

Molecular Integral Evaluation

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Molecular integral evaluation

- one-electron interactions
 - overlap, multipole-moment, momentum, and kinetic-energy integrals
 - Coulomb attraction integrals

$$O_{\mu\nu} = \int \chi_{\mu}(\mathbf{r}) \hat{O}(\mathbf{r}) \chi_{\nu}(\mathbf{r}) \, d\mathbf{r}$$

- two-electron interactions
 - Coulomb integrals

$$g_{\mu\nu\lambda\sigma} = \iint \frac{\chi_{\mu}(\mathbf{r}_1) \chi_{\nu}(\mathbf{r}_1) \chi_{\lambda}(\mathbf{r}_2) \chi_{\sigma}(\mathbf{r}_2)}{r_{12}} \, d\mathbf{r}_1 \, d\mathbf{r}_2$$

- Coulomb potential

$$J_{\mu\nu} = \sum_{\lambda\sigma} g_{\mu\nu\lambda\sigma} D_{\lambda\sigma}$$

- one-electron functions
 - primitive Cartesian GTOs
- integration schemes
 - McMurchie–Davidson, Obara–Saika and Rys schemes

Overview

- Cartesian and Hermite Gaussians
 - properties of Cartesian Gaussians
 - properties of Hermite Gaussians
- Simple one-electron integrals
 - Gaussian product rule and overlap distributions
 - overlap distributions expanded in Hermite Gaussians
 - overlap and kinetic-energy integrals
- Coulomb integrals
 - Gaussian electrostatics and the Boys function
 - one- and two-electron Coulomb integrals over Cartesian Gaussians
- Sparsity and screening
- Coulomb potential
 - early density matrix contraction
 - density fitting

Cartesian Gaussians

- Primitive Cartesian Gaussians centered at \mathbf{A} :

$$G_{ijk}(\mathbf{r}, a, \mathbf{A}) = x_A^i y_A^j z_A^k \exp(-ar_A^2), \begin{cases} a > 0 & \text{orbital exponent} \\ \mathbf{r}_A = \mathbf{r} - \mathbf{A} & \text{electronic coordinates} \\ i \geq 0, j \geq 0, k \geq 0 & \text{quantum numbers} \end{cases}$$

- total angular-momentum quantum number

$$l = i + j + k \geq 0$$

- The full set of Gaussians of a given a and l constitutes a *shell* of GTOs:

- each shell contains $(l + 1)(l + 2)/2$ GTOs

s shell: G_{000}

p shell: $G_{100}, G_{010}, G_{001}$

d shell: $G_{200}, G_{110}, G_{101}, G_{020}, G_{011}, G_{002}$

Contracted spherical-harmonic GTOs

- We only discuss integration over primitive Cartesian GTOs:

$$G_{ijk}(\mathbf{r}_A, a) = x_A^i y_A^j z_A^k \exp(-ar_A^2)$$

- Final integrals are needed over contracted spherical-harmonic GTOs:

$$\chi_{lm}(\mathbf{r}_A) = S_{lm}(\mathbf{r}_A) \sum_{\mu} d_{\mu} \exp(-a_{\mu} r_A^2)$$

- This may be accomplished by a simple linear transformation

$$\chi_{lm}(\mathbf{r}_A) = \sum_{ijk} C_{ijk}^{lm} \sum_{\mu} d_{\mu} G_{ijk}(\mathbf{r}_A, a_{\mu})$$

- The number of contracted spherical-harmonic GTOs is usually much smaller than the number of primitive Cartesian GTOs
- Properly implemented, the transformation to a contracted spherical-harmonic basis reduces CPU time (relative to that required for the corresponding primitive Cartesian basis).

Properties of Cartesian Gaussians

- Definition of a primitive Cartesian Gaussian:

$$G_{ijk}(a, \mathbf{r}_A) = x_A^i y_A^j z_A^k \exp(-ar_A^2), \quad \mathbf{r}_A = \mathbf{r} - \mathbf{A}$$

- Each Gaussian factorizes in the Cartesian directions:

$$G_{ijk}(a, \mathbf{r}_A) = G_i(a, x_A)G_j(a, y_A)G_k(a, z_A)$$

$$G_i(a, x_A) = x_A^i \exp(-ax_A^2)$$

– note: this is not true for solid-harmonic Gaussians nor for STOs

- Differentiation of Gaussians:

$$\frac{\partial G_i(a, x_A)}{\partial A_x} = -\frac{\partial G_i(a, x_A)}{\partial x} = 2aG_{i+1}(a, x_A) - iG_{i-1}(a, x_A)$$

– a linear combination two undifferentiated Gaussians

- Gaussian recurrence relation:

$$x_A G_i(a, x_A) = G_{i+1}(a, x_A)$$

Hermite Gaussians

- The Hermite Gaussians are defined as

$$\Lambda_{tuv}(\mathbf{r}, p, \mathbf{P}) = \left(\frac{\partial}{\partial P_x} \right)^t \left(\frac{\partial}{\partial P_y} \right)^u \left(\frac{\partial}{\partial P_z} \right)^v \exp(-pr_P^2), \quad \mathbf{r}_P = \mathbf{r} - \mathbf{P}$$

- Like Cartesian Gaussians, they also factorize in the Cartesian directions:

$$\Lambda_t(x_P) = (\partial/\partial P_x)^t \exp(-px_P^2) \leftarrow \text{times a polynomial of degree } t$$

- The Hermite Gaussians are not much used as basis functions by themselves
 - rather, they are used as intermediates in the evaluation of Gaussian integrals

$$\text{Cartesian product} \rightarrow G_i(x_A)G_j(x_B) = \sum_{t=0}^{i+j} E_t^{ij} \Lambda_t(x_P) \leftarrow \text{Hermite expansion}$$

- useful for integration

$$\int_{-\infty}^{\infty} \Lambda_t(x) dx = \delta_{t0} \sqrt{\frac{\pi}{p}}$$

- McMurchie and Davidson (1978)

- We shall make extensive use of the McMurchie–Davidson scheme for integration

Hermite recurrence relation

- An important property of the Hermite Gaussians is the recurrence relation

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

- The proof is simple:
 - from the definition of Hermite Gaussians, we have

$$\Lambda_{t+1} = \left(\frac{\partial}{\partial P_x} \right)^t \frac{\partial}{\partial P_x} \exp(-p x_P^2) = 2p \left(\frac{\partial}{\partial P_x} \right)^t x_P \Lambda_0$$

- inserting the identity

$$\left(\frac{\partial}{\partial P_x} \right)^t x_P = x_P \left(\frac{\partial}{\partial P_x} \right)^t - t \left(\frac{\partial}{\partial P_x} \right)^{t-1}$$

we then obtain

$$\Lambda_{t+1} = 2p \left[x_P \left(\frac{\partial}{\partial P_x} \right)^t - t \left(\frac{\partial}{\partial P_x} \right)^{t-1} \right] \Lambda_0 = 2p (x_P \Lambda_t - t \Lambda_{t-1})$$

Integration over Hermite Gaussians

- From the definition of Hermite Gaussians, we have

$$\int_{-\infty}^{\infty} \Lambda_t(x) dx = \int_{-\infty}^{\infty} \left(\frac{\partial}{\partial P_x} \right)^t \exp(-px_P^2) dx$$

- We now change the order of differentiation and integration (Leibniz' rule):

$$\int_{-\infty}^{\infty} \Lambda_t(x) dx = \left(\frac{\partial}{\partial P_x} \right)^t \int_{-\infty}^{\infty} \exp(-px_P^2) dx$$

