SCF methods, basis sets, and integrals

Lecture IV: Integrals

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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).
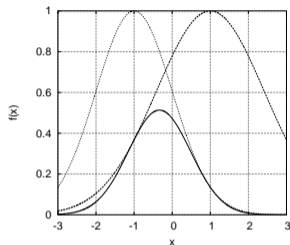
- The figure shows the product of the (unnormalised) s-type GTOs χ_a with exponent $\alpha = 0.25$ at $\mathbf{A} = (1, 0, 0)$ and χ_b with exponent $\beta = 0.50$ at $\mathbf{B} = (-1, 0, 0)$,

$$\chi_a(\mathbf{r}) = e^{-\alpha(\mathbf{r}-\mathbf{A})^2}, \qquad \chi_b(\mathbf{r}) = e^{-\beta(\mathbf{r}-\mathbf{B})^2}$$

- The two-centre product $\chi_a(\mathbf{r})\chi_b(\mathbf{r})$ is again a Gaussian χ_p centred at the "centre of gravity" $\mathbf{P}$.

The Gaussian-product theorem

- The product of the GTOs χ_a and χ_b can be written as

$$\chi_a(\mathbf{r})\chi_b(\mathbf{r}) = e^{-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2} e^{-(\alpha+\beta)(\mathbf{r}-\mathbf{P})^2}$$

with

$$\mathbf{P} = \frac{\alpha\mathbf{A} + \beta\mathbf{B}}{\alpha + \beta}$$

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

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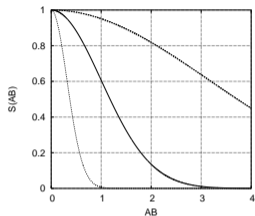
The overlap integral

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

$$\int \chi_a(\mathbf{r})\chi_b(\mathbf{r})d\mathbf{r} = e^{-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2} \int e^{-(\alpha+\beta)(\mathbf{r}-\mathbf{P})^2} d\mathbf{r}$$

$$= e^{-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2} \int e^{-(\alpha+\beta)\mathbf{r}^2} d\mathbf{r}$$

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

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

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

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 $|\mathbf{A} - \mathbf{B}|$ (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 small number of integrals over CGTOs.

Primitive Cartesian GTOs

- The primitive Cartesian GTO is

$$\chi_a(\mathbf{r}) = x_A^i y_A^j z_A^k \exp(-\alpha r_A^2), \qquad \mathbf{r}_A = \mathbf{r} - \mathbf{A}$$

- Integrals over real-valued spherical-harmonic GTOs

$$\chi_a'(\mathbf{r}) = S_{lm}(x_A, y_A, z_A) \exp(-\alpha r_A^2)$$

(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.

$$\mathbf{S}' = \mathbf{C}^T \mathbf{S} \mathbf{C}$$

- 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,

$$\chi_a = \left\{ x_A^i \exp(-\alpha x_A^2) \right\} \left\{ y_A^i \exp(-\alpha y_A^2) \right\} \left\{ z_A^i \exp(-\alpha z_A^2) \right\}$$

- We can thus focus our attention on only one Cartesian component, say x,

$$G_i(x, \alpha, A_x) = x_A^i \exp(-\alpha x_A^2)$$

- The self overlap of the x component is

$$\langle G_i | G_i \rangle = \frac{(2i-1)!!}{(4\alpha)^i} \sqrt{\frac{\pi}{2\alpha}}, \qquad \langle G_0 | G_0 \rangle = \sqrt{\frac{\pi}{2\alpha}}$$

- 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, differentation 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 $G_{i+1} = x_A G_i$):

$$G_i^{n+1} = 2\alpha G_{i+1}^n - i\, G_{i-1}^n, \qquad \text{with} \quad G_i^n = \frac{\partial^n G_i}{\partial A_x^n}$$

