Compact Coulomb integrals using short-range real-space and long-range Fourier representations

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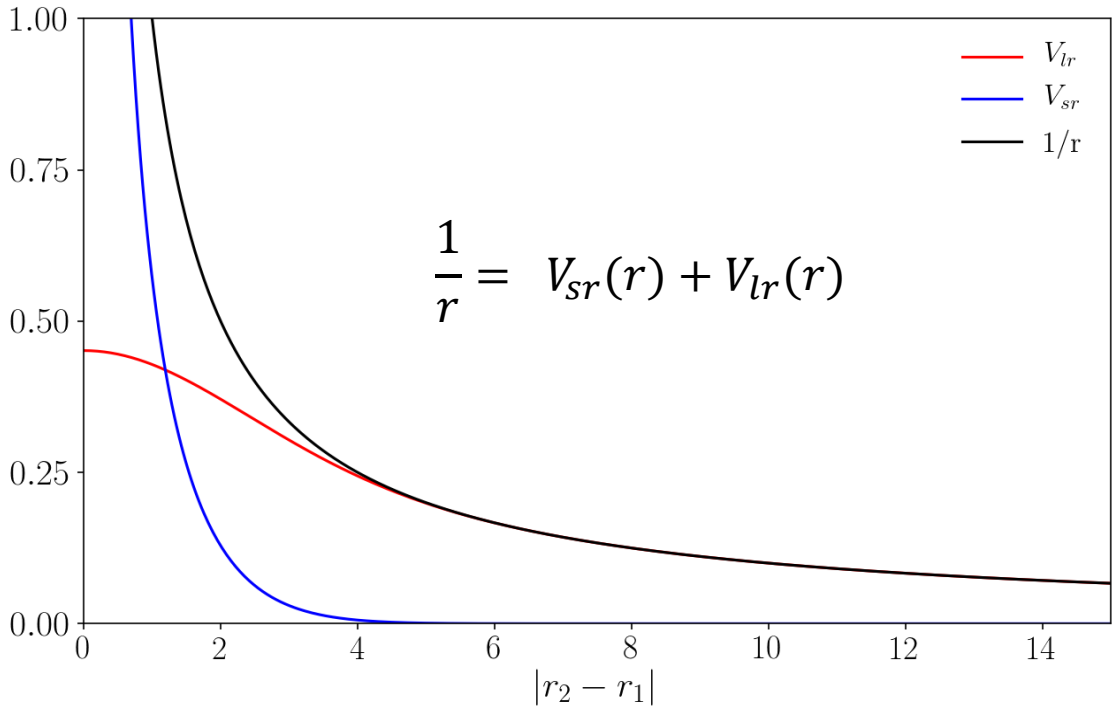
Overview

Atomic orbital integrals required for electronic structure calculations do not scale linearly w.r.t system size.

- The slow $\frac{1}{|r_2 - r_1|}$ decay is detrimental for large systems



- Nuclear nuclear potential

$$V^{NN} = \frac{1}{2}\sum_{a \neq b} \frac{Z_a Z_b}{|R_b - R_a|}$$

- Nuclear electron integrals

$$V^{Ne} = -\sum_b Z_b \int d^3r\, \phi_\alpha(r_1)\phi_\beta(r_1)\frac{1}{|r_1 - R_b|}$$

- Two electron AO integrals

$$V^{ee} = (\alpha\beta\,|\gamma\delta\,) = \int d^3r\, \phi_\alpha(r_1)\phi_\beta(r_1)\frac{1}{|r_2 - r_1|}\phi_\gamma(r_2)\phi_\delta(r_2)$$

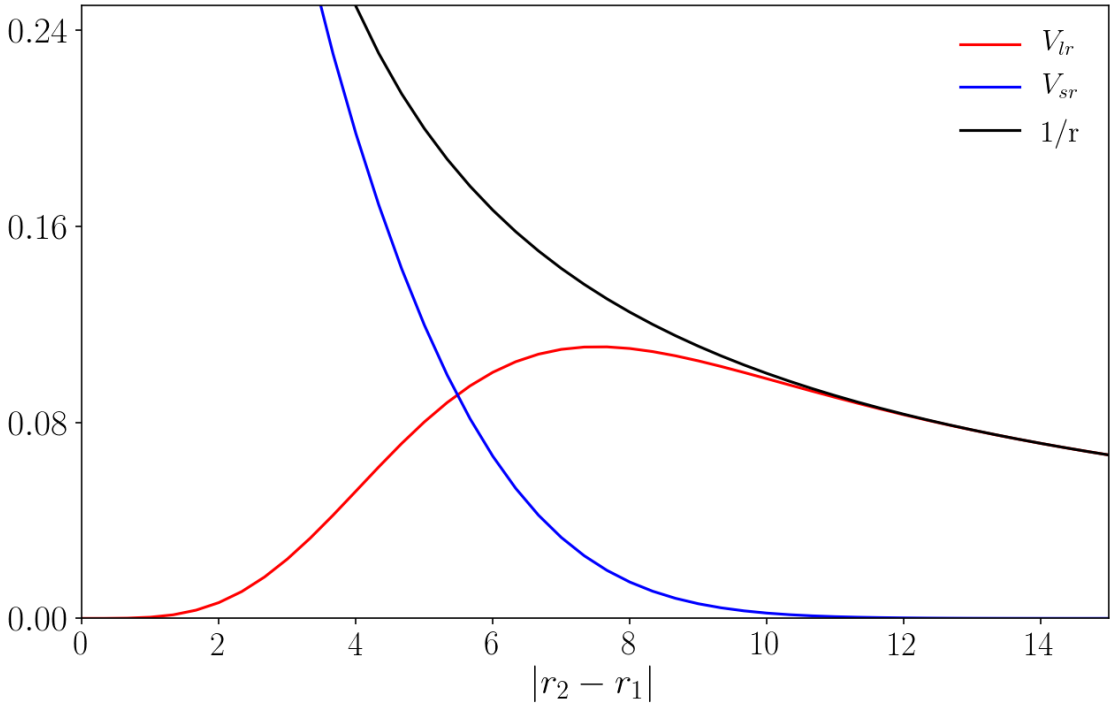
Range Separation

- Range separate the $\frac{1}{r}$ potential

$$\frac{1}{r} = V_{sr}(r) + V_{lr}(r)$$

$$V_{sr}(r) = \frac{\mathrm{erfc}(\alpha r)}{r} + X_0 e^{-\gamma r^2}$$

$$V_{lr}(r) = \frac{\mathrm{erf}(\alpha r)}{r} - X_0 e^{-\gamma r^2}$$



$X_0 = \frac{\alpha^2}{\sqrt{\pi}}$ Sets $V_{lr}(r = 0)$ to zero

$\gamma = \frac{\alpha^2}{3}$ Flattest V_{lr} near $r = 0$

- Short-range treated in real space
- Long-range treated in reciprocal space

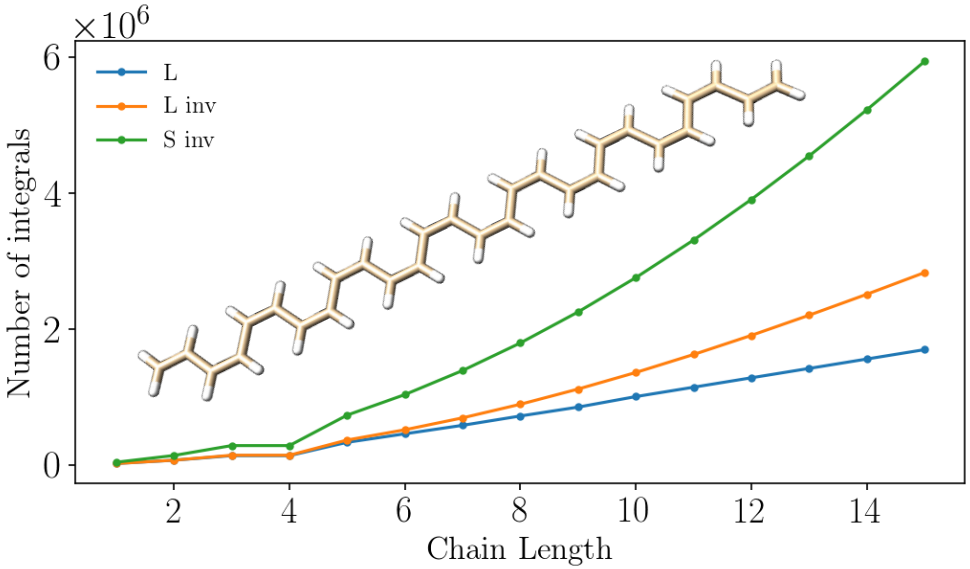
