijklmn}^N + \frac{1}{2\eta} (i \Theta_{i-1,jklmn}^N + j \Theta_{i,j-1,klmn}^N) \\
- X_{PC} \Theta_{ijklmn}^{N+1} - \frac{1}{2\eta} (i \Theta_{i-1,jklmn}^{N+1} + j \Theta_{i,j-1,klmn}^{N+1}) \\
\Theta_{i,j+1,klmn}^N = X_{PB} \Theta_{ijklmn}^N + \frac{1}{2\eta} (i \Theta_{i-1,jklmn}^N + j \Theta_{i,j-1,klmn}^N) \\
- X_{PC} \Theta_{ijklmn}^{N+1} - \frac{1}{2\eta} (i \Theta_{i-1,jklmn}^{N+1} + j \Theta_{i,j-1,klmn}^{N+1})
\]

and similarly for \( y \) and \( z \).
The McMurchie–Davidson scheme

- Before we turn our attention to the two-electron repulsion integrals, we note that the following three integral-evaluation techniques are currently in use:
  1. The Obara–Saika scheme
  2. The McMurchie–Davidson scheme
  3. Rys quadrature

- The idea of the McMurchie–Davidson scheme is to expand the overlap distribution $\Omega_{ab}$ in Hermite Gaussians,

\[
\Omega_{ij}^x = \sum_{t=0}^{i+j} E_{ij}^t \Lambda_t, \quad \Lambda_t = \left(\frac{\partial}{\partial P_x}\right)^t \exp(-\eta x_P^2)
\]

and similarly for $\Omega_{kl}^y$ and $\Omega_{mn}^z$.

- In the McMurchie–Davidson (MD) scheme, integrals over Hermite Gaussians are evaluated and transformed to the Cartesian Gaussian basis using the expansion coefficients $E_{ij}^t$. 
The MD expansion coefficients

• In order to compute the expansion coefficients $E_t^{ij}$, we consider the incremented distribution

$$\Omega_{i+1,j}^x = \sum_{t=0}^{i+j+1} E_t^{i+1,j} \Lambda_t$$

• Of course, $\Omega_{i+1,j}^x = \Omega_{ij}^x + \Omega_{ij}^x$,

$$x_P \Lambda_t = t \Lambda_{t-1} + \frac{1}{2\eta} \Lambda_{t+1}$$

• We thus obtain

$$x_P \Omega_{ij}^x = \sum_{t=0}^{i+j} E_t^{ij} \left( t \Lambda_{t-1} + \frac{1}{2\eta} \Lambda_{t+1} \right) = \sum_{t=0}^{i+j+1} \left\{ (t+1) E_{t+1}^{ij} + \frac{1}{2\eta} E_{t-1}^{ij} \right\} \Lambda_t$$

• Here, we assume that $E_t^{ij} = 0$ when $t < 0$ or $t > i + j$. 
The MD expansion coefficients

• We have established that

\[ \Omega_{i+1,j}^x = \sum_{t=0}^{i+j+1} E_{t}^{i+1,j} \Lambda_t \]

and

\[ \Omega_{i+1,j}^x = \sum_{t=0}^{i+j+1} \left\{ (t + 1) E_{t+1}^{i,j} + \frac{1}{2\eta} E_{t}^{i,j} - 1 + X_{PA} E_{t}^{i,j} \right\} \Lambda_t \]

• We therefore arrive at the following McMurchie–Davidson recurrence relations for the expansion coefficients:

\[ E_{t}^{i+1,j} = \frac{1}{2\eta} E_{t-1}^{i,j} + X_{PA} E_{t}^{i,j} + (t + 1) E_{t+1}^{i,j} \]

\[ E_{t}^{i,j+1} = \frac{1}{2\eta} E_{t-1}^{i,j} + X_{PB} E_{t}^{i,j} + (t + 1) E_{t+1}^{i,j} \]

\[ E_{0}^{00} = K_{ab}^x \]
The McMurchie–Davidson scheme

- For all three Cartesian coordinates, we have
  \[ \Lambda_{tuv} = \Lambda_t \Lambda_u \Lambda_v = \left( \frac{\partial}{\partial P_x} \right)^t \left( \frac{\partial}{\partial P_y} \right)^u \left( \frac{\partial}{\partial P_z} \right)^v \exp(-\eta r_P^2) \]
  and
  \[ \Omega_{ab} = \sum_{t=0}^{i+j} \sum_{u=0}^{k+l} \sum_{v=0}^{m+n} E_{t}^{ij} E_{u}^{kl} E_{v}^{mn} \Lambda_{tuv} \]