Gaussian overlap distributions

- We define the Gaussian overlap distribution

  which factorises as
  $$\Omega_{ab}(\mathbf{r}) = \chi_a(\mathbf{r})\chi_b(\mathbf{r})$$

  $$\Omega_{ab}(\mathbf{r}) = G_i(x, \alpha, A_x)G_j(x, \beta, B_x)\cdots = \Omega_{ij}^x(x, \alpha, \beta, A_x, B_x)\ldots$$

- Due to the GPT, Ω_{ij}^x may be written as

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

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

- In the above equation, we give x relative to A_x, B_x and P_x. 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

$$x_\mathrm{A}\Omega_{ij}^x = \Omega_{i+1,j}^x, \quad x_\mathrm{B}\Omega_{ij}^x = \Omega_{i,j+1}^x, \quad X_\mathrm{AB}\Omega_{ij}^x = \Omega_{i,j+1}^x - \Omega_{i+1,j}^x$$

- Differentiating the overlap distributions yields

$$\frac{\partial \Omega_{ij}^x}{\partial A_x} = 2\alpha\Omega_{i+1,j}^x - i\,\Omega_{i-1,j}^x, \quad \frac{\partial \Omega_{ij}^x}{\partial B_x} = 2\beta\Omega_{i,j+1}^x - j\,\Omega_{i,j-1}^x$$

- We furthermore note that

$$X_\mathrm{PA} = P_x - A_x = \frac{\alpha A_x + \beta B_x}{\eta} - \frac{\alpha + \beta}{\eta}A_x = \frac{\beta}{\eta}(B_x - A_x) = -\frac{\beta}{\eta}X_\mathrm{AB}$$

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

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 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*,

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

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

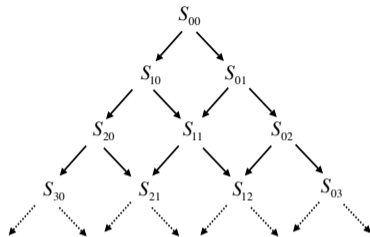$$S_{i+1,j} = X_{\mathrm{PA}} S_{ij} + \frac{1}{2\eta} \left(i\,S_{i-1,j} + j\,S_{i,j-1} \right)$$

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

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

$$S_{10} = X_{\mathrm{PA}} S_{00}, \quad S_{20} = X_{\mathrm{PA}} S_{10} + \frac{1}{2\eta} S_{00}, \quad \text{etc.}$$

The Obara–Saika scheme for S_{ij}

- The fundamental ideas are:

  1. Translational invariance:
     $\partial S_{ij}/\partial A_x + \partial S_{ij}/\partial B_x = 0$

  2. Horizontal recurrrence:
     $x_{\mathrm{B}} - x_{\mathrm{A}} = X_{\mathrm{AB}}$

- 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 recurrrence relation can be applied to transfer "quantum numbers" from i to j and vice versa for all kinds of basis functions, also contracted Gaussians.

$$\langle x_{\mathrm{A}}\chi_\mu|\chi_\nu\rangle = \langle \chi_\mu|x_{\mathrm{B}}\chi_\nu\rangle - X_{\mathrm{AB}}\langle \chi_\mu|\chi_\nu\rangle$$

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

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

- 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

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

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

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

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

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

and

$$S_{i,j+1}^e = X_{\mathrm{AB}}S_{ij}^e + S_{i+1,j}^e$$

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

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

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

$$D_{i+1,j}^e = X_{\mathrm{PA}} D_{ij}^e + \frac{1}{2\eta}\left(i\,D_{i-1,j}^e + j\,D_{i,j-1}^e - 2\beta e\,D_{ij}^{e-1}\right)$$

$$D_{i,j+1}^e = X_{\mathrm{PB}} D_{ij}^e + \frac{1}{2\eta}\left(i\,D_{i-1,j}^e + j\,D_{i,j-1}^e + 2\alpha e\,D_{ij}^{e-1}\right)$$