Short-Range Integrals

- Use density fitting

$$V_{sr}^{ee} = (\alpha\beta\,|\gamma\delta\,)_{sr}$$

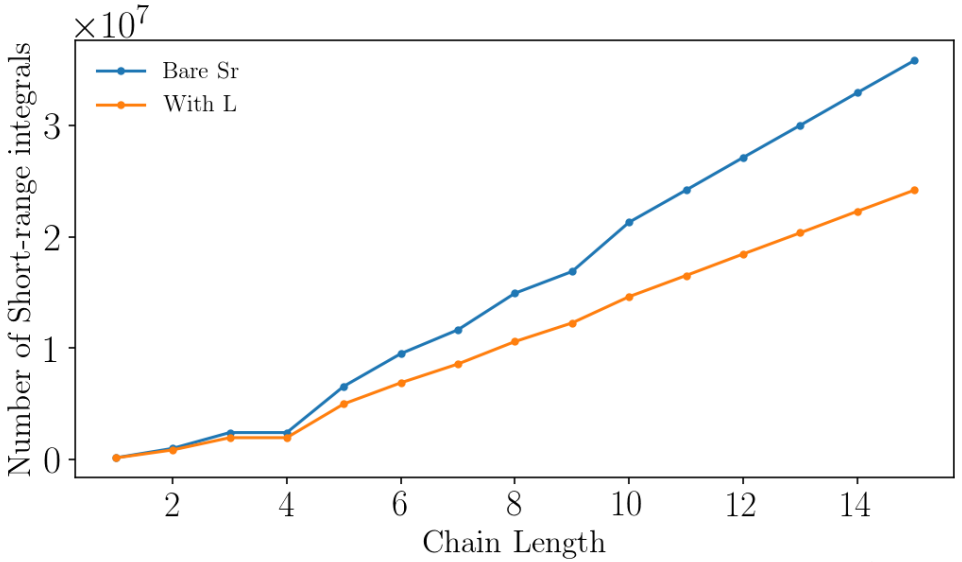
$$= \sum_{X,Y} (\alpha\beta\,|X)_{sr} (X|Y)_{sr}^{-1} (Y|\gamma\delta\,)_{sr}$$

X,Y are auxiliary fitting functions



Treated with Cholesky decomposition

$$(X|Y)_{sr}^{-1} = L^{-1^T} L^{-1}$$



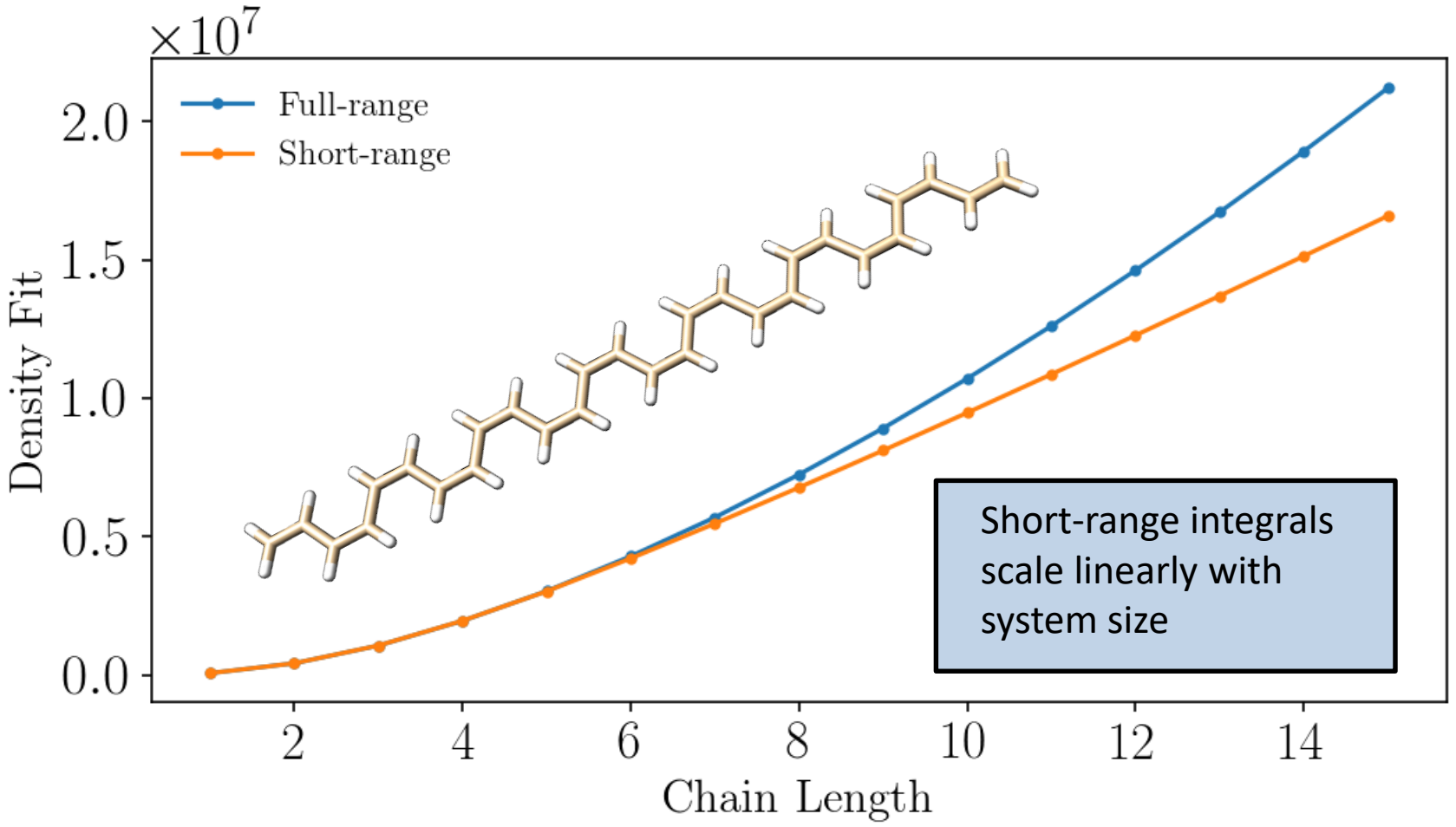
$$(\alpha\beta|X)_{sr} = (\alpha\beta|X) L^{-1^T}$$

Short-Range Integrals

$(\alpha\beta \mid X)_{sr}$

α, β **cannot** be too far apart, AO integrals are local.