- Thus, using the MD scheme, the Coulomb integrals becomes
  \[ \Theta_{ijklmn}^0 = \sum_{t=0}^{i+j} \sum_{u=0}^{k+l} \sum_{v=0}^{m+n} E_{t}^{ij} E_{u}^{kl} E_{v}^{mn} \int \frac{\Lambda_{tuv}}{r_C} \, dr \]

- Furthermore,
  \[ \int \frac{\Lambda_{tuv}}{r_C} \, dr = \frac{2\pi}{\eta} \left( \frac{\partial}{\partial P_x} \right)^t \left( \frac{\partial}{\partial P_y} \right)^u \left( \frac{\partial}{\partial P_z} \right)^v F_0(\eta R^2_{PC}) \]
The McMurchie–Davidson recurrence relations

- The Coulomb integrals are written as

\[ \Theta_{ijklmn}^0 = \sum_{t=0}^{i+j} \sum_{k=0}^{k+l} \sum_{m=0}^{m+n} E_t^{ij} E_u^{kl} E_v^{mn} \int \frac{\Lambda_{tuv}}{r_C} dr \]

\[ = \frac{2\pi}{\eta} \sum_{t=0}^{i+j} \sum_{u=0}^{k+l} \sum_{v=0}^{m+n} E_t^{ij} E_u^{kl} E_v^{mn} R_{tuv}^0 \]

- Here, we have introduced the auxiliary integrals

\[ R_{000}^N = (-2\eta)^N F_N (\eta R_{PC}^2) \]

- The integrals \( R_{tuvw}^0 \) are obtained from the recurrence relations

\[ R_{t+1,uv}^N = t R_{t-1,uv}^{N+1} + X_{PC} R_{tuvw}^{N+1} \]

\[ R_{t,u+1,v}^N = u R_{t,u-1,v}^{N+1} + Y_{PC} R_{tuvw}^{N+1} \]

\[ R_{tu,v+1}^N = v R_{tu,v-1}^{N+1} + Z_{PC} R_{tuvw}^{N+1} \]
Gauß–Rys quadrature

- We have seen that the Coulomb integrals are obtained as a linear combination of Boys functions

\[
\Theta_{ijklmn}^0 = \sum_{N=0}^{M} c_N F_N(\eta R_{PC}^2), \quad M = i + j + k + l + m + n
\]

where the coefficients \( c_N \) depend on the exponents and coordinates involved.

- Since \( F_N(x) = \int_0^1 t^{2N} \exp(-xt^2)dt \), we may write

\[
\Theta_{ijklmn}^0 = \int_0^1 p_M(t^2) \exp(-\eta R_{PC}^2 t^2) dt
\]

- \( p_M(t^2) \) is a polynomial in \( t^2 \) of degree \( M \). The integral can be evaluated by means of a Gauß–Rys quadrature using \( L = \left\lceil \frac{M}{2} \right\rceil + 1 \) quadrature points (roots \( t_\lambda \) and weights \( w_\lambda \)),

\[
\Theta_{ijklmn}^0 = \sum_{\lambda=1}^{L} w_\lambda p_M(t_\lambda^2) \exp(-\eta R_{PC}^2 t_\lambda^2)
\]
Two-electron Coulomb integrals

- We now turn our attention to the two-electron integral $V_{pq}$, which is the energy of repulsion between the (normalised) charge distributions $\rho_p$ and $\rho_q$,

\[
V_{pq} = \int \int \frac{\rho_p(r) \rho_q(r')}{|r - r'|} dr dr'
\]

- Integration over $r'$ yields

\[
V_{pq} = \sqrt{\frac{4\zeta}{\pi}} \int F_0(\zeta r_Q^2) \rho_p(r) dr
\]

- The charge distribution $\rho_p(r)$ is a Gaussian, $F_0(\zeta r_Q^2)$ is an integral over a Gaussian, and their product is again (an integral over) a Gaussian by virtue of the GPT.