- The Gaussian integral is given by

$$\int_{-\infty}^{\infty} \exp(-px_P^2) dx = \sqrt{\frac{\pi}{p}}$$

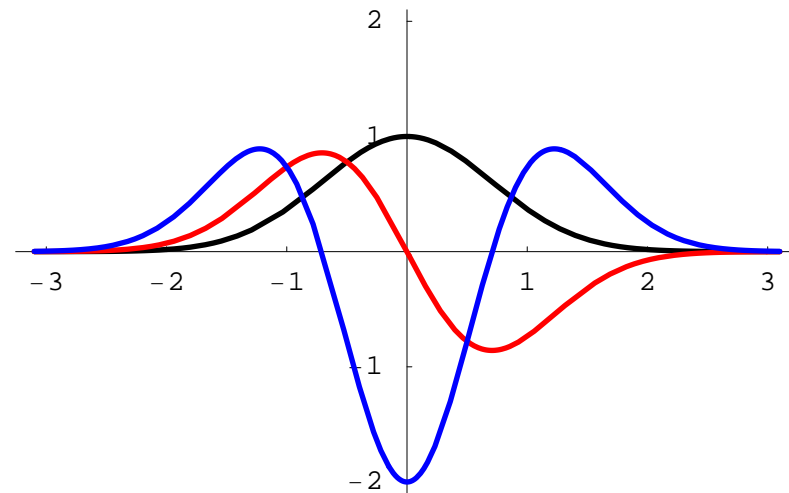
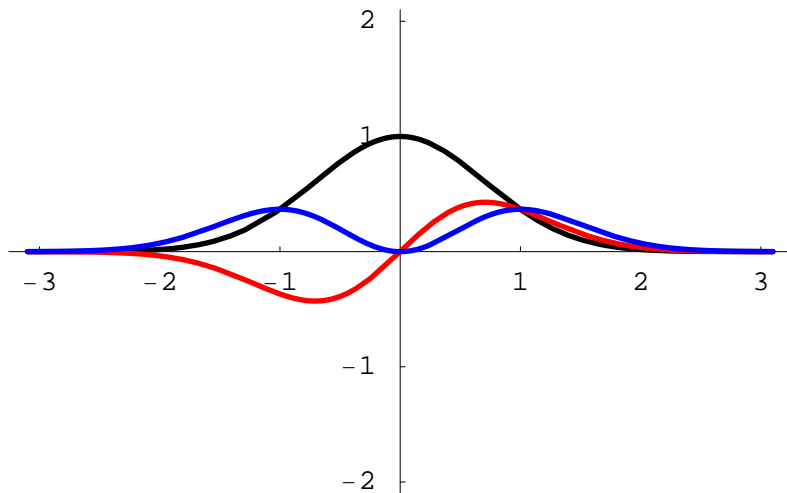
- Since the integral is independent of \mathbf{P} , differentiation with respect to \mathbf{P} gives zero:

$$\int_{-\infty}^{\infty} \Lambda_t(x) dx = \delta_{t0} \sqrt{\frac{\pi}{p}}$$

– only integrals over s functions do not vanish

Comparison of Cartesian and Hermite Gaussians

	Cartesian Gaussians	Hermite Gaussians
definition	$G_i = x_A^i \exp(-ax_A^2)$	$\Lambda_t = \frac{\partial^t}{\partial P_x^t} \exp(-px_P^2)$
recurrence	$x_A G_i = G_{i+1}$	$x_P \Lambda_t = \frac{1}{2p} \Lambda_{t+1} + t \Lambda_{t-1}$
differentiation	$\frac{\partial G_i}{\partial A_x} = 2a G_{i+1} - i G_{i-1}$	$\frac{\partial \Lambda_t}{\partial P_x} = \Lambda_{t+1}$



The Gaussian product rule

- The product of two Gaussians is another Gaussian centered somewhere on the line segment connecting the original Gaussians; its exponent is the sum of the original exponents:

$$\exp(-ax_A^2) \exp(-bx_B^2) = \underbrace{\exp(-\mu X_{AB}^2)}_{\text{exponential prefactor}} \underbrace{\exp(-px_P^2)}_{\text{product Gaussian}}$$

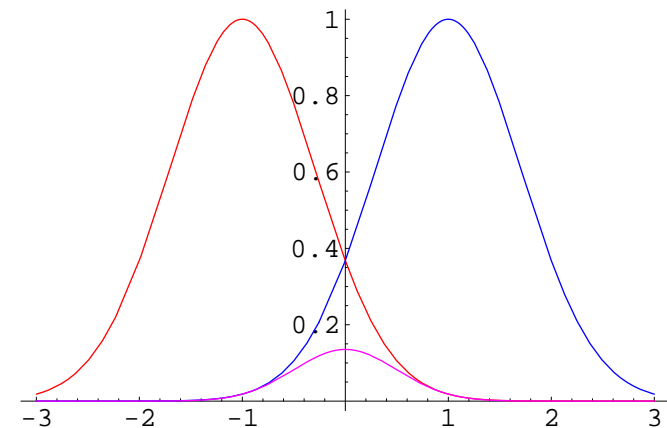
where

$$P_x = \frac{aA_x + bB_x}{p} \quad \leftarrow \text{“center of mass”}$$

$$p = a + b \quad \leftarrow \text{total exponent}$$

$$X_{AB} = A_x - B_x, \quad \leftarrow \text{relative separation}$$

$$\mu = \frac{ab}{a + b} \quad \leftarrow \text{reduced exponent}$$



- The Gaussian product rule greatly simplifies the calculation of integrals
 - two-center integrals are reduced to one-center integrals
 - four-center integrals are reduced to two-center integrals

Overlap distributions

- The product of two Cartesian Gaussians is known as an **overlap distribution**:

$$\Omega_{ij}(x) = G_i(x, a, A_x)G_j(x, b, B_x)$$

- The Gaussian product rule reduces two-center integrals to one-center integrals

$$\int \Omega_{ij}(x) dx = K_{AB} \int x_A^i x_B^j \exp(-px_P^2) dx$$

- the Cartesian monomials still make the integration awkward
- we would like to utilize the simple integration properties of Hermite Gaussians

- To simplify integration, we expand overlap distributions in Hermite Gaussians

$$\text{overlap distribution} \rightarrow \Omega_{ij}(x) = \sum_{t=0}^{i+j} E_t^{ij} \Lambda_t(x_P) \leftarrow \text{in Hermite Gaussians}$$

- note: $\Omega_{ij}(x)$ is a single Gaussian times a polynomial in x of degree $i + j$
- it may be exactly represented as a linear combination of Λ_t with $0 \leq t \leq i + j$

- Recurrence relations may be used for the expansion coefficients

$$E_t^{i+1,j} = \frac{1}{2p} E_{t-1}^{ij} + X_{PA} E_t^{ij} + (t+1) E_{t+1}^{ij}$$

Recurrence relations for Hermite coefficients

- Hermite expansion of $\Omega_{i+1,j}$:

$$\Omega_{i+1,j} = K_{AB} x_A^{i+1} x_B^j \exp(-pr_P^2) = \sum_t E_t^{i+1,j} \Lambda_t$$

- Alternative Hermite expansion of $\Omega_{i+1,j}$ (with use of $x_P \Lambda_t = \frac{1}{2p} \Lambda_{t+1} + t \Lambda_{t-1}$)

$$\begin{aligned} \Omega_{i+1,j} &= x_A \Omega_{ij} = (x - A_x) \Omega_{ij} \\ &= (x - P_x) \Omega_{ij} + (P_x - A_x) \Omega_{ij} = x_P \Omega_{ij} + X_{PA} \Omega_{ij} \\ &= \sum_t E_t^{ij} x_P \Lambda_t + X_{PA} \sum_t E_t^{ij} \Lambda_t \\ &= \sum_t E_t^{ij} \left(\frac{1}{2p} \Lambda_{t+1} + t \Lambda_{t-1} + X_{PA} \Lambda_t \right) \\ &= \sum_t \left[\frac{1}{2p} E_{t-1}^{ij} + X_{PA} E_t^{ij} + (t+1) E_{t+1}^{ij} \right] \Lambda_t \end{aligned}$$

- A comparison of the two expansions yields the recurrence relations

$$E_t^{i+1,j} = \frac{1}{2p} E_{t-1}^{ij} + X_{PA} E_t^{ij} + (t+1) E_{t+1}^{ij}$$

Overlap integrals

- Overlap integrals

$$S_{ab} = \langle G_a | G_b \rangle$$

$$G_a = G_{ikm}(\mathbf{r}, a, \mathbf{A}) = G_i(x_A)G_k(y_A)G_m(z_A)$$

$$G_b = G_{jln}(\mathbf{r}, b, \mathbf{B}) = G_j(x_B)G_l(y_B)G_n(z_B)$$

- The overlap integral factorizes in the Cartesian directions:

$$S_{ab} = S_{ij}S_{kl}S_{mn}, \quad S_{ij} = \langle G_i(x_A) | G_j(x_B) \rangle$$