X **cannot** be too far from α, β, short-range.



Long-Range Integrals

- Treated in Fourier space, numerical integration over g

$$V_{lr}(r_1, r_2) = \int d^3g\, \eta(g)\, e^{ig\cdot r_1} e^{-ig\cdot r_2}$$

$$\eta(g) = \frac{4\pi}{(2\pi)^3}\frac{1}{g^2} e^{-\frac{1}{4\alpha^2}g^2} - \frac{X_0}{(4\pi\gamma)^{3/2}} e^{-\frac{1}{4\gamma^2}g^2}$$

- g^2 singularity: Use spherical coordinates

$$d^3g = g_r^2 dg_r \sin(\phi)\, d\phi d\theta$$

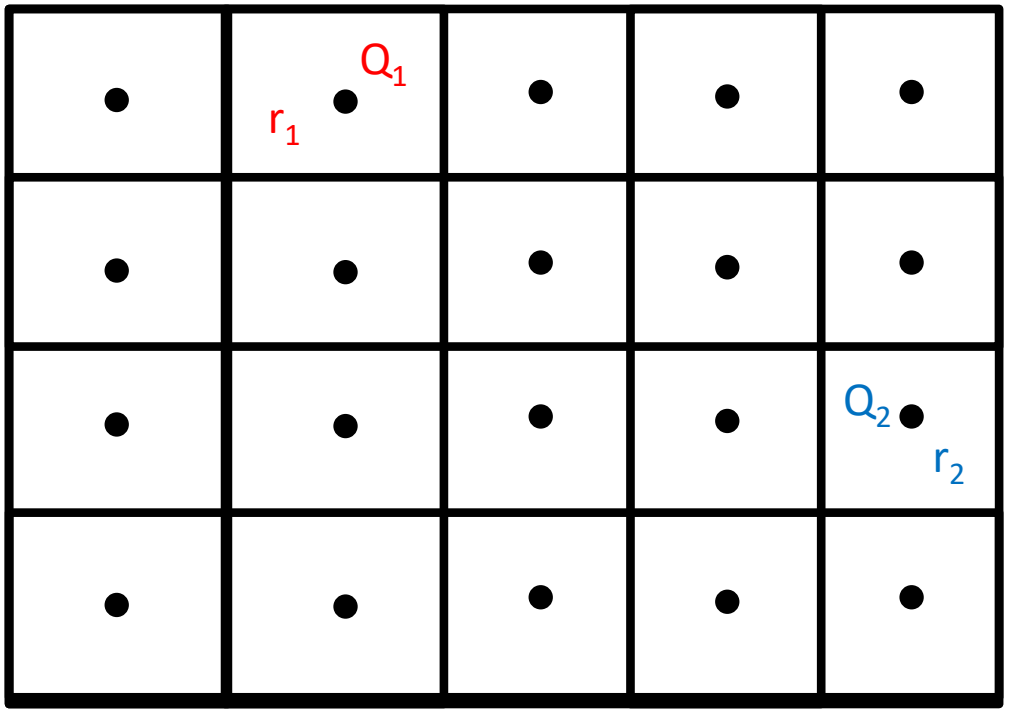
- Large $g \cdot r$, even for small g:

Gauge cells

- Large $g \cdot r$, even for small g:

$$V_{lr}(r_1, r_2) = \int d^3g\, \eta(g)\, e^{ig\cdot r_1} e^{-ig\cdot r_2}$$

- Introduce a grid of gauge points



$$(e^{ig\cdot r_1} - e^{ig\cdot Q_1}) + e^{ig\cdot Q_1}$$

- r is never **very far** from q

$$r_1 = Q_1 + x$$

$$e^{ig\cdot Q_1}(e^{ig\cdot x} - 1)$$

Rapid Slow

Regularized long-range potential

$$V_{lr}(r_1, r_2) = \int d^3g\, \eta(g)\, (e^{ig\cdot r_1} - e^{ig\cdot Q_1})(e^{-ig\cdot r_2} - e^{-ig\cdot Q_2})$$
$$+ \int d^3g\, \eta(g)\, (e^{ig\cdot r_1} - e^{ig\cdot Q_1})\, e^{ig\cdot Q_2}$$
$$+ \int d^3g\, \eta(g)\, (e^{-ig\cdot r_2} - e^{-ig\cdot Q_2})\, e^{ig\cdot Q_1}$$
$$+ \int d^3g\, \eta(g)\, e^{-ig\cdot Q_2} e^{ig\cdot Q_1}$$

$$V_{lr}(r_1, r_2) = V_{Rlr}(r_1, r_2) + V_{lr}(r_2, Q_1) + V_{lr}(r_1, Q_2) - V_{lr}(Q_1, Q_2)$$