- The integration over $r$ is easy and the integration over $t$ [hidden in $F_0(\zeta r_Q^2)$] remains.
Two-electron Coulomb integrals

- We obtain

\[ V_{pq} = \sqrt{\frac{4\eta\zeta}{\pi}} \int_0^1 \frac{\zeta}{(\eta t^2 + \zeta)^{3/2}} \exp \left( -\frac{\eta\zeta t^2 R_{PQ}^2}{\eta t^2 + \zeta} \right) dt \]

- This integral can be written as

\[ V_{pq} = \sqrt{\frac{4\omega}{\pi}} F_0(\omega R_{PQ}^2), \quad \omega = \frac{\eta\zeta}{\eta + \zeta} \]

which can be verified by substituting \( u^2 = \frac{\eta + \zeta}{\eta t^2 + \zeta} \). \( \omega \) is the reduced exponent.

- Recurrence relations for Cartesian Gaussians other than \( s \)-type functions may be obtained in a manner similar to the one-electron Coulomb integrals, e.g., with the auxiliary functions

\[ \Theta_{0000;0000;0000}^N = \frac{2\pi^{5/2}}{\eta\zeta \sqrt{\eta + \zeta}} K_{ab}^xyz K_{cd}^xyz F_N(\omega R_{PQ}^2) \]
Two-electron Coulomb integrals

• The two-electron Coulomb integrals are

\[ \langle ab| r_{12}^{-1} | cd \rangle = g_{abcd} = \Theta_{iji'j';kk'l'l';mm'n'n'}^{0} \]

• Since there are four Gaussians involved \((G_a, G_b, G_c, \text{ and } G_d)\) the total number of integrals scales as \(N^4\), where \(N\) is the size of the basis set.

• When we increase the basis set in a series of calculations of the same small molecule, there is little we can do about the \(O(N^4)\) scaling.

• When we run calculations on a series of molecules of different size (e.g., on the alkanes \(\text{C}_N \text{H}_{2N+2}\)) in a given Gaussian basis, then many two-electron Coulomb integrals are very small and can be ignored.

• In that case, the number of significant integrals scales as \(O(N^2)\).
Scaling of two-electron Coulomb integrals

- To facilitate the discussion, we consider two-electron Coulomb integrals over (unnormalized) $s$-type Gaussians,

$$g_{abcd} = \langle ab | r_{12}^{-1} | cd \rangle = \Theta_{0000;0000;0000}^0 = \frac{2\pi^{5/2}}{\eta \zeta \sqrt{\eta + \zeta}} K_{xyz}^0 K_{xy}^0 F_0(\omega R_{PQ}^2)$$

- We note that

$$\frac{2\pi^{5/2}}{\eta \zeta \sqrt{\eta + \zeta}} = \sqrt{\frac{4\omega}{\pi}} \left(\frac{\pi}{\eta}\right)^{3/2} \left(\frac{\pi}{\zeta}\right)^{3/2}$$

and

$$S_{ab} = \left(\frac{\pi}{\eta}\right)^{3/2} K_{ab}^{xyz}$$

- The two-electron Coulomb integral can thus be written as

$$g_{abcd} = \sqrt{\frac{4\omega}{\pi}} S_{ab} S_{cd} F_0(\omega R_{PQ}^2)$$

- We furthermore know that

$$F_0(x) \leq 1 \quad \text{and} \quad F_0(x) \leq \frac{1}{2} \sqrt{\frac{\pi}{x}}$$
Scaling of two-electron Coulomb integrals

- We find that the Coulomb integral is bounded by

\[ g_{abcd} \leq S_{ab}S_{cd} \min \left( \sqrt{\frac{4\omega}{\pi}}, \frac{1}{R_{PQ}} \right) \]

- For large molecular systems, the number of nonzero overlap integrals \( S_{ab} \) scales as \( \mathcal{O}(N) \).

- When the number of significant overlap integrals begins to increase as \( N \), the number of significant two-electron Coulomb integrals will begin to increase as \( N^2 \).

- Note that \( R_{PQ}^{-1} \) will not be smaller than \( 10^{-6} \) in any practical calculation.

- The number of significant two-electron Coulomb integrals will depend at least quadratically on the size of the system.
Prescreening of integrals

- In large systems, the number of significant two-electron integrals increases only quadratically.
- In order to exploit this fact, we need a strict upper bound for the magnitude of the integrals.
- Such a bound is provided by the Schwarz inequality,

\[ |(ab|cd)| \leq Q_{ab} Q_{cd} \]

with \( Q_{ab} = \sqrt{(ab|ab)} \) and \( Q_{cd} = \sqrt{(cd|cd)} \).

