

Molecular Integral Evaluation

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Molecular integral evaluation

▶ one-electron integrals

- ▶ overlap, multipole-moment, and kinetic-energy integrals
- ▶ nuclear-attraction integrals

$$O_{ab} = \int \chi_a(\mathbf{r}) \hat{O}(\mathbf{r}) \chi_b(\mathbf{r}) d\mathbf{r}$$

▶ two-electron integrals

- ▶ Coulomb integrals

$$g_{abcd} = \iint \frac{\chi_a(\mathbf{r}_1) \chi_b(\mathbf{r}_1) \chi_c(\mathbf{r}_2) \chi_d(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

- ▶ Coulomb and exchange contributions to Fock/KS matrix

$$F_{ab} = \sum_{cd} (2g_{abcd} D_{cd} - g_{acbd} D_{cd})$$

▶ basis functions

- ▶ primitive Cartesian GTOs

▶ integration schemes

- ▶ McMurchie–Davidson, Obara–Saika and Rys schemes
- ▶ screening, density fitting, fast multipole methods

1 Cartesian and Hermite Gaussians

- ▶ properties of Cartesian Gaussians
- ▶ properties of Hermite Gaussians

2 Simple one-electron integrals

- ▶ Gaussian product rule and overlap distributions
- ▶ overlap distributions expanded in Hermite Gaussians
- ▶ overlap and kinetic-energy integrals

3 Coulomb integrals

- ▶ Gaussian electrostatics and the Boys function
- ▶ one- and two-electron Coulomb integrals over Cartesian Gaussians

4 Sparsity and screening

- ▶ Cauchy–Schwarz screening

5 Coulomb potential

- ▶ early density-matrix contraction
- ▶ density fitting

Cartesian Gaussian-type orbitals (GTOs)

- ▶ We shall consider integration over **primitive Cartesian Gaussians** centered at **A**:

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

- ▶ total **angular-momentum** quantum number $\ell = i + j + k \geq 0$
- ▶ Gaussians of a given ℓ constitute a **shell**:
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}
- ▶ Each Gaussian **factorizes** in the Cartesian directions:

$$G_{ijk}(a, \mathbf{r}_A) = G_i(a, x_A)G_j(a, y_A)G_k(a, z_A), \quad G_i(a, x_A) = x_A^i \exp(-ax_A^2)$$

- ▶ note: this is not true for spherical-harmonic Gaussians nor for Slater-type orbitals
- ▶ Gaussians satisfy a simple **recurrence relation**:

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

- ▶ The **differentiation** of a Gaussian yields a linear combination of two Gaussians

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

Hermite Gaussians

- ▶ The **Hermite Gaussians** are defined as

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

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

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

- ▶ Hermite Gaussians yield the **same spherical-harmonic functions** as do Cartesian Gaussians
 - ▶ they may therefore be used as basis functions in place of Cartesian functions
- ▶ We shall only consider their use as **intermediates** in the evaluation of Gaussian integrals

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

- ▶ such expansions are useful because of simple integration properties (next slide)

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

- ▶ McMurchie and Davidson (1978)
- ▶ We shall make extensive use of the **McMurchie–Davidson scheme** for integration

Integration over Hermite Gaussians

- ▶ From the **definition** of Hermite Gaussians, we have

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

- ▶ We now change the order of differentiation and integration by **Leibniz' rule**:

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

- ▶ The **basic Gaussian integral** is given by

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

- ▶ Since the integral is independent of P_x , differentiation with respect to P_x gives zero:

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

- ▶ only integrals over Hermite s functions do not vanish

Hermite recurrence relation

- ▶ We recall the simple recurrence relation of Cartesian Gaussians:

$$x_A G_i = G_{i+1}$$

- ▶ The corresponding **Hermite recurrence relation** is slightly more complicated:

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

- ▶ 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

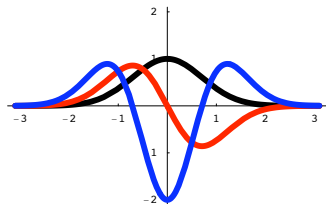
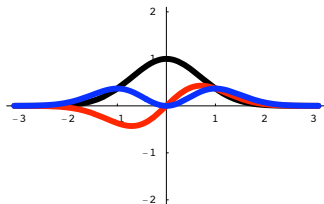
$$\left(\frac{\partial}{\partial P_x} \right)^t x_P = x_P \left(\frac{\partial}{\partial P_x} \right)^t - t \left(\frac{\partial}{\partial P_x} \right)^{t-1}$$

we then obtain

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

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	$\frac{\partial G_i}{\partial A_x} = 2a G_{i+1} - i G_{i-1}$	$\frac{\partial \Lambda_t}{\partial P_x} = \Lambda_{t+1}$