- Use the Gaussian product rule and Hermite expansion:

$$S_{ij} = \int \Omega_{ij}(x) dx = \sum_{t=0}^{i+j} E_t^{ij} \int \Lambda_t(x_P) dx = \sum_{t=0}^{i+j} E_t^{i+j} \delta_{t0} \sqrt{\frac{\pi}{p}} = E_0^{ij} \sqrt{\frac{\pi}{p}}$$

– only one term survives

- The total overlap integral is therefore given by

$$S_{ab} = E_0^{ij} E_0^{kl} E_0^{mn} \left(\frac{\pi}{p} \right)^{3/2}$$

Dipole integrals

- Multipole integrals follow the same scheme as overlap integrals

$$\begin{aligned}
 D_{ij} &= \langle G_i(x_A) | x_C | G_j(x_B) \rangle = \int \Omega_{ij}(x_P) x_C dx \\
 &= \sum_{t=0}^{i+j} E_t^{ij} \int \Lambda_t(x_P) x_C dx \quad (\text{use } x_C = x_P + X_{PC}) \\
 &= \sum_{t=0}^{i+j} E_t^{ij} \int [x_P \Lambda_t(x_P) + X_{PC} \Lambda_t(x_P)] dx \quad (\text{use } x_P \Lambda_t = \frac{1}{2p} \Lambda_{t+1} + t \Lambda_{t-1}) \\
 &= \sum_{t=0}^{i+j} E_t^{ij} \int \left[\frac{1}{2p} \Lambda_{t+1}(x_P) + X_{PC} \Lambda_t(x_P) + t \Lambda_{t-1}(x_P) \right] dx \\
 &= E_0^{ij} X_{PC} \sqrt{\frac{\pi}{p}} + E_1^{ij} \sqrt{\frac{\pi}{p}}
 \end{aligned}$$

- Final dipole integral

$$D_{ij} = \left(E_1^{ij} + X_{PC} E_0^{ij} \right) \sqrt{\frac{\pi}{p}}$$

Kinetic-energy integrals

- Kinetic-energy integral

$$T_{ab} = -\frac{1}{2} \left\langle G_a \left| \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right| G_b \right\rangle$$

$$T_{ab} = T_{ij} S_{kl} S_{mn} + S_{ij} T_{kl} S_{mn} + S_{ij} S_{kl} T_{mn}$$

$$S_{ij} = \langle G_i(x_A) | G_j(x_B) \rangle$$

$$T_{ij} = -\frac{1}{2} \left\langle G_i(x_A) \left| \frac{\partial^2}{\partial x^2} \right| G_j(x_B) \right\rangle$$

- Differentiation of Cartesian Gaussians

$$\frac{\partial}{\partial x} G_j(x_B) = -2bG_{j+1} + jG_{j-1}$$

$$\frac{\partial^2}{\partial x^2} G_j(x_B) = 4b^2 G_{j+2} - 2b(2j+1)G_j + j(j-1)G_{j-2}$$

– the second derivative is linear combination of three undifferentiated Gaussians

- Kinetic-energy integrals are linear combinations of overlap integrals

$$T_{ij} = 4b^2 S_{i,j+2} - 2b(2j+1)S_{i,j} + j(j-1)S_{i,j-2}$$

Review of simple one-electron integrals

- Gaussian product rule and expansion of overlap distributions

$$\exp(-ax_A^2) \exp(-bx_B^2) = K_{AB} \exp(-px_P^2)$$

$$G_i(x_A)G_j(x_B) = \sum_{t=0}^{i+j} E_t^{ij} \Lambda_t(x_P)$$

- Overlap and dipole integrals

$$S_{ab} = E_0^{ij} E_0^{kl} E_0^{mn} \left(\frac{\pi}{p}\right)^{3/2}$$

$$X_{ab} = \left(E_1^{ij} + X_{PC} E_0^{ij}\right) E_0^{kl} E_0^{mn} \left(\frac{\pi}{p}\right)^{3/2}$$

- Kinetic-energy integrals by differentiation
- We shall now consider the Coulomb integrals ...

Coulomb integrals

- One-electron nuclear-attraction integrals

$$\langle G_a(\mathbf{r}_A) | r_C^{-1} | G_b(\mathbf{r}_B) \rangle$$

- Two-electron repulsion integrals

$$\langle G_a(\mathbf{r}_{1A}) G_b(\mathbf{r}_{1B}) | r_{12}^{-1} | G_c(\mathbf{r}_{2C}) G_d(\mathbf{r}_{2D}) \rangle$$

- Coulomb integrals are not separable in the Cartesian directions
- The Gaussian Coulomb integrals may be reduced to a one-dimensional finite integral: **the Boys function**

$$F_n(x) = \int_0^1 \exp(-xt^2) t^{2n} dt$$

– makes the evaluation of Gaussian Coulomb integrals relatively simple

- We begin by evaluating the simplest Coulomb integral:

$$V_p = \int r_C^{-1} \exp(-pr_P^2) d\mathbf{r} = \frac{2\pi}{p} F_0(pR_{PC}^2)$$

– we shall then go on to consider the usual Coulomb integrals

Coulomb integral over a spherical Gaussian I

$$V_p = \int r_C^{-1} \exp(-pr_P^2) \, d\mathbf{r}$$

1. The presence of r_C^{-1} is awkward and is avoided by the substitution

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

to yield the **four-dimensional** integral

$$V_p = \frac{1}{\sqrt{\pi}} \int \exp(-pr_P^2) \int_{-\infty}^{\infty} \exp(-t^2 r_C^2) \, dt \, d\mathbf{r}$$

2. To prepare for integration over \mathbf{r} , we invoke the Gaussian product rule

$$\exp(-pr_P^2) \exp(-t^2 r_C^2) = \exp\left(-\frac{pt^2}{p+t^2} R_{CP}^2\right) \exp\left[-(p+t^2) r_S^2\right]$$

to obtain (where the exact value of \mathbf{S} in r_S does not matter):

$$V_p = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \int \exp\left[-(p+t^2) r_S^2\right] \, d\mathbf{r} \exp\left(-\frac{pt^2}{p+t^2} R_{CP}^2\right) \, dt$$

Coulomb integral over a spherical Gaussian II

$$V_p = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \int [-(p+t^2)r_S^2] \, d\mathbf{r} \exp\left(-\frac{pt^2}{p+t^2} R_{CP}^2\right) dt$$

3. Integration over all space \mathbf{r} now yields a **one-dimensional** integral

$$V_p = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \left(\frac{\pi}{p+t^2}\right)^{3/2} \exp\left(-pR_{CP}^2 \frac{t^2}{p+t^2}\right) dt$$

4. To introduce a finite integration range, we perform the substitution

$$u^2 = \frac{t^2}{p+t^2} \Rightarrow 1 + pt^{-2} = u^{-2} \Rightarrow pt^{-3} dt = u^{-3} du \Rightarrow dt = p^{-1} \left(\frac{t^2}{u^2}\right)^{3/2} du$$

and obtain

$$V_p = \frac{2\pi}{p} \int_0^1 \exp(-pR_{CP}^2 u^2) du = \frac{2\pi}{p} F_0(pR_{PC}^2)$$