- Before an integral is computed, the product \( Q_{ab} Q_{cd} \) is compared with some threshold \( \tau \). The integral is only computed if

\[ Q_{ab} Q_{cd} \geq \tau \]

- Typical values are \( \tau = 10^{-7} - 10^{-8} \) for small molecules.
- The upper bound is also useful when we ask how the integral contributes to the energy or the Fock matrix.
Prescreening of integrals

• In closed-shell Hartree–Fock theory, the Fock matrix is

\[
F_{\mu\nu} = h_{\mu\nu} + \sum_{\kappa\lambda} D_{\kappa\lambda} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)]
\]

• Using real basis functions, we have the following permutational symmetry among the two-electron integrals:

\[
(\mu\nu|\kappa\lambda) = (\nu\mu|\kappa\lambda) = (\nu\mu|\lambda\kappa) = (\mu\nu|\lambda\kappa) = (\kappa\lambda|\mu\nu) = (\kappa\lambda|\nu\mu) = (\lambda\kappa|\nu\mu) = (\lambda\kappa|\mu\nu)
\]

• Hence, we compute only ca. 1/8 of the total number of integrals and use each integral in various manners,

\[
\begin{align*}
F_{\mu\nu} &\leftarrow F_{\mu\nu} + 4D_{\kappa\lambda}(\mu\nu|\kappa\lambda) \\
F_{\kappa\lambda} &\leftarrow F_{\kappa\lambda} + 4D_{\mu\nu}(\mu\nu|\kappa\lambda) \\
F_{\mu\kappa} &\leftarrow F_{\mu\kappa} - D_{\nu\lambda}(\mu\nu|\kappa\lambda) \\
F_{\mu\lambda} &\leftarrow F_{\mu\lambda} - D_{\nu\kappa}(\mu\nu|\kappa\lambda) \\
F_{\nu\kappa} &\leftarrow F_{\nu\kappa} - D_{\mu\lambda}(\mu\nu|\kappa\lambda) \\
F_{\nu\lambda} &\leftarrow F_{\nu\lambda} - D_{\mu\kappa}(\mu\nu|\kappa\lambda)
\end{align*}
\]
Prescreening of integrals

- The density matrix elements are known when the integrals are evaluated. They can be incorporated in the prescreening tests.

- The evaluation of the integral $(\mu\nu|\kappa\lambda)$ is only needed if

$$Q_{\mu\nu}Q_{\kappa\lambda}D_{\text{max}} \geq \tau$$

where

$$D_{\text{max}} = \max \left\{ 4|D_{\mu\nu}|, 4|D_{\kappa\lambda}|, |D_{\mu\kappa}|, |D_{\mu\lambda}|, |D_{\nu\kappa}|, |D_{\nu\lambda}| \right\}$$

- Concerning the Hartree–Fock energy, we could screen with

$$Q_{\mu\nu}Q_{\kappa\lambda}\max \left\{ 4|D_{\mu\nu}D_{\kappa\lambda}|, |D_{\mu\kappa}D_{\nu\lambda}|, |D_{\nu\kappa}D_{\mu\lambda}| \right\} \geq \tau$$

but this leaves an unmonitored error in the Fock matrix.

- This last screening is however useful for energy-related properties such as the nuclear forces.
The direct SCF procedure

• In conventional SCF procedures, the integrals are computed only once and stored on disk for later use. In such procedures, the Schwarz screening helps to eliminate integrals once and for all.

• In direct SCF procedures, the integrals are re-evaluated in each SCF iteration.

• The prescreening is then performed in conjunction with the density matrix, which is usually done for batches of integrals,

$$D_{MN} = \max_{\mu \in M, \nu \in N} |D_{\mu\nu}| \quad Q_{MN} = \max_{\mu \in M, \nu \in N} |Q_{\mu\nu}|$$

• Furthermore, important savings in the number of calculated integrals may be obtained by considering the change of the Fock matrix in two consecutive iterations.

• The screening can then be performed using the change of the density matrix,

$$\Delta D^{(i)}_{\mu\nu} = D^{(i)}_{\mu\nu} - D^{(i-1)}_{\mu\nu}$$
The direct SCF procedure

- In the direct SCF procedure, the Fock matrix in iteration number \( i \) is computed from

\[
F_{\mu\nu}^{(i)} = F_{\mu\nu}^{(i-1)} + \sum_{\kappa\lambda} \Delta D_{\kappa\lambda}^{(i)} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)]
\]

- Only those integrals are required which are related to significant changes in the density matrix from one iteration to the next.