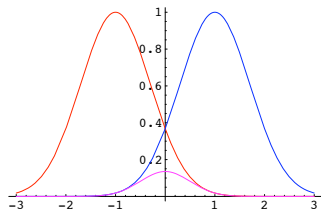
The Gaussian product rule

- ▶ An important property of Gaussians is the **Gaussian product rule**
- ▶ The product of two Gaussians is **another Gaussian** centered somewhere on the line 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 integral evaluation**
 - ▶ 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

$$\int \Omega_{ij}(x) dx = K_{AB}^x \int x_A^i x_B^j \exp(-px^2) dx, \quad K_{AB}^x = \exp(-\mu X_{AB}^2)$$

- ▶ the Cartesian monomials still make the integration awkward
- ▶ we would like to utilize the simple integration properties of Hermite Gaussians
- ▶ We therefore **expand Cartesian overlap distributions in Hermite Gaussians**

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

- ▶ 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 $0 \leq t \leq i+j$
- ▶ The expansion coefficients may be evaluated **recursively** from $E_0^{00} = K_{AB}^x$:

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

- ▶ we shall now prove these **recurrence relations**

Recurrence relations for Hermite expansion coefficients

- ▶ A straightforward Hermite expansion of $\Omega_{i+1,j}$

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

- ▶ An alternative Hermite expansion of $\Omega_{i+1,j}$

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

- ▶ we have here used the recurrence $x_P \Lambda_t = \frac{1}{2p} \Lambda_{t+1} + t \Lambda_{t-1}$

- ▶ 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

- ▶ We now have everything we need to evaluate **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**, the **Hermite expansion**, and the **Hermite integration rule**:

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

- ▶ 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-moment integrals

- ▶ Many other integrals may be evaluated in the same manner
- ▶ For example, **dipole-moment integrals** are obtained as

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

- ▶ The final **dipole-moment integral** is given by

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

Kinetic-energy integrals

- ▶ As a final example of non-Coulomb integrals, we consider the **kinetic-energy integrals**:

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

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

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

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

- ▶ **Differentiation of Cartesian Gaussians** gives

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

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

- ▶ the first derivative is linear combination of two undifferentiated Gaussians
 - ▶ the second derivative is linear combination of three undifferentiated Gaussians
- ▶ Kinetic-energy integrals are **linear combinations of up to three overlap integrals**:

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

Coulomb integrals

- ▶ We shall consider two types of **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

- ▶ however, they may be reduced to a **one-dimensional integral on a finite interval**:

$$F_n(x) = \int_0^1 \exp(-xt^2) t^{2n} dt \leftarrow \text{the Boys function}$$

- ▶ this makes the evaluation of Gaussian Coulomb integrals relatively simple

- ▶ We begin by evaluating the **one-electron spherical Coulomb integral**:

$$V_p = \int \frac{\exp(-pr_p^2)}{r_C} dr = \frac{2\pi}{p} F_0(pR_{pC}^2)$$

- ▶ we shall next go on to consider more general Coulomb integrals

Coulomb integral over a spherical Gaussian I

- ▶ We would like to evaluate the **three-dimensional** Coulomb-potential integral

$$V_p = \int \frac{\exp(-pr_p^2)}{r_C} dr$$

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

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

to yield the **four-dimensional** integral

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

- 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):

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

– to be continued...

Coulomb integral over a spherical Gaussian II

- carried over from previous slide:

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

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

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

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

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

and obtain

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

- ▶ 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 $[0, 1]$

Gaussian electrostatics

- ▶ The Boys function is related to the **error function**

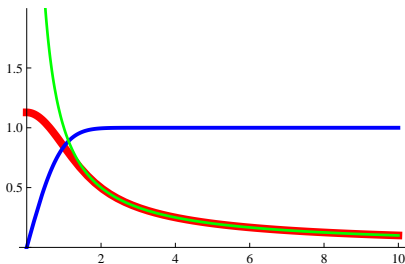
$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) dt = \frac{2x F_0(x^2)}{\sqrt{\pi}}$$