• We have here introduced the Boys function

$$F_n(x) = \int_0^1 \exp(-xt^2) t^{2n} dt$$

– a 3D integral over all space has been reduced to a 1D integral over $[0, 1]$

The Boys function $F_n(x)$

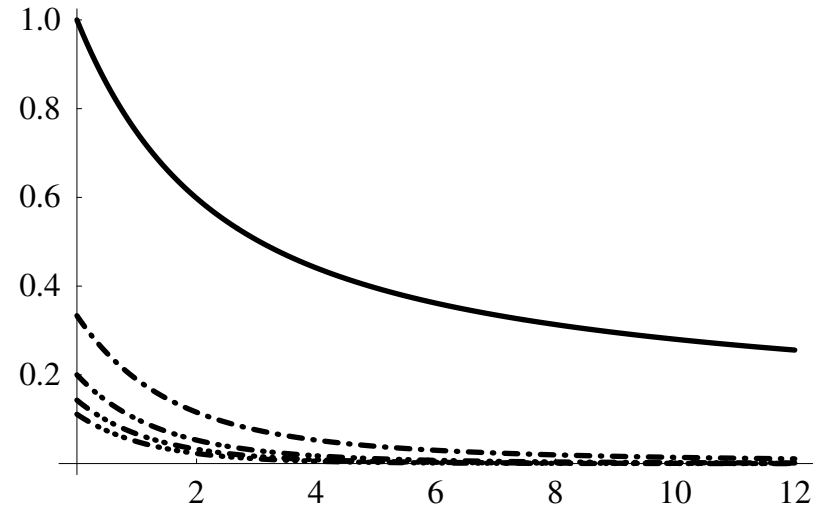
- $F_n(x) > 0$ since the integrand is positive:

$$F_n(x) = \int_0^1 \exp(-xt^2) t^{2n} dt > 0$$

- $F_n(x)$ is convex and decreasing:

$$F'_n(x) = -F_{n+1}(x) < 0$$

$$F''_n(x) = F_{n+2}(x) > 0$$



- Small and large values:

$$F_n(x) = \frac{1}{2n+1} + \sum_{k=1}^{\infty} \frac{(-x)^k}{k!(2n+2k+1)} \quad (x \text{ small})$$

$$F_n(x) \approx \int_0^{\infty} \exp(-xt^2) t^{2n} dt = \frac{(2n-1)!!}{2^{n+1}} \sqrt{\frac{\pi}{x^{2n+1}}} \quad (x \text{ large})$$

- Downward recurrence relation:

$$F_{n-1}(x) = \frac{2xF_n(x) + \exp(-x)}{2n-1}$$

Gaussian electrostatics

- Spherical-Gaussian integrals are nicely expressed in terms of the error function

$$\int r_C^{-1} \exp(-pr_P^2) \, d\mathbf{r} = \frac{2\pi}{p} F_0(pR_{PC}^2)$$

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) \, dt = \frac{2}{\sqrt{\pi}} x F_0(x^2)$$

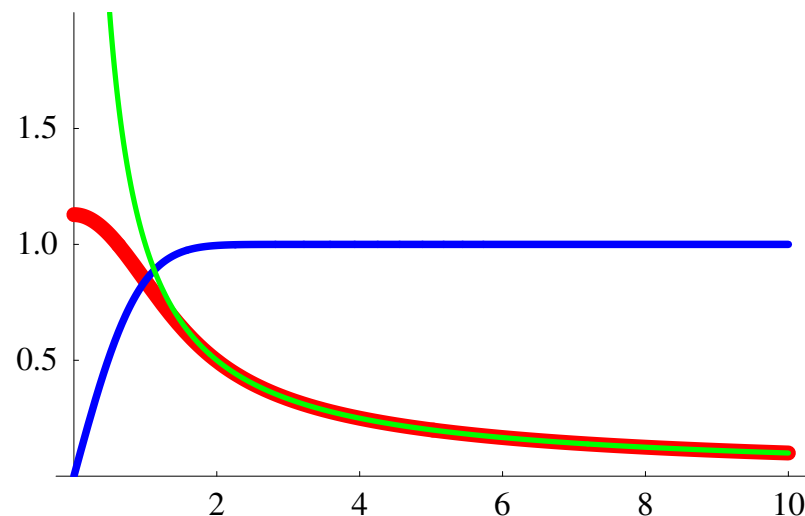
- Introducing unit charge distributions and the reduced exponent as

$$\rho_p(\mathbf{r}_P) = (p/\pi)^{3/2} \exp(-pr_P^2), \quad \alpha = pq/p + q$$

we obtain formulas similar to those of electrostatics (but damped)

$$\int \frac{\rho_p(\mathbf{r}_P)}{r_C} \, d\mathbf{r} = \frac{\operatorname{erf}(\sqrt{p}R_{PC})}{R_{PC}}$$

$$\iint \frac{\rho_p(\mathbf{r}_{1P}) \rho_q(\mathbf{r}_{2Q})}{r_{12}} \, d\mathbf{r}_1 d\mathbf{r}_2 = \frac{\operatorname{erf}(\sqrt{\alpha}R_{PQ})}{R_{PQ}}$$



Cartesian Coulomb integrals

- We have obtained a simple result for one-center spherical Gaussians:

$$\int r_C^{-1} \exp(-pr_P^2) \, d\mathbf{r} = \frac{2\pi}{p} F_0(pR_{PC}^2)$$

- We shall now consider general two-center one-electron Coulomb integrals:

$$V_{ab} = \langle G_a | r_C^{-1} | G_b \rangle = \int \frac{\Omega_{ab}(\mathbf{r})}{r_C} \, d\mathbf{r}$$

- The overlap distribution expanded in Hermite Gaussians

$$\Omega_{ab}(\mathbf{r}) = \Omega_{ij}(x)\Omega_{kl}(y)\Omega_{mn}(z), \quad \Omega_{ij}(x) = \sum_{t=0}^{i+j} E_t^{ij} \Lambda_t(x_P)$$

- The total overlap distribution may therefore be written in the form

$$\Omega_{ab}(\mathbf{r}) = \sum_{tuv} E_t^{ij} E_u^{kl} E_v^{mn} \Lambda_{tuv}(\mathbf{r}_P) = \sum_{tuv} E_{tuv}^{ab} \Lambda_{tuv}(\mathbf{r}_P)$$

- Expansion of two-center Coulomb integrals in one-center Hermite integrals:

$$\text{two-center integral} \rightarrow V_{ab} = \sum_{tuv} E_{tuv}^{ab} \int \frac{\Lambda_{tuv}(\mathbf{r}_P)}{r_C} \, d\mathbf{r} \leftarrow \text{one-center integrals}$$

Coulomb integrals over Hermite Gaussians

- Expansion of two-center Coulomb integrals in one-center Hermite integrals

$$V_{ab} = \sum_{tuv} E_{tuv}^{ab} \int \frac{\Lambda_{tuv}(\mathbf{r}_P)}{r_C} d\mathbf{r}, \quad \int \frac{\exp(-pr_P^2)}{r_C} d\mathbf{r} = \frac{2\pi}{p} F_0(pR_{PC}^2)$$

- Changing the order of integration and differentiation by Leibniz rule, we obtain

$$\begin{aligned} \int \frac{\Lambda_{tuv}(\mathbf{r}_P)}{r_C} d\mathbf{r} &= \frac{\partial^{t+u+v}}{\partial P_x^t \partial P_y^u \partial P_z^v} \int \frac{\exp(-pR_P^2)}{r_C} d\mathbf{r} \\ &= \frac{2\pi}{p} \frac{\partial^{t+u+v} F_0(pR_{PC}^2)}{\partial P_x^t \partial P_y^u \partial P_z^v} = \frac{2\pi}{p} R_{tuv}(p, \mathbf{R}_{PC}) \end{aligned}$$

where the one-center **Hermite Coulomb integral** is given by

$$R_{tuv}(p, \mathbf{R}_{PC}) = \frac{\partial^{t+u+v} F_0(pR_{PC}^2)}{\partial P_x^t \partial P_y^u \partial P_z^v}$$

- the Hermite integrals are derivatives of the Boys function

Evaluation of Hermite Coulomb integrals

- The Hermite integrals are derivatives of the Boys function
 - can be obtained by repeated differentiation, using $F'_n(x) = -F_{n+1}(x)$
 - recursion is simpler and more efficient
- To set up recursion, we introduce the **auxiliary Hermite integrals**

$$R_{tuv}^n(p, \mathbf{P}) = (-2p)^n \frac{\partial^{t+u+v} F_n(pR_{PC}^2)}{\partial P_x^t \partial P_y^u \partial P_z^v}$$

which include as special cases the **source** and **target** integrals

$$R_{000}^n = (-2p)F_n \rightarrow R_{tuv}^0 = \frac{\partial^t}{\partial P_x^t} \frac{\partial^u}{\partial P_y^u} \frac{\partial^v}{\partial P_z^v} F_0$$