$$D_{ij}^{e+1} = 2\alpha D_{i+1,j}^e - i\,D_{i-1,j}^e$$

- The horizontal recurrence relation becomes

$$D_{i,j+1}^e - D_{i+1,j}^e = X_{\mathrm{AB}} D_{ij}^e + e\,D_{ij}^{e-1}$$

Momentum and kinetic-energy integrals

- Consider the one-electron integrals

$$\mathbf{P}_{ab} = -i\langle\chi_a|\boldsymbol{\nabla}|\chi_b\rangle \qquad \text{(linear momentum)}$$

$$\mathbf{L}_{ab} = -i\langle\chi_a|\mathbf{r}\times\boldsymbol{\nabla}|\chi_b\rangle \qquad \text{(angular momentum)}$$

$$T_{ab} = -\frac{1}{2}\langle\chi_a|\Delta|\chi_b\rangle \qquad \text{(kinetic energy)}$$

- The z components of the momentum integrals, for example, may be computed from

$$
\begin{aligned}
P_{ab}^z &= -i S_{ij} S_{kl} D_{mn}^1 \\
L_{ab}^z &= -i\langle\chi_a|x\frac{\partial}{\partial y} - \frac{\partial}{\partial x}y|\chi_b\rangle = -i\left(S_{ij}^1 D_{kl}^1 S_{mn} - D_{ij}^1 S_{kl}^1 S_{mn}\right)
\end{aligned}
$$

- 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

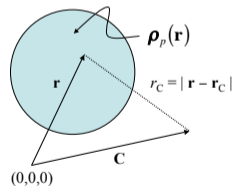- We consider the electrostatics of the (normalised) spherical Gaussian charge distributions

$$\rho_p(\mathbf{r}) = \left(\frac{\eta}{\pi}\right)^{3/2} \exp(-\eta r_\mathrm{P}^2), \qquad \rho_q(\mathbf{r}) = \left(\frac{\zeta}{\pi}\right)^{3/2} \exp(-\zeta r_\mathrm{Q}^2)$$

- The normalisation means that

$$\int \rho_p(\mathbf{r}) d\mathbf{r} = \int \rho_q(\mathbf{r}) d\mathbf{r} = 1$$

- The electrostatic potential at **C** due to ρ_p is

$$V_p(\mathbf{C}) = \int \frac{\rho_p(\mathbf{r})}{r_\mathrm{C}} d\mathbf{r}$$

Coulomb integrals over spherical Gaussians

- The energy of repulsion between the charge distributions ρ_p and ρ_q is

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

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

- 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 $V_p(\mathbf{C})$, we have a product of two Gaussians: $\rho_p(\mathbf{r})$ and $\exp(-r_{\mathrm{C}}^2 t^2)$.

- This product yields a new Gaussian centred at

$$\mathbf{S} = (\eta \mathbf{P} + t^2 \mathbf{C})/(\eta + t^2)$$

according to the Gaussian-product theorem (GPT),

$$V_p(\mathbf{C}) = \frac{\eta^{3/2}}{\pi^2} \int_{-\infty}^{\infty} \left\{ \int \exp[-(\eta + t^2)r_{\mathrm{S}}^2] d\mathbf{r} \right\} \exp\left(-\frac{\eta t^2}{\eta + t^2} R_{\mathrm{PC}}^2 \right) dt$$

- The spatial integral can easily be computed and we obtain

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

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

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

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

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

$$F_m(x) = \int_0^1 t^{2m} \exp(-xt^2)dt, \qquad F_0(x) = \sqrt{\frac{\pi}{4x}}\mathrm{erf}(\sqrt{x})$$

 (erf is the error function).

- We can thus write
$$V_p(\mathbf{C}) = \sqrt{\frac{4\eta}{\pi}} F_0(\eta R_{\mathrm{PC}}^2)$$

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 $m = 0, 1, 2, \ldots, m_{\max} + 5$ at regular intervals $x_1 = 0.0, x_2 = 0.1, x_3 = 0.2, \ldots, x_n = 2m_{\max} + 36$.