- The Regularized long-range contribution is evaluated numerically and is small
- The additional terms are evaluated analytically and are the larger contributions

Two electron long-range integrals

$$V_{lr}^{ee}(r_1, r_2) = \int d^3g\, \eta(g)\, \bar{M}_{\alpha\beta}(g)\bar{M}_{\gamma\delta}(-g)$$
$$+ X_{\alpha\beta}(Q_i)S_{\gamma\delta}(Q_i) + S_{\alpha\beta}(Q_i)X_{\gamma\delta}(Q_i)$$
$$-S_{\alpha\beta}(Q_i)V_{lr}(|Q_i - Q_j|)\, S_{\gamma\delta}(Q_j)$$

$$\bar{M}_{\alpha\beta}(g) = (\alpha\beta|g) - S_{\alpha\beta}e^{ig\cdot Q}$$

$$(\alpha\beta|g) = \int d^3r_1\phi_\alpha(r_1)\phi_\beta(r_1)e^{ig\cdot r_1}$$

- Compact 3 index integrals (analytical Fourier transforms) with a fixed g point grid, **independent of system size**

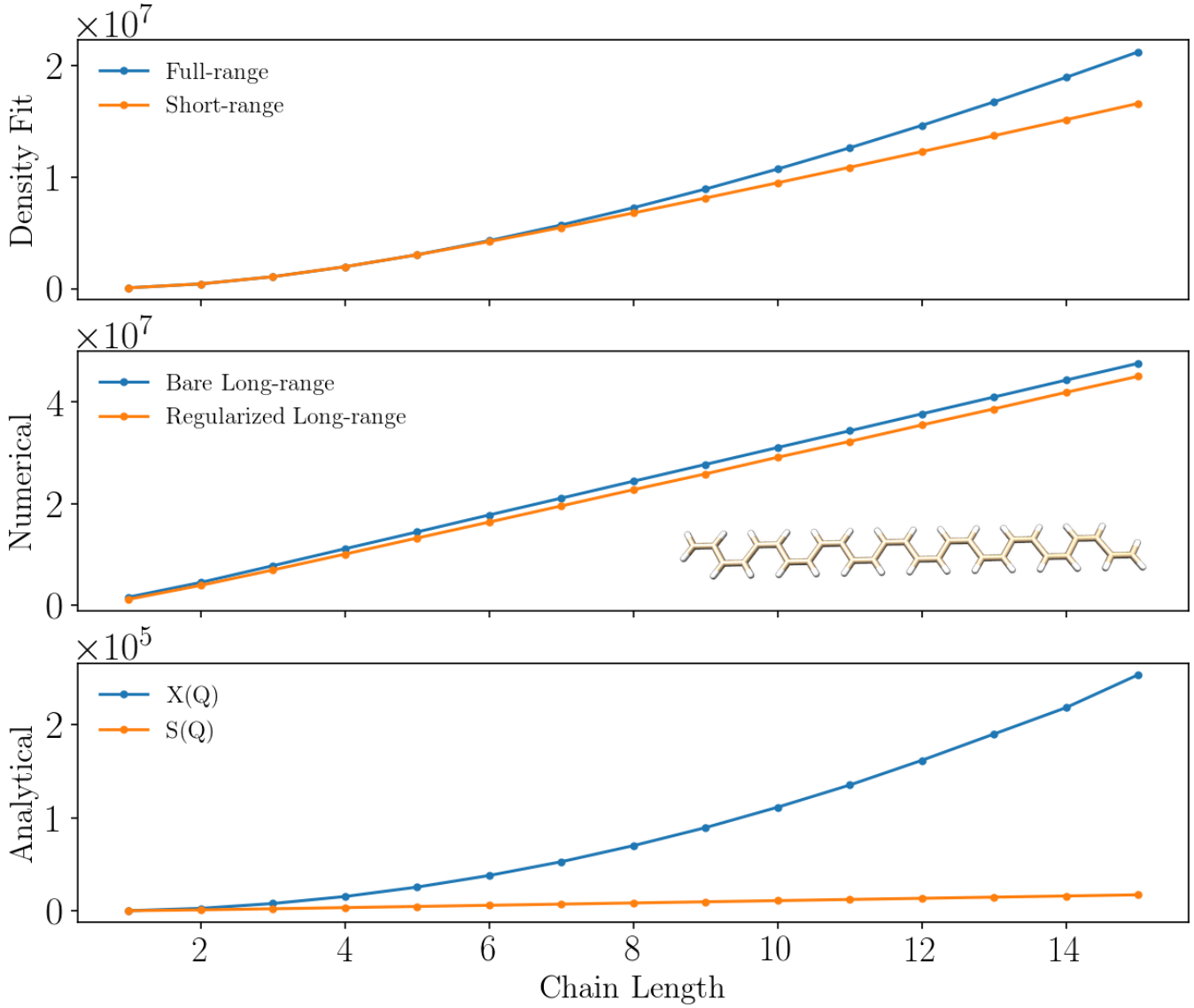
$X_{\alpha\beta}(Q)$ • Long range nuclear electron attraction integrals with a charge centred at Q