- The Hermite integrals can now be generated from the recurrence relations

$$R_{t+1,u,v}^n = tR_{t-1,u,v}^{n+1} + X_{PC}R_{tuv}^{n+1}$$

$$R_{t,u+1,v}^n = uR_{t,u-1,v}^{n+1} + Y_{PC}R_{tuv}^{n+1}$$

$$R_{t,u,v+1}^n = vR_{t,u,v-1}^{n+1} + Z_{PC}R_{tuv}^{n+1}$$

Final expressions for Coulomb integrals

- One-electron integrals

$$\begin{aligned}\langle G_a | r_C^{-1} | G_b \rangle &= \int \frac{\Omega_{ab}}{r_C} d\mathbf{r} \\ &= \sum_{tuv} E_{tuv}^{ab} \int \frac{\Lambda_{tuv}}{r_C} d\mathbf{r} = \frac{2\pi}{p} \sum_{tuv} E_{tuv}^{ab} R_{tuv}(p, \mathbf{R}_{PC})\end{aligned}$$

- Two-electron integrals

$$\begin{aligned}\langle G_a(a)G_b(1) | r_{12}^{-1} | G_c(2)G_d(2) \rangle &= \iint \frac{\Omega_{ab}(1)\Omega_{cd}(2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \sum_{tuv} E_{tuv}^{ab} \sum_{\tau\nu\phi} E_{\tau\nu\phi}^{cd} \iint \frac{\Lambda_{tuv}(1)\Lambda_{\tau\nu\phi}(2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \sum_{tuv} E_{tuv}^{ab} \sum_{\tau\nu\phi} E_{\tau\nu\phi}^{cd} (-1)^{\tau+\nu+\phi} R_{t+\tau, u+\nu, v+\phi}(\alpha, \mathbf{R}_{PQ})\end{aligned}$$

- two-electron integrals very similar to one-electron integrals
- Hermit expansion for both electrons, around centers \mathbf{P} and \mathbf{Q}
- integrals depend on \mathbf{R}_{PQ} and $\alpha = pq/(p+q)$, with $p = a + b$ and $q = c + d$

Summary one-electron Coulomb integral evaluation

1. Calculate expansion coefficients

$$E_0^{00} = \exp(-\mu X_{AB}^2)$$

$$E_t^{i+1,j} = \frac{1}{2p} E_{t-1}^{ij} + X_{PA} E_t^{ij} + (t+1) E_{t+1}^{ij}$$

2. Calculate the Boys function

$$F_n(x) = \int_0^1 \exp(-xt^2) t^{2n} dt \quad (\text{with } x = pR_{PC}^2)$$

$$F_n(x) = \frac{2xF_{n+1}(x) + \exp(-x)}{2n+1}$$

3. Calculate Hermite integrals

$$R_{000}^n = (-2p)^n F_n$$

$$R_{t+1,u,v}^n = X_{PC} R_{tuv}^{n+1} + t R_{t-1,u,v}^{n+1}$$

4. Calculate Cartesian integrals

$$\langle G_a | r_C^{-1} | G_b \rangle = \sum_{tuv} E_t^{ij} E_u^{kl} E_v^{mn} R_{tuv}^0$$

Evaluation of two-electron contributions Fock/Kohn–Sham matrices

- The general expression for two-electron integrals is given by

$$g_{abcd} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \sum_{tuv} E_{tuv}^{ab} \sum_{\tau\nu\phi} E_{\tau\nu\phi}^{cd} (-1)^{\tau+\nu+\phi} R_{t+\tau, u+\nu, v+\phi}(\alpha, \mathbf{R}_{PQ})$$

- In SCF theories, these integrals make contributions to the Fock/KS matrix:

$$F_{ab} = \sum_{cd} \left(\underbrace{2g_{abcd}D_{cd}}_{\text{Coulomb}} - \underbrace{g_{acbd}D_{cd}}_{\text{exchange}} \right)$$

- in early days, one would write all integrals to disk and read back as required
- in **direct SCF** theories, integrals are calculated as needed
- this development (1980) made much larger calculations possible
- Many developments have since improved the efficiency of direct SCF
 - efficient screening of integrals
 - early contraction with density matrices (Coulomb)
 - density fitting (Coulomb)
 - multipole methods (Coulomb)

Scaling properties

- Product of two s functions from Gaussian product rule

$$\exp(-ar_A^2) \exp(-br_B^2) = \exp(-ab/(a+b)R_{AB}^2) \exp(-(a+b)r_P^2)$$

- Overlap integral between two s orbitals:

$$S_{ab} = \left(\frac{\pi}{a+b}\right)^{3/2} \exp\left(-\frac{ab}{a+b}R_{AB}^2\right)$$

- the number of such integrals scales quadratically with system size
- however, S_{ab} decreases rapidly with R_{AB}

- Let us assume that we may neglect all integrals

$$|S_{ab}| < 10^{-k} \quad \leftarrow \text{insignificant integrals}$$

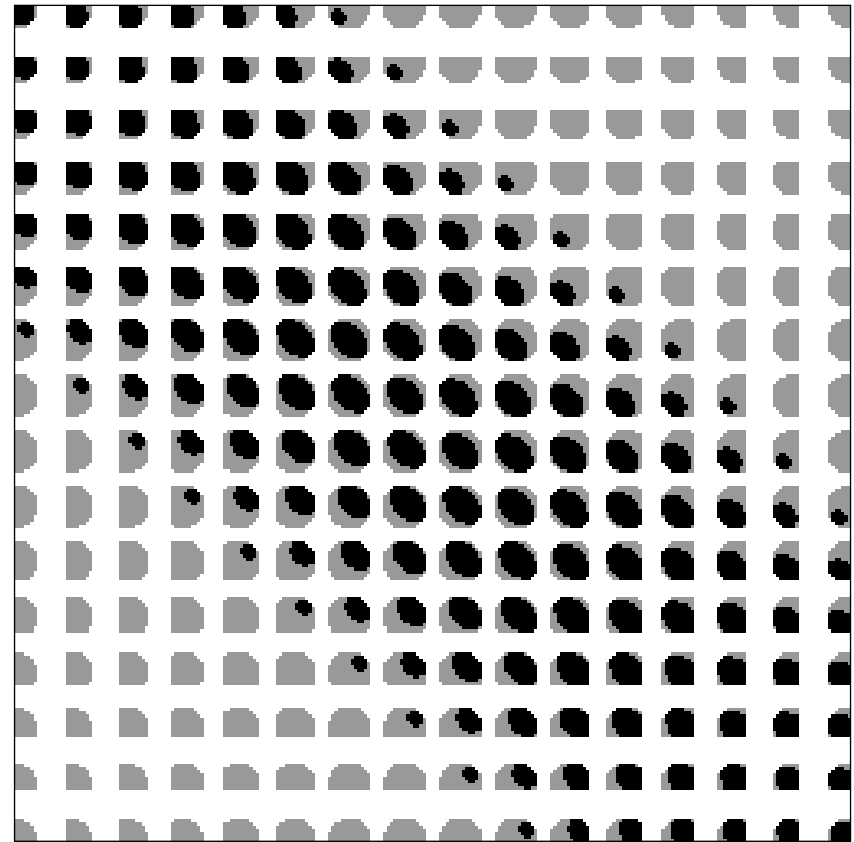
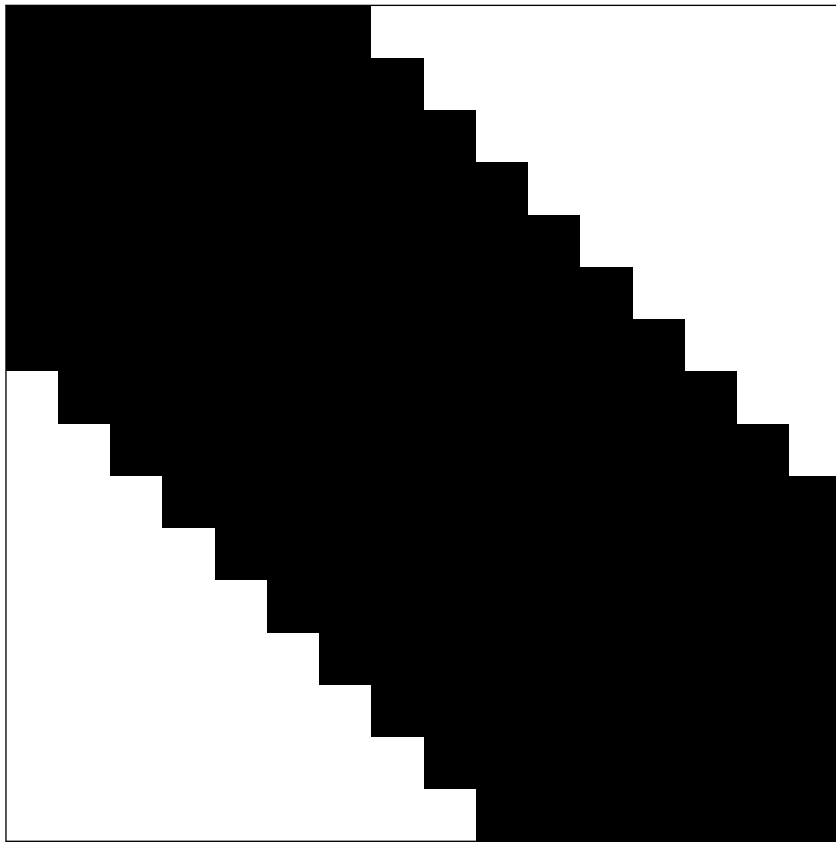
- We may neglect all integrals separated by more than