- Close to convergence, screening with \( \Delta D^{(i)} \) is extremely efficient.

- Furthermore, if the Coulomb and exchange matrices are constructed separately, we have the following two screening criteria:

\[
Q_{\mu\nu}Q_{\kappa\lambda} \{4|D_{\mu\nu}|, 4|D_{\kappa\lambda}|\} \geq \tau
\]

\[
Q_{\mu\nu}Q_{\kappa\lambda} \{|D_{\mu\kappa}|, |D_{\mu\lambda}|, |D_{\nu\kappa}|, |D_{\nu\lambda}|\} \geq \tau
\]
The RI approximation

- The idea of the resolution-of-the-identity (RI) approximation is to avoid four-index (or four-centre) two-electron integrals.

- In a naive approach, we can insert an approximation to the unity operator represented in an orthonormal auxiliary basis \(\{\varphi_P\}\),

\[
\hat{1} \approx \sum_P |\varphi_P\rangle\langle \varphi_P|
\]

- We then obtain, for example,

\[
(\mu\nu|\kappa\lambda) \approx \sum_P (\mu\nu|P)\langle P\kappa\lambda|,
\langle P\kappa\lambda| = \int \varphi_P(1)\chi_\kappa(1)\chi_\lambda(1)d\mathbf{r}_1
\]

- \((\mu\nu|P)\) is a three-index two-electron repulsion integral,

\[
(\mu\nu|P) = \int \int \chi_\mu(1)\chi_\nu(1)r_{12}^{-1}\varphi_P(2)d\mathbf{r}_1d\mathbf{r}_2
\]
RI approximation with non-orthonormal basis

- If we approximate the unity operator by a projection operator onto a non-orthonormal auxiliary basis \( \{ \chi_P \} \), then we have

\[
\hat{1} \approx \sum_{P,Q} |\chi_P\rangle S_{PQ}^{-1} \langle \chi_Q |
\]

- Note that \( S_{PQ}^{-1} \) is a matrix element of the inverse overlap matrix,

\[
S_{PQ}^{-1} \equiv (S^{-1})_{PQ}
\]

- We obtain

\[
(\mu\nu | \kappa\lambda) \approx \sum_{PQ} (\mu\nu | P) S_{PQ}^{-1} \langle Q \kappa \lambda |
\]

- It has turned out that the most accurate RI approximation is obtained by using the Coulomb metric.
RI approximation with Coulomb metric

- Using the Coulomb metric, we approximate the unity operator as follows:

\[ \hat{1} \approx \sum_{P,Q} |\chi_P\rangle (P|Q)^{-1} (\chi_Q|, \]

where

\[ (\chi_Q| = \int \chi_Q(2) r_{12}^{-1} \, dr_2 \]

- Note that \((P|Q)^{-1}\) is a matrix element of the inverse of the two-index Coulomb integrals,

\[ (P|Q)^{-1} \equiv (C^{-1})_{PQ}, \quad C_{PQ} = \int \int \chi_P(1) r_{12}^{-1} \chi_Q(2) \, dr_1 \, dr_2 \]

- We obtain

\[ (\mu\nu|\kappa\lambda) \approx \sum_{PQ} (\mu\nu|P) (P|Q)^{-1} (Q|\kappa\lambda) \]
RI approximation with Coulomb metric

- Alternatively, we expand the orbital product $\chi_\kappa \chi_\lambda$ in a basis $\{\chi_P\}$,

  $$\chi_\kappa \chi_\lambda \approx \tilde{\chi}_\kappa \chi_\lambda = \sum_P c_{P}^{\kappa \lambda} \chi_P$$

- We then minimise the self-repulsion of the error,

  $$(\kappa \lambda - \bar{\kappa} \bar{\lambda} | \kappa \lambda - \bar{\kappa} \bar{\lambda}) = \min$$

- This immediately leads to the set of linear equations

  $$\sum_Q (P | Q) c_{Q}^{\kappa \lambda} = (P | \kappa \lambda) \quad \forall P \quad \Rightarrow \quad c_{P}^{\kappa \lambda} = \sum_Q (P | Q)^{-1} (Q | \kappa \lambda)$$