$S_{\alpha\beta}(Q)$ $= \int d^3r_1\phi_\alpha(r_1)\phi_\beta(r_1)$: if $\alpha, \beta \in Q_i$

$=0$: otherwise

- Overlap integrals associated with gauge centre Q

Two electron long-range integrals



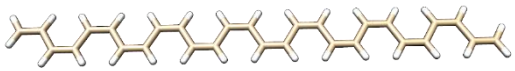
$$(\alpha\beta|X) = (\beta\alpha|X)$$

$$\bar{M}_{\alpha\beta}(g) = \bar{M}_{\beta\alpha}(g) = \bar{M}^*{}_{\alpha\beta}(-g)$$

Same shape/sym as short-range integrals

$X_{\alpha\beta}(Q)$ is the only non-linear scaling quantity.

Results: $C_{28}H_{30}$



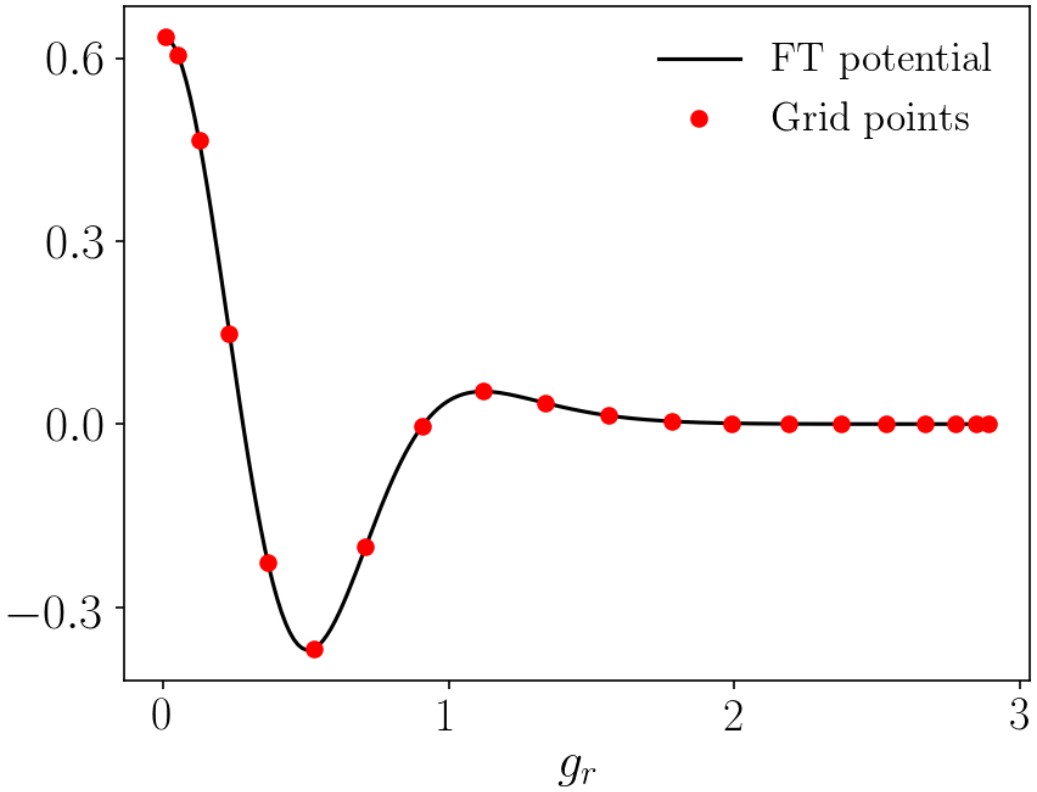
		Analytical		Numerical		
		% Contribution	Value (Eh)	% Contribution	Value (Eh)	Error (Eh)
Fourier	NN			100.00	874.33	-4.12
	Ne			100.00	-1761.52	8.29
	J			100.00	887.13	-4.16
	K			100.00	-0.30	0.00
	Total					0.016
Multiple Gauge	NN	99.87	869.09	0.13	1.12	0.001
	Ne	99.84	-1750.50	0.16	-2.76	0.03
	J	99.83	881.47	0.17	1.51	-0.02
	K	77.06	-0.43	22.94	0.13	0.003
	Total					0.019

Total short-range contribution: NN 51.92%, Ne 71.33%,
Direct Coulomb 61.89%, Exchange 99.81%

Numerical Integration $\int d^3 g F(g) = \sum_i w_i F(g_i)$

$$\eta(g_r) = \frac{4\pi}{(2\pi)^3} e^{-\frac{1}{4\alpha^2} g_r^2} - \frac{X_0 g_r^2}{(4\pi\gamma)^{3/2}} e^{-\frac{1}{4\gamma^2} g_r^2}$$

$$d^3 g = g_r^2 dg_r \sin(\phi)\, d\phi d\theta$$

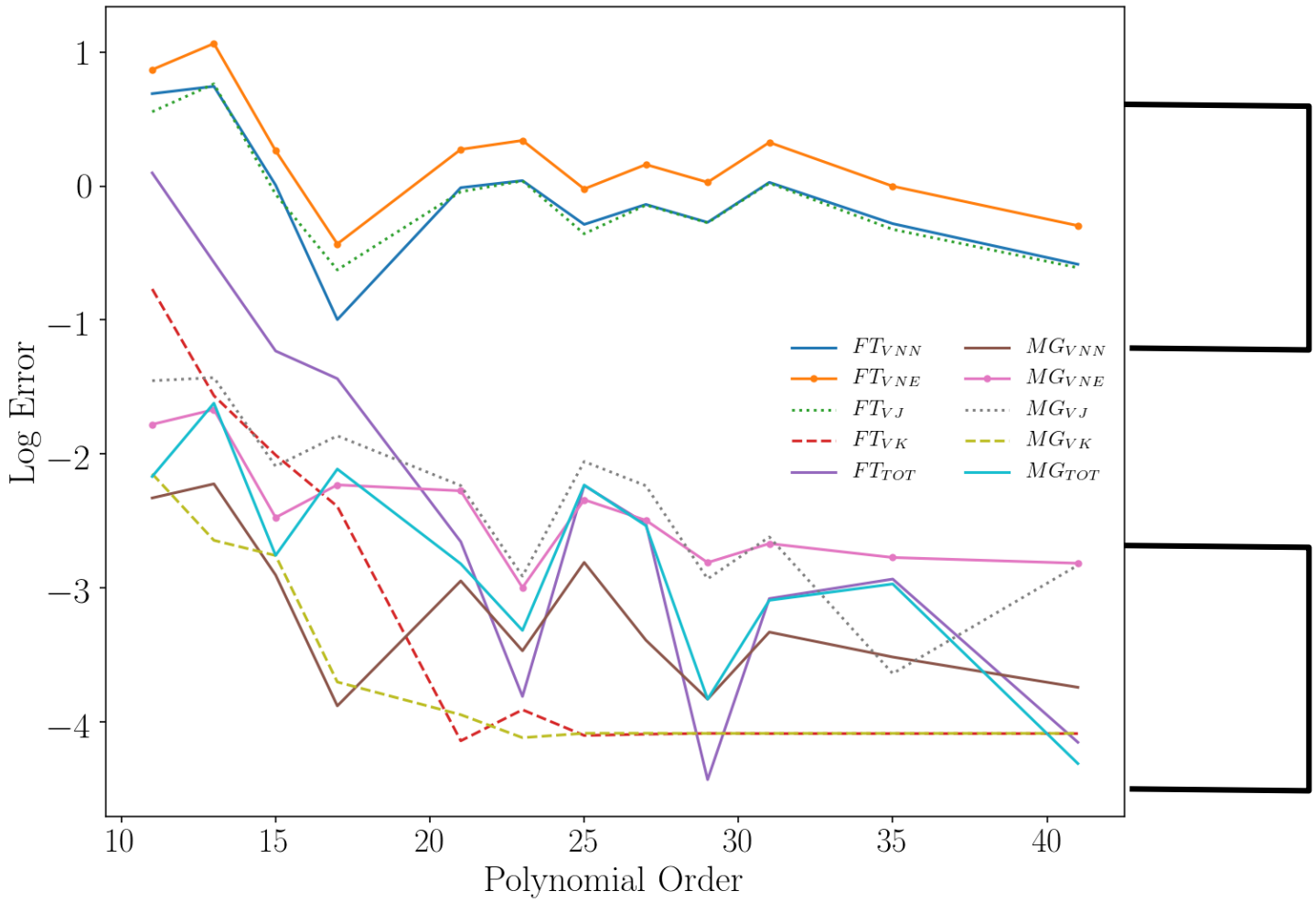


- Radial grids: Legendre, Chebyshev or Hermite
- Angular grids: Lebedev

Fixed grid (polynomial degree) **independent** of molecular size

Numerical Integration

- Two waters far apart (250A)