$$R_{AB} > \sqrt{a_{\min}^{-1} \ln \left[\left(\frac{\pi}{2a_{\min}} \right)^3 10^{2k} \right]}$$

- in a large system, most integrals becomes small and may be neglected
- the number of significant integrals increases linearly with system size

The sparsity of overlap and electron-repulsion integrals

- linear system of 16 Gaussian 1s functions of unit exponent, separated by $1a_0$



Two-electron integral scaling

- Two-electron *ssss* integrals:

$$g_{abcd} = \operatorname{erf}(\sqrt{\alpha}R_{PQ}) \frac{S_{ab}S_{cd}}{R_{PQ}}$$

- the total number of integrals scales quartically with system size
- the number of significant integrals scales quadratically

$$S_{ab}, S_{cd} \rightarrow 0 \text{ rapidly}$$

$$R_{PQ}^{-1} \rightarrow 0 \text{ very slowly}$$

- Decompose integral into classical and nonclassical parts:

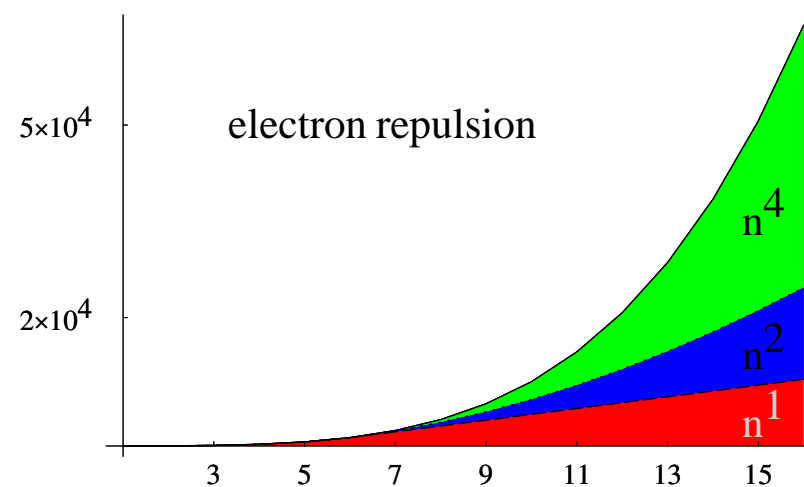
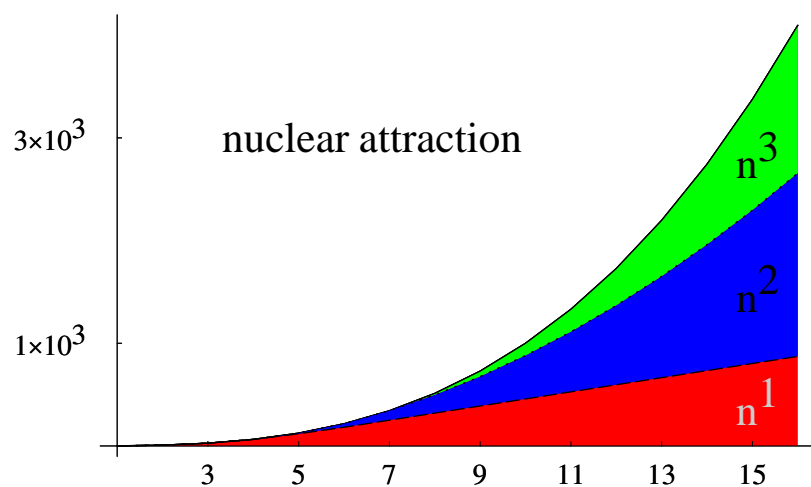
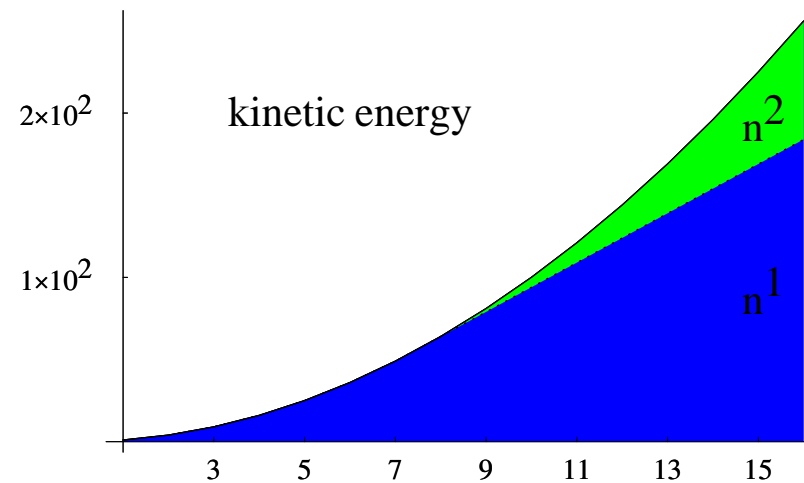
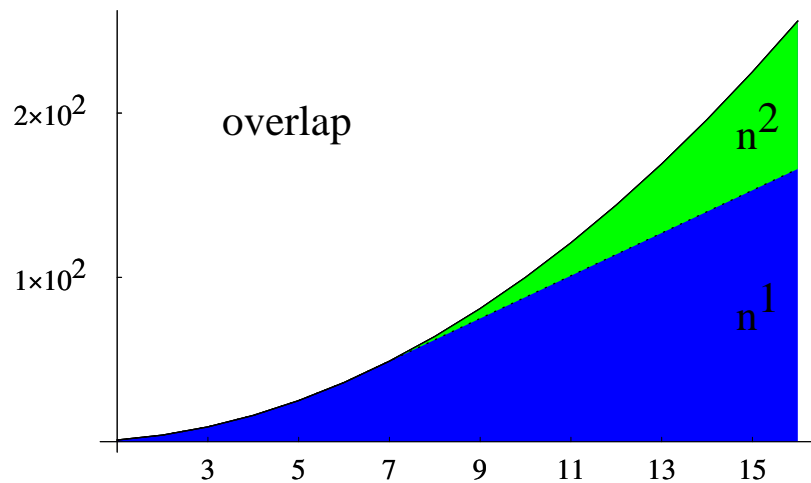
$$g_{abcd} = \underbrace{\frac{S_{ab}S_{cd}}{R_{PQ}}}_{\text{classical}} - \underbrace{\operatorname{erfc}(\sqrt{\alpha}R_{PQ}) \frac{S_{ab}S_{cd}}{R_{PQ}}}_{\text{nonclassical}}$$

- quadratic scaling of classical part, can be treated by multipole methods
- linear scaling of nonclassical part since $S_{ab} \rightarrow 0$, $S_{cd} \rightarrow 0$, $\operatorname{erfc} \rightarrow 0$ rapidly

$$\operatorname{erfc}(\sqrt{\alpha}R_{PQ}) \leq \frac{\exp(-\alpha R_{PQ}^2)}{\sqrt{\pi\alpha}R_{PQ}}$$