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

$$
\begin{aligned}
F_m(x) = F_m(x_k + \Delta x) &= F_m(x_k) - F_{m+1}(x_k)\Delta x + \tfrac{1}{2}F_{m+2}(x_k)(\Delta x)^2 \\
&- \tfrac{1}{6}F_{m+3}(x_k)(\Delta x)^3 + \tfrac{1}{24}F_{m+4}(x_k)(\Delta x)^4 - \ldots
\end{aligned}
$$
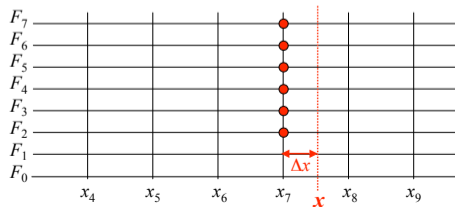
The figure shows the grid points involved in computing $F_2(x)$ with $x_7 < x < x_8$.

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,

$$F_m(x) = \frac{2x F_{m+1}(x) + \exp(-x)}{2m+1}, \qquad F_\infty(x) = 0$$

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

- For large x, we have

$$F_m(x) \approx \frac{(2m-1)!!}{2^{m+1}} \sqrt{\frac{\pi}{x^{2m+1}}}, \qquad (x \text{ large})$$

The OS scheme for one-electron Coulomb integrals

- We write the Coulomb integral as

$$\Theta^0_{ijklmn} = \langle \chi_a | \frac{1}{r_{\mathbf{C}}} | \chi_b \rangle = \int \frac{\Omega_{ab}(\mathbf{r})}{r_{\mathbf{C}}} d\mathbf{r} = \int \frac{\Omega^x_{ij}\Omega^y_{kl}\Omega^z_{mn}}{r_{\mathbf{C}}} d\mathbf{r}$$

- We obtain Θ^0_{ijklmn} from $\Theta^N_{000000} = \frac{2\pi}{\eta} K^{xyz}_{ab} F_N(\eta R^2_{\mathrm{PC}})$ and

$$\Theta^N_{i+1,jklmn} = X_{\mathrm{PA}}\Theta^N_{ijklmn} + \frac{1}{2\eta}(i\,\Theta^N_{i-1,jklmn} + j\,\Theta^N_{i,j-1,klmn})$$
$$- X_{\mathrm{PC}}\Theta^{N+1}_{ijklmn} - \frac{1}{2\eta}(i\,\Theta^{N+1}_{i-1,jklmn} + j\,\Theta^{N+1}_{i,j-1,klmn})$$

$$\Theta^N_{i,j+1,klmn} = X_{\mathrm{PB}}\Theta^N_{ijklmn} + \frac{1}{2\eta}(i\,\Theta^N_{i-1,jklmn} + j\,\Theta^N_{i,j-1,klmn})$$
$$- X_{\mathrm{PC}}\Theta^{N+1}_{ijklmn} - \frac{1}{2\eta}(i\,\Theta^{N+1}_{i-1,jklmn} + j\,\Theta^{N+1}_{i,j-1,klmn})$$

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 Ω_{ab} in Hermite Gaussians,

$$\Omega_{ij}^x = \sum_{t=0}^{i+j} E_t^{ij} \Lambda_t, \qquad \Lambda_t = (\partial/\partial P_x)^t \exp(-\eta x_P^2)$$

and similarly for Ω_{kl}^y and Ω_{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_t^{ij}.

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, $\Omega_{i+1,j}^x = x_A \Omega_{ij}^x = x_P \Omega_{ij}^x + X_{PA} \Omega_{ij}^x$, and furthermore

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

- We thus obtain

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

- 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

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

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

$$
\begin{aligned}
E_t^{i+1,j} &= \frac{1}{2\eta} E_{t-1}^{ij} + X_{\mathrm{PA}} E_t^{ij} + (t+1) E_{t+1}^{ij} \\[2mm]
E_t^{i,j+1} &= \frac{1}{2\eta} E_{t-1}^{ij} + X_{\mathrm{PB}} E_t^{ij} + (t+1) E_{t+1}^{ij} \\[2mm]
E_0^{00} &= K_{ab}^x
\end{aligned}
$$

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

$$\Theta_{ijklmn}^0 = \sum_{t=0}^{i+j} \sum_{u=0}^{k+l} \sum_{v=0}^{m+n} E_t^{ij} E_u^{kl} E_v^{mn} \int \frac{\Lambda_{tuv}}{r_C} d\mathbf{r}$$

- Furthermore,

$$\int \frac{\Lambda_{tuv}}{r_C} d\mathbf{r} = \frac{2\pi}{\eta} \left(\frac{\partial}{\partial P_x}\right)^t \left(\frac{\partial}{\partial P_y}\right)^u \left(\frac{\partial}{\partial P_z}\right)^v F_0(\eta R_{PC}^2)$$

The McMurchie–Davidson recurrence relations

- The Coulomb integrals are written as

$$
\begin{aligned}
\Theta_{ijklmn}^0 &= \sum_{t=0}^{i+j}\sum_{u=0}^{k+l}\sum_{v=0}^{m+n} E_t^{ij} E_u^{kl} E_v^{mn} \int \frac{\Lambda_{tuv}}{r_{\mathrm{C}}} d\mathbf{r} \\
&= \frac{2\pi}{\eta} \sum_{t=0}^{i+j}\sum_{u=0}^{k+l}\sum_{v=0}^{m+n} E_t^{ij} E_u^{kl} E_v^{mn} R_{tuv}^0
\end{aligned}
$$

- Here, we have introduced the auxiliary integrals

$$
R_{000}^N = (-2\eta)^N F_N(\eta R_{\mathrm{PC}}^2)
$$

- The integrals R_{tuv}^0 are obtained from the recurrence relations

$$
\begin{aligned}
R_{t+1,uv}^N &= t\, R_{t-1,uv}^{N+1} + X_{\mathrm{PC}}\, R_{tuv}^{N+1} \\
R_{t,u+1,v}^N &= u\, R_{t,u-1,v}^{N+1} + Y_{\mathrm{PC}}\, R_{tuv}^{N+1} \\
R_{tu,v+1}^N &= v\, R_{tu,v-1}^{N+1} + Z_{\mathrm{PC}}\, R_{tuv}^{N+1}
\end{aligned}
$$

Gauß–Rys quadrature

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

$$\Theta^0_{ijklmn} = \sum_{N=0}^{M} c_N F_N(\eta R^2_{\mathrm{PC}}), \qquad M = i + j + k + l + m + n$$

  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

$$\Theta^0_{ijklmn} = \int_0^1 p_M(t^2) \exp(-\eta R^2_{\mathrm{PC}} t^2)dt$$

- $p_M(t^2)$ is a polynomial in t^2 of degree M. The integral can be evaluated from a Gauß–Rys quadrature with $L = \left[\frac{M}{2}\right] + 1$ quadrature points (roots t_λ and weights w_λ),

$$\Theta^0_{ijklmn} = \sum_{\lambda=1}^{L} w_\lambda \, p_M(t^2_\lambda) \exp(-\eta R^2_{\mathrm{PC}} t^2_\lambda)$$

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 ρ_p and ρ_q,

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

- Integration over $\mathbf{r}'$ yields

$$V_{pq} = \sqrt{\frac{4\zeta}{\pi}} \int F_0(\zeta r_Q^2)\rho_p(\mathbf{r})d\mathbf{r}$$

- The charge distribution $\rho_p(\mathbf{r})$ 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 $\mathbf{r}$ 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

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

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

- Recurrence relations for Cartesian Gaussians other than s-type functions may be obtained in a mannner 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

$$\langle ab|r_{12}^{-1}|cd\rangle = g_{abcd} = \Theta^0_{iji'j';klk'l';mnm'n'}$$

- Since there are four Gaussians involved (χ_a, χ_b, χ_c and χ_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 $\mathcal{O}(N^4)$ scaling.

- When we run calculations on a series of molecules of different size (*e.g.*, on the alkanes $C_N H_{2N+2}$) 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 $\mathcal{O}(N^2)$.