- ▶ Introducing **unit charge distributions** and the reduced exponent as

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

we obtain formulas similar to those of **point-charge electrostatics (but damped)**

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



The Boys function $F_n(x)$

- ▶ The Boys function is **central to molecular integral evaluation**
 - ▶ it is evaluated by a **combination of numerical techniques**

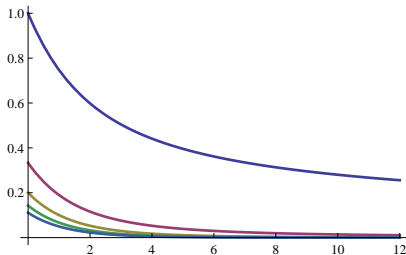
- ▶ $F_n(x) > 0$ since the integrand is positive:

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

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

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

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



- ▶ Evaluation for small and large values:

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

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

- ▶ Different n -values are related by downward recurrence relations:

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

Cartesian Coulomb integrals

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

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

- ▶ 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 is 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

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

- ▶ We now expand two-center Coulomb integrals in **one-center Hermite Coulomb integrals**:

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

- ▶ Our next task is therefore to evaluate **Hermite Coulomb 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

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

- ▶ Expansion of the Coulomb integrals in one-center **Hermite Coulomb integrals** R_{tuv} :

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

- ▶ The Hermite Coulomb 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

Evaluation of Hermite Coulomb integrals

- ▶ To set up recursion for the Hermite integrals, 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**:

$$\begin{aligned} R_{t+1,u,v}^n &= tR_{t-1,u,v}^{n+1} + X_{PC}R_{tuv}^{n+1} \\ R_{t,u+1,v}^n &= uR_{t,u-1,v}^{n+1} + Y_{PC}R_{tuv}^{n+1} \\ R_{t,u,v+1}^n &= vR_{t,u,v-1}^{n+1} + Z_{PC}R_{tuv}^{n+1} \end{aligned}$$

Summary one-electron Coulomb integral evaluation

- 1 Calculate **Hermite expansion coefficients** for overlap distributions by recurrence

$$E_0^{00} = \exp(-\mu X_{AB}^2)$$
$$E_t^{i+1,j} = \frac{1}{2p} E_{t-1}^{ij} + X_{PA} E_t^{ij} + (t+1) E_{t+1}^{ij}$$

- 2 Calculate the **Boys function** by a variety of numerical techniques

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

- 3 Calculate **Hermite Coulomb integrals** by recurrence

$$R_{000}^n = (-2p)^n F_n$$
$$R_{t+1,u,v}^n = X_{PC} R_{tuv}^{n+1} + t R_{t-1,u,v}^{n+1}$$

- 4 Obtain the **Cartesian Coulomb integrals** by expansion in Hermite integrals

$$\langle G_a | r_C^{-1} | G_b \rangle = \frac{2\pi}{p} \sum_{tuv} E_t^{ij} E_u^{kl} E_v^{mn} R_{tuv}^0$$

Two-electron Coulomb integrals

- ▶ Two-electron integrals are treated in the same way as one-electron integrals
- ▶ Evaluation of **one-electron integrals**:

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

- ▶ Evaluation of **two-electron integrals**:

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

- ▶ Hermit expansion for both electrons, around centers **P** and **Q**
- ▶ integrals depend on \mathbf{R}_{PQ} and $\alpha = pq/(p+q)$, with $p = a + b$ and $q = c + d$
- ▶ translational invariance simplifies two-electron Hermite integrals

Direct SCF and other techniques

- ▶ 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
 - ▶ **screening of integrals**
 - ▶ **early contraction with density matrices**
 - ▶ **density fitting**
 - ▶ **multipole methods**

Screening of overlap integrals

- ▶ The product of two s functions is by the **Gaussian product rule**

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

- ▶ This gives a simple expression for the **overlap integral** between two such 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 the separation R_{AB}
- ▶ Let us assume that we may neglect all integrals smaller than 10^{-k} :

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

- ▶ We may then **neglect 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

Screening of two-electron integrals

- ▶ A **two-electron ssss integral** may be written in the form:

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

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

$$\begin{aligned} S_{ab}, S_{cd} &\rightarrow 0 \text{ rapidly} \\ R_{PQ}^{-1} &\rightarrow 0 \text{ very slowly} \end{aligned}$$