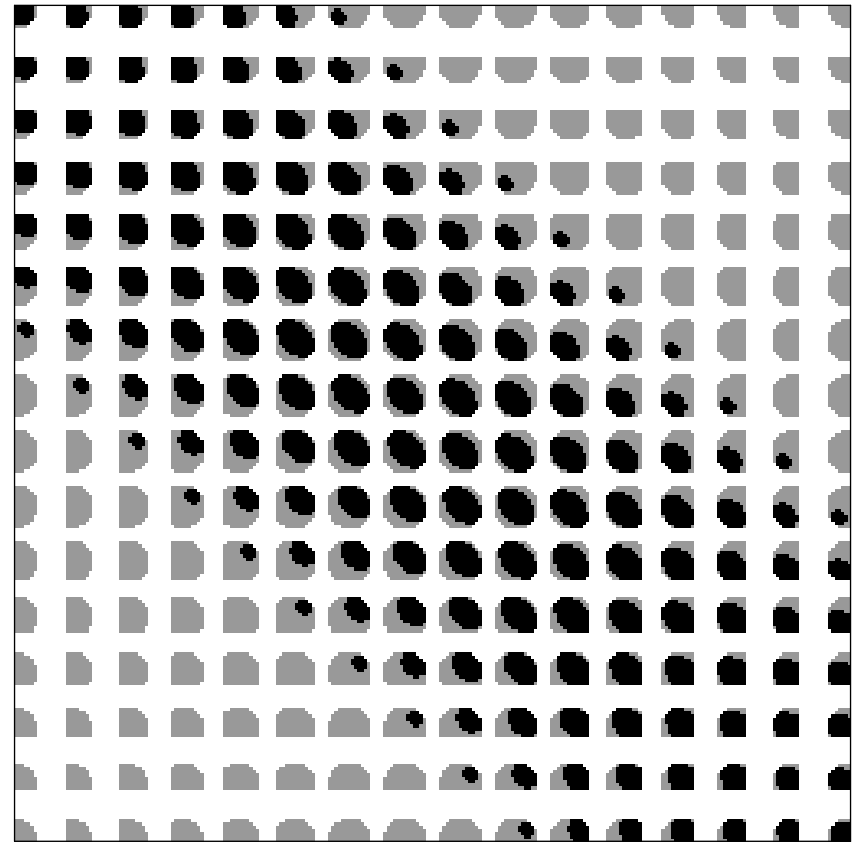
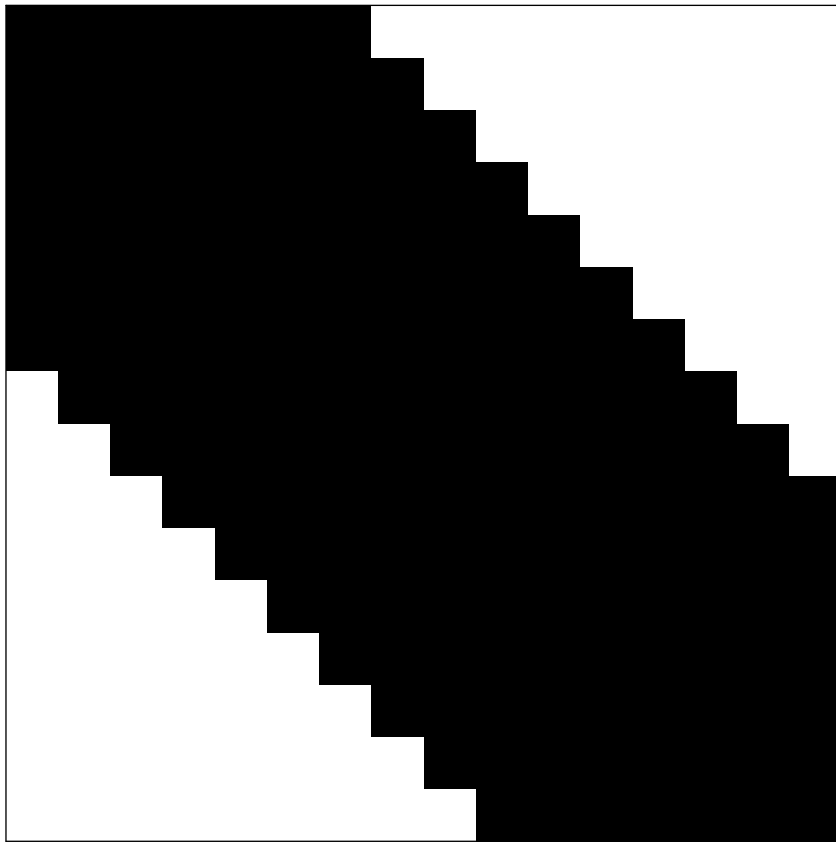
The scaling properties of molecular integrals

- linear system of up to 16 1s GTOs of unit exponent, separated by $1a_0$



The sparsity of overlap and electron-repulsion integrals

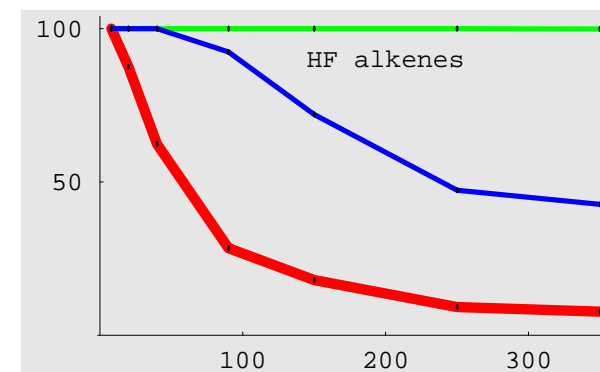
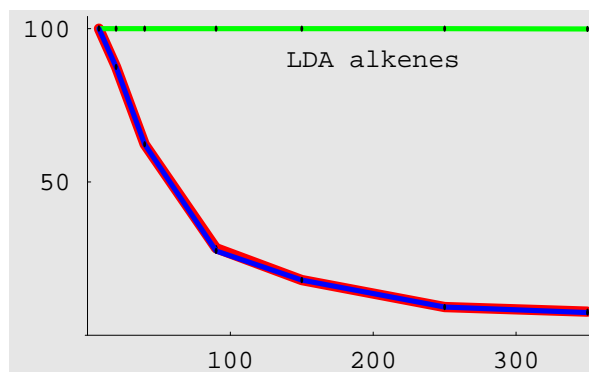
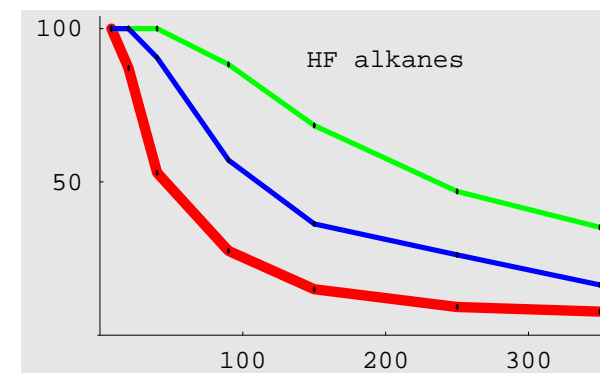
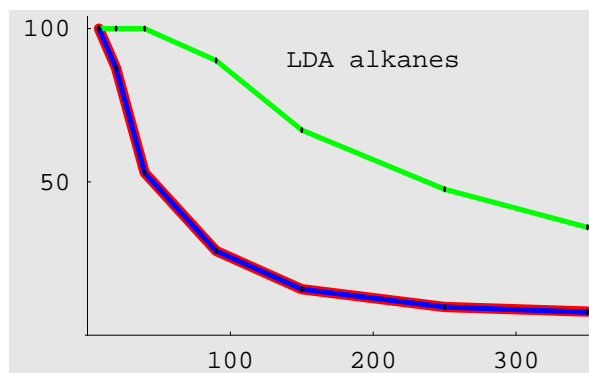
- linear system of 16 Gaussian 1s functions of unit exponent, separated by $1a_0$



Sparsity in linear alkanes and alkenes

- Percentage of matrix elements greater than 10^{-6} in alkane and alkene chains

- **overlap matrix:**
 - sparse
- **density matrix:**
 - nonsparse for alkenes
 - sparse for alkanes
- **Fock/KS matrices:**
 - KS matrix like overlap
 - Fock matrix intermediate between overlap and density matrices