Scaling of two-electron Coulomb integrals

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

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

- We note that

$$\frac{2\pi^{5/2}}{\eta\zeta\sqrt{\eta+\zeta}} = \sqrt{\frac{4\omega}{\pi}} \left(\frac{\pi}{\eta}\right)^{3/2} \left(\frac{\pi}{\zeta}\right)^{3/2} \quad \text{and} \quad S_{ab} = \left(\frac{\pi}{\eta}\right)^{3/2} K_{ab}^{xyz}$$

- 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

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

- 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,

$$|(ab|cd)| \leq Q_{ab}Q_{cd} \quad \text{with} \quad Q_{ab} = \sqrt{(ab|ab)} \quad \text{and} \quad Q_{cd} = \sqrt{(cd|cd)}$$

- Before an integral is computed, the product $Q_{ab}Q_{cd}$ is compared with some threshold τ. 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, only ca. 1/8 of the total number of integrals is used:

$$F_{\mu\nu} \leftarrow F_{\mu\nu} + 4D_{\kappa\lambda}(\mu\nu|\kappa\lambda)$$
$$F_{\kappa\lambda} \leftarrow F_{\kappa\lambda} + 4D_{\mu\nu}(\mu\nu|\kappa\lambda)$$
$$F_{\mu\kappa} \leftarrow F_{\mu\kappa} - D_{\nu\lambda}(\mu\nu|\kappa\lambda)$$
$$F_{\mu\lambda} \leftarrow F_{\mu\lambda} - D_{\nu\kappa}(\mu\nu|\kappa\lambda)$$
$$F_{\nu\kappa} \leftarrow F_{\nu\kappa} - D_{\mu\lambda}(\mu\nu|\kappa\lambda)$$
$$F_{\nu\lambda} \leftarrow F_{\nu\lambda} - D_{\mu\kappa}(\mu\nu|\kappa\lambda)$$

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

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

where

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

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

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

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,

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

- 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,

$$\Delta D_{\mu\nu}^{(i)} = D_{\mu\nu}^{(i)} - D_{\mu\nu}^{(i-1)}$$

The direct SCF procedure

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

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

- 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 $\Delta \mathbf{D}^{(i)}$ is extremely efficient.

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

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

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,

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

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

$$(\mu\nu|P) = \int\int \chi_\mu(1)\chi_\nu(1)r_{12}^{-1}\varphi_P(2)d\mathbf{r}_1 d\mathbf{r}_2$$

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,

$$S_{PQ}^{-1} \equiv \left(\mathbf{S}^{-1}\right)_{PQ}$$

- We obtain

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

- 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

$$(\chi_Q| = \int \chi_Q(2) r_{12}^{-1} d\mathbf{r}_2$$

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

$$(P|Q)^{-1} \equiv \left(\mathbf{C}^{-1}\right)_{PQ}, \qquad C_{PQ} = \int \int \chi_P(1) r_{12}^{-1} \chi_Q(2) d\mathbf{r}_1 d\mathbf{r}_2$$

- 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 $\{\chi_P\}$,

$$\chi_\kappa \chi_\lambda \approx \widetilde{\chi_\kappa \chi_\lambda} = \sum_P c_P^{\kappa\lambda} \chi_P$$

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

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

- 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,

$$(\mu\nu|\kappa\lambda) \approx \sum_P c_P^{\mu\nu}(P|\kappa\lambda) + \sum_Q (\mu\nu|Q)c_Q^{\kappa\lambda} - \sum_{PQ} c_P^{\mu\nu}(P|Q)c_Q^{\kappa\lambda}$$

- 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 $f(r_{12})$,

$$(\mu\nu|f(r_{12})|\kappa\lambda) \approx \sum_P c_P^{\mu\nu}(P|f(r_{12})|\kappa\lambda) + \sum_Q (\mu\nu|f(r_{12})|Q)c_Q^{\kappa\lambda} - \sum_{PQ} c_P^{\mu\nu}(P|f(r_{12})|Q)c_Q^{\kappa\lambda}$$

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 mE_{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.

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.