LR Fock Matrix Construction

$J_{\mu\nu} = \sum_g \bar{M}_{\mu\nu}(g) \sum_{\sigma\tau} \bar{M}_{\sigma\tau}(g)\, D_{\sigma\tau}$ + Analytical

$$K_{\mu\nu} = \sum_{g,\sigma\tau} \bar{M}_{\mu\tau}(g)\, D_{\sigma\tau} \bar{M}_{\sigma\nu}(-g) + \sum_i S_{\mu\tau}(Q_i) D_{\sigma\tau}\, X_{\sigma\nu}(Q_i) + \sum_i X_{\mu\tau}(Q_i)\, S_{\sigma\nu}(Q_i)\, D_{\sigma\tau}$$

$$- \sum_i S_{\mu\tau}(Q_i) D_{\sigma\tau}\, S_{\sigma\nu}(Q_i)\, V_{lr}(|Q_i - Q_j|)$$

Contract over the sparse terms first

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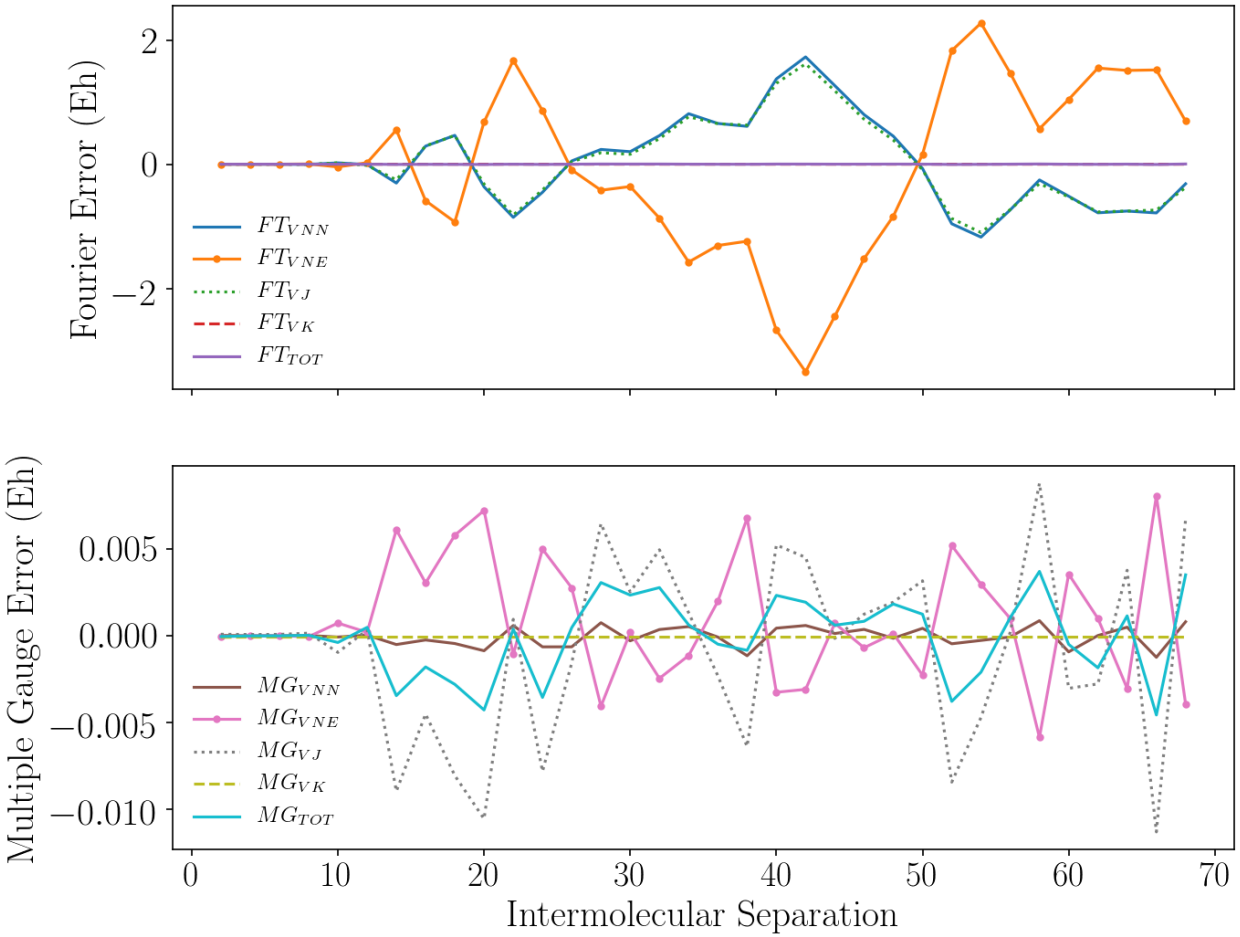
Results: Stretching a H_2O dimer



- Bare Fourier, has large errors on individual terms
- Multiple gauge approach reduces numerical error