Integral prescreening

- Small integrals ($< 10^{-10}$) are not needed and should be avoided by some prescreening technique
- The two-electron integrals

$$g_{abcd} = \iint \frac{\Omega_{ab}(1)\Omega_{cd}(2)}{r_{12}} \mathbf{dr}_1 \mathbf{dr}_2$$

are the elements of a positive definite matrix with diagonal elements

$$g_{ab,ab} \geq 0$$

- The conditions for an inner product are thus satisfied
- The Cauchy–Schwarz inequality yields

$$\|g_{ab,ab}\| \leq \sqrt{g_{ab,ab}}\sqrt{g_{cd,cd}}$$

- Precalculate

$$G_{ab} = \sqrt{g_{ab,ab}}$$

and prescreen

$$\|g_{ab,cd}\| \leq G_{ab}G_{cd}$$

Calculation of Coulomb potential

- The traditional Coulomb-potential evaluation is a two-step procedure
 1. evaluate significant two-electron integrals (in batches)

$$g_{abcd} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \sum_{tuv} E_{tuv}^{ab} \sum_{\tau\nu\phi} E_{\tau\nu\phi}^{cd} (-1)^{\tau+\nu+\phi} R_{t+\tau, u+\nu, v+\phi}(\alpha, \mathbf{R}_{PQ})$$

2. add their contribution to the Fock or Kohn–Sham matrix:

$$J_{ab} = \sum_{cd} g_{abcd} D_{cd}$$

- The cost of the different steps (L is ang. mom., p number of primitives):

Boys	E coef	R int	$\tau\nu\phi$	cont	S_{lm}	tuv	cont	S_{lm}	J_{ab}
Lp^4	L^3p^2	L^4p^4	$L^{10}p^4$	L^7p^4	L^8p^2	L^9p^2	L^6p^2	L^7	L^4

- for low L , evaluation of the Boys function dominates
- for large L , the $\tau\nu\phi$ contraction dominates

- It is not necessary to assemble the integrals fully before contraction with D_{cd}

Early contraction with density matrix for Coulomb potential

- Two-electron Coulomb contribution to Fock/Kohn–Sham matrix:

$$J_{ab} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \sum_{tuv} E_{tuv}^{ab} \sum_{\tau\nu\phi} \sum_{cd} D_{cd} E_{\tau\nu\phi}^{cd} (-1)^{\tau+\nu+\phi} R_{t+\tau, u+\nu, v+\phi}(\alpha, \mathbf{R}_{PQ})$$

- Early contraction of density matrix with E coefficients:

$$K_{\tau\nu\phi}^Q = (-1)^{\tau+\nu+\phi} \sum_{cd \in Q} D_{cd} E_{\tau\nu\phi}^{cd}$$

$$J_{ab} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \sum_{tuv} E_{tuv}^{ab} \sum_Q \sum_{\tau\nu\phi} K_{\tau\nu\phi}^Q R_{t+\tau, u+\nu, v+\phi}(\alpha, \mathbf{R}_{PQ})$$

– the $\tau\nu\phi$ (tuv) cost reduced from $L^{10}p^4$ to L^6p^4 (from L^9p^2 to L^7p^2)

- Timings (seconds) for benzene:

	cc-pVDZ	cc-pVTZ	cc-pVQZ
late contraction	27	374	3823
early contraction	10	90	687

Density fitting

- Traditionally, the electron density is expanded in overlap distributions

$$\rho(\mathbf{r}) = \sum_{ab} D_{ab} \Omega_{ab}(\mathbf{r})$$

- the number of terms is n^2 , where n is the number of AOs

- The Coulomb contribution to the Fock/KS matrix is evaluated as

$$J_{ab} = \langle \Omega_{ab}(\mathbf{r}_1) | r_{12}^{-1} | \rho(\mathbf{r}_2) \rangle$$

- the formal cost of this evaluation is therefore quartic (n^4)

- Consider now an **approximate density** $\tilde{\rho}(\mathbf{r})$, expanded in an **auxiliary basis** $\omega_\alpha(\mathbf{r})$:

$$\tilde{\rho}(\mathbf{r}) = \sum_{\alpha} c_{\alpha} \omega_{\alpha}(\mathbf{r}), \quad \tilde{\rho}(\mathbf{r}) \approx \rho(\mathbf{r})$$

- the size of the auxiliary basis N increases linearly with system size

- We may now evaluate the Coulomb contribution approximately as

$$\tilde{J}_{ab} = \langle \Omega_{ab}(\mathbf{r}_1) | r_{12}^{-1} | \tilde{\rho}(\mathbf{r}_2) \rangle$$

- the cost of the evaluation is therefore cubic ($n^2 N$)

- if the $\tilde{\rho}$ is sufficiently accurate and easy to obtain, this may give huge savings

Coulomb density fitting

- Consider the evaluation of the Coulomb potential

$$J_{ab} = \sum_{cd} (ab|cd) D_{cd}$$

- We now introduce an auxiliary basis and invoke the resolution of identity:

$$(ab|cd) \approx \sum_{\alpha\beta} (ab|\alpha) (\alpha|\beta)^{-1} (\beta|cd)$$

– in a complete auxiliary basis, the two expressions are identical

- We may now calculate the Coulomb potential in two different ways:

$$J_{ab} = \sum_{cd} (ab|cd) D_{cd} = (ab|\rho)$$

$$\approx \sum_{cd} \sum_{\alpha\beta} (ab|\alpha) (\alpha|\beta)^{-1} (\beta|cd) D_{cd} = \sum_{\alpha} (ab|\alpha) c_{\alpha} = (ab|\tilde{\rho}) = \tilde{J}_{ab}$$

where the coefficients c_{α} are obtained from the linear sets of equations

$$\sum_{\alpha} (\beta|\alpha) c_{\alpha} = \sum_{cd} (\beta|cd) D_{cd} \Leftrightarrow (\beta|\tilde{\rho}) = (\beta|\rho)$$

- no four-center integrals, the formal cost is cubic or smaller
- note: the solution of the linear equations scales cubically

- This particular approach to density fitting is called **Coulomb density fitting**

Robust density fitting

- In Coulomb density fitting, the exact and fitted Coulomb matrices are given by

$$J_{ab} = (ab|\rho), \quad \tilde{J}_{ab} = (ab|\tilde{\rho}), \quad (\alpha|\rho) = (\alpha|\tilde{\rho})$$

- We may then calculate the exact and density-fitted Coulomb energies as

$$E = \sum_{ab} J_{ab} D_{ab} = (\rho|\rho), \quad \tilde{E} = \sum_{ab} \tilde{J}_{ab} D_{ab} = (\rho|\tilde{\rho})$$

- The true Coulomb energy is an upper bound to the density-fitted energy:

$$E - \tilde{E} = (\rho|\rho) - (\rho|\tilde{\rho}) = (\rho|\rho) - (\rho|\tilde{\rho}) - (\tilde{\rho}|\rho) + (\tilde{\rho}|\tilde{\rho}) = (\rho - \tilde{\rho}|\rho - \tilde{\rho})$$

- the error in the density-fitted energy is **quadratic** in the error in the density
- Coulomb fitting is thus equivalent to minimization of $E - \tilde{E} = (\rho - \tilde{\rho}|\rho - \tilde{\rho})$

- It is possible to determine the approximate density in other ways

- quadratic energy error is ensured by using the **robust formula**

$$\tilde{E} = (\tilde{\rho}|\rho) + (\rho|\tilde{\rho}) - (\tilde{\rho}|\tilde{\rho}) = E - (\rho - \tilde{\rho}|\rho - \tilde{\rho})$$

- however, the error in the energy is no longer minimized

Density fitting: sample calculations

- no symmetry used; exact energy: $-230.208E_h$

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
exact density late	27	374	3823	na
exact density early	10	90	687	5320
fitted density	1	7	34	166
exact energy	-230.09671	-230.17927	-230.19463	na
density-fitted energy	-230.09733	-230.17933	-230.19466	-230.20116

- Clearly, very large gains can be achieved with density fitting
- Formal scaling is cubical
 - for large systems, screening yields quadratic scaling for integral evaluation
 - the cubic cost of solving linear equations remains for large systems
- Linear scaling is achieved by boxed density-fitting and fast multipole methods
 - the density is partitioned into boxes, which are fitted one at a time
 - fast multipole methods for matrix elements