- Hence,

  $$(\mu \nu | \kappa \lambda) \approx \sum_P (\mu \nu | P) c_{P}^{\kappa \lambda} = \sum_{PQ} (\mu \nu | P) (P | Q)^{-1} (Q | \kappa \lambda)$$
Robust fitting

• The RI approximation can be inserted in such a manner, that the error in the target integral is only quadratic in the error of the fit,

\[
(\mu\nu|\kappa\lambda) \approx \sum_P c^{\mu\nu}_P (P|\kappa\lambda) + \sum_Q (\mu\nu|Q)c^{\kappa\lambda}_Q - \sum_{PQ} c^{\mu\nu}_P (P|Q)c^{\kappa\lambda}_Q
\]

• For Coulomb integrals, as before, this leads to

\[
(\mu\nu|\kappa\lambda) \approx \sum_{PQ} (\mu\nu|P)(P|Q)^{-1}(Q|\kappa\lambda)
\]

• The robust fitting is, however, important for other two-electron integrals, for example those over the operator \( f(r_{12}) \),

\[
(\mu\nu||\kappa\lambda) \approx \sum_P c^{\mu\nu}_P (P||\kappa\lambda) + \sum_Q (\mu\nu||Q)c^{\kappa\lambda}_Q - \sum_{PQ} c^{\mu\nu}_P (P||Q)c^{\kappa\lambda}_Q
\]

where \((\ldots||\ldots)\) indicates the integral over \( f(r_{12}) \).
Various applications of the RI approximation

- The RI approximation is for example used to accelerate the calculation of the Coulomb operator $\hat{J}$ (RI-$J$ approximation), especially in DFT.
- The RI approximation can also be used to accelerate the calculation of the exchange operator $\hat{K}$ (RI-$JK$ approximation) in Hartree–Fock theory or DFT with hybrid functional (e.g., B3LYP).
- Finally, it can also be used to approximate integrals of the type $(IA|JB)$, where $I, J$ are occupied Hartree–Fock orbitals and $A, B$ are virtual Hartree–Fock orbitals. These integrals occur in the MP2 and CC2 theories.
- Clearly, different basis sets are needed to approximate orbital products of the types $\varphi_I\varphi_I$ (RI-$J$), $\varphi_I\chi_\mu$ (RI-$JK$) and $\varphi_I\varphi_A$ (cbas in Turbomole).
- These three types of auxiliary basis sets have been designed and optimised for the Turbomole basis sets.
RI- $J$ approximation

- In the RI- $J$ approximation, the electron density is expanded in an appropriate auxiliary basis,

$$J_{\mu\nu} = (\mu\nu|\rho) \approx \sum_P (\mu\nu|P)c_P^\rho = \sum_P \sum_{\kappa\lambda} (\mu\nu|P)c_{P}^{\kappa\lambda} D_{\kappa\lambda}$$

$$= \sum_{PQ} \sum_{\kappa\lambda} (\mu\nu|P)(P|Q)^{-1}(Q|\kappa\lambda) D_{\kappa\lambda}$$

- The formal scaling is no longer $N^4$ but rather $N^3$, assuming that the auxiliary basis increases linearly with system size.

- It is possible to obtain accurate results (with an error of ca. 0.1 m$E_h$ per atom) with auxiliary basis sets that are about three times larger than the orbital basis.

- Asymptotically, the construction of the Coulomb matrix will scale as $N^2$, as before, but with a much smaller prefactor.

- The RI- $J$ approximation can be combined with multipole methods (MARI- $J$: multipole-accelerated RI- $J$).
RI-\(JK\) approximation

- In the RI-\(JK\) approximation, the RI approximation is not only used for the Coulomb matrix but also for the exchange matrix,

\[
K_{\mu\nu} = \sum_{\kappa\lambda} D_{\kappa\lambda} (\mu\kappa | \nu\lambda) \approx \sum_{PQ} \sum_{\kappa\lambda} (\mu\kappa | P) (P | Q)^{-1} (Q | \nu\lambda) D_{\kappa\lambda}
\]

- The formal scaling is still \(N^4\), as before.

- The RI-\(JK\) approximation is very useful when relatively large basis sets are used, for example when the Hartree–Fock calculation is followed by a post-Hartree–Fock treatment.

- Similar algorithms have been developed for the RI-MP2 and RI-CC2 methods. The formal scaling is still \(N^5\) for these methods, as before, but with a much smaller prefactor.

- The RI-MP2-F12 methods utilises robust fitting for integrals over other operators than \(1/r_{12}\).