- ▶ Let us decompose the integral into **classical** and **nonclassical** parts:

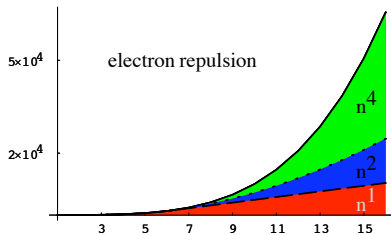
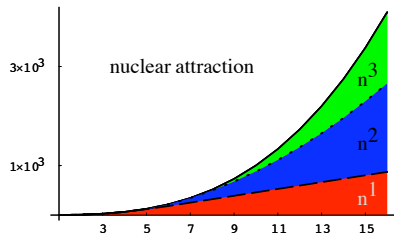
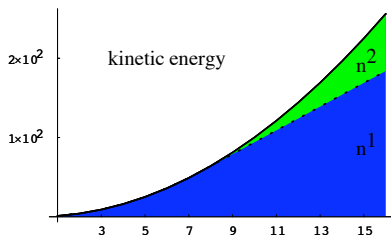
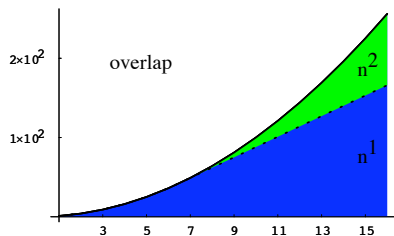
$$g_{abcd} = \underbrace{\frac{S_{ab}S_{cd}}{R_{PQ}}}_{\text{classical}} - \underbrace{\operatorname{erfc}(\sqrt{\alpha}R_{PQ}) \frac{S_{ab}S_{cd}}{R_{PQ}}}_{\text{nonclassical}}$$

- ▶ **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 $1a_0$



Integral prescreening

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

$$g_{abcd} = \iint \frac{\Omega_{ab}(1)\Omega_{cd}(2)}{r_{12}} dr_1 dr_2$$

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

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

Early contraction with density matrix

- ▶ In direct SCF, two-electron integrals are only used for **Fock/KS-matrix construction**

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

- ▶ only integrals that contribute significantly are evaluated
- ▶ screening is made based on the size of the density matrix
- ▶ It is not necessary to evaluate significant integrals fully before contraction with D_{cd}
- ▶ An **early contraction** of D_{cd} with the coefficients $E_{\tau\nu\phi}^{cd}$ is more efficient:

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

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

- ▶ Timings 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 **orbital products**

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

- ▶ 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

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

- ▶ 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

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

- ▶ the cost of the evaluation is therefore cubic ($n^2 N$)
 - ▶ if $\tilde{\rho}$ is sufficiently accurate and easy to obtain, this may give large 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:

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

where we have introduced the **approximate density**

$$\tilde{\rho}(\mathbf{r}) = \sum_{\alpha} c_{\alpha} \alpha(\mathbf{r})$$

whose 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** (multiplied by two) as

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

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

$$E_{\text{cou}} - \tilde{E}_{\text{cou}} = (\rho|\rho) - (\rho|\tilde{\rho}) = (\rho|\rho) - (\rho|\tilde{\rho}) - (\tilde{\rho}|\rho) + (\tilde{\rho}|\tilde{\rho}) = (\rho - \tilde{\rho}|\rho - \tilde{\rho})$$

where we have used the relation $(\tilde{\rho}|\rho) = (\tilde{\rho}|\tilde{\rho})$ which follows from $(\alpha|\rho) = (\alpha|\tilde{\rho})$

- ▶ the error in the density-fitted energy is **quadratic** in the error in the density
- ▶ Coulomb fitting is thus equivalent to **minimization of the self-interaction error**:

$$E_{\text{cou}} - \tilde{E}_{\text{cou}} = (\rho - \tilde{\rho}|\rho - \tilde{\rho}) \geq 0$$

- ▶ It is possible to determine the approximate density in other ways (not by Coulomb fitting)
 - ▶ quadratic energy error is always ensured by using the **robust formula**

$$\tilde{E}_{\text{cou}} = (\tilde{\rho}|\rho) + (\rho|\tilde{\rho}) - (\tilde{\rho}|\tilde{\rho}) = E_{\text{cou}} - (\rho - \tilde{\rho}|\rho - \tilde{\rho})$$

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

Density fitting: sample calculations

- ▶ Calculation on benzene

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

- ▶ 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