

CCP9 flagship: Hybrid & range-separated (R-S) functionals

My focus is on one of the three development work packages:

WP2: Hybrid & R-S functionals

Two major goals:

1. Accelerate hybrid XC functionals
2. Add support for R-S XC functionals

Builds on ONETEP's existing Hartree-Fock exchange (HFX) implementation:

- ▶ Scales linearly with number of atoms, N
- ▶ *But* restricted to small systems ($N \sim 100$)

Current focus:

- ▶ Enable HFX to scale to 1000s cores
- ▶ Practical HFX for large N (ideally ~ 1000)

CCP9 flagship: Hybrid & range-separated (R-S) functionals

WP2 interacts with the other development work packages:

WP1: Embedding methods

Partition local orbitals into spatial regions:

- ▶ Different levels of theory in different regions
- ▶ Embed excited state in ground state environment
e.g. LR-TDDFT in ground state DFT

WP3: Excited state forces & geometries

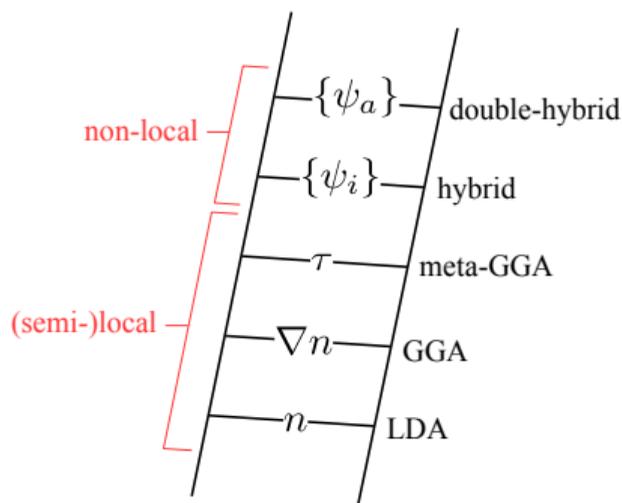
Forces in LR-TDDFT calculations:

- ▶ Geometry optimization and *ab initio* MD
- ▶ Longer timescale excited state behaviour
e.g. dissipation, reaction dynamics

Hybrid (and R-S) XC functionals must be compatible with other WPs, i.e.

- ▶ **WP1:** Support for spatially partitioned NGWF sets
- ▶ **WP3:** Evaluation of XC contribution in excited state

Why do we need hybrid functionals?



R-S hybrids partition Coulomb operator:

- ▶ Long-range correction (e.g. CAM-B3LYP)
- ▶ Screened-exchange (e.g. HSE)

Hybrids include Hartree-Fock exchange:

$$E_x^{\text{HF}}[n[\{\psi_i\}]] = - \sum_{i=1, j=1}^{N_{\text{occ}}} (\psi_i \psi_j | \psi_j \psi_i)$$

$$\int d\mathbf{r} d\mathbf{r}' \psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_j(\mathbf{r}) \psi_i(\mathbf{r}')$$

- ▶ Corrects self-interaction error in Coulomb term
- ▶ Can mix local and HF exchange contributions

$$\frac{1}{r} = \underbrace{\frac{\text{erfc}(\omega r)}{r}}_{\text{short range}} + \underbrace{\frac{\text{erf}(\omega r)}{r}}_{\text{long range}}$$

Hybrid functionals are (can be) more accurate!

Overview of linear-scaling Hartree-Fock exchange in ONETEP

HFX with SWRI

- ▶ ONETEP minimizes $E[\mathbf{K}, \{\varphi_\alpha\}]$
- ▶ HFX expressed in terms of \mathbf{K} and $\{\varphi_\alpha\}$
- ▶ HFX expanded via spherical wave (SW) resolution-of-the-identity (RI)

$$E_x^{\text{HF}} = -K^{\beta\alpha}(\varphi_\alpha\varphi_\delta|\varphi_\beta\varphi_\gamma)K^{\delta\gamma}$$
$$\stackrel{\text{SWRI}}{=} -K^{\beta\alpha}(\varphi_\alpha\varphi_\delta|f_p)V^{pq}(f_q|\varphi_\beta\varphi_\gamma)K^{\delta\gamma}$$

$$f_p(\mathbf{r}) = \begin{cases} j_{l_p}(q_p r)Z_{l_p m_p}(\hat{\mathbf{r}}) & r < a \\ 0 & r \geq a \end{cases}$$

Truncated SW basis

- ▶ Analytic Coulomb potentials
- ▶ Strictly localized (within $r < a$)
- ▶ Systematically improvable (like plane waves)

A two-electron integral engine with generalized Wannier functions

Challenges for linear-scaling Hartree-Fock exchange in ONETEP

$O(N)$ computational cost, with caveats

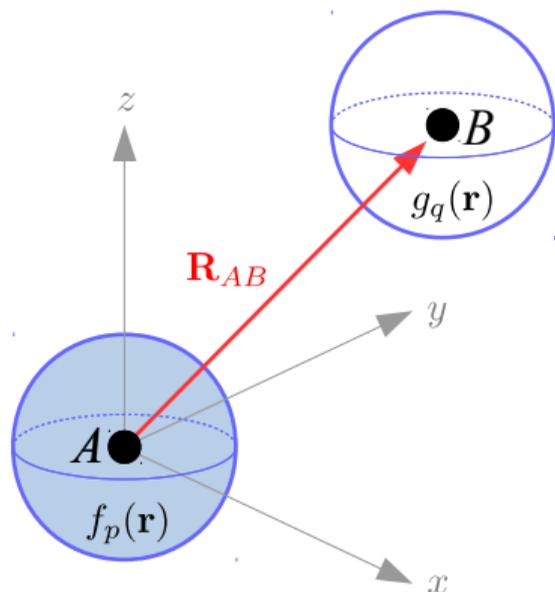
- ▶ Very high computational cost (CPU and memory)
- ▶ Restricted to $N \sim 100$ atoms (ONETEP capable of $N > 10000$)

Major issues to address

1. Non-optimal parallelization of overall scheme
2. Large prefactor and memory usage for evaluation of Coulomb metric (\mathbf{V})

My primary focus so far has been the development of new scheme for evaluating $\mathbf{V} \dots$

Existing Coulomb metric evaluation scheme (3Dc)



$$V_{Ap,Bq} = \int_V dx dy dz f_p(x_A, y_A, z_A) g_q(x_B, y_B, z_B)$$

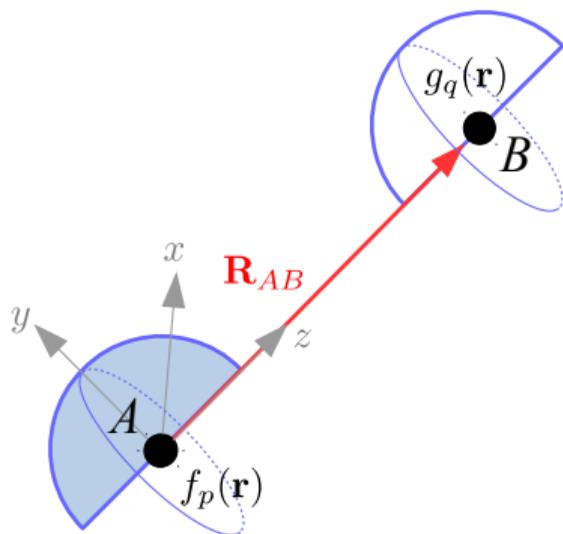
$$V_{Ap,Bq} = \int d\mathbf{r} f_p(\mathbf{r}_A) g_q(\mathbf{r}_B)$$

$$g_q(\mathbf{r}) = \int d\mathbf{r}' \frac{f_q(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Piecewise Chebyshev polynomial expansion of f_p and g_q in Cartesian coordinate system:

- ▶ Integrate expanded integrand analytically
- ▶ $N_i^3 N_o^3$ Chebyshev nodes per expansion
- ▶ $N_i = N_o = 12$ gives $\sim 3 \times 10^6$ coefficients
i.e. **22 MiB per SW expansion.**
- ▶ Burdensome with 100s of SWs per atom!

New Coulomb metric evaluation scheme (2Dn-1Da)



2-D numerical, 1-D analytic integration in a spherical polar coordinate system:

- ▶ Use SWs with RSHs with z aligned along \mathbf{R}_{AB}
- ▶ Separate into (r, θ) - & ϕ -dependent parts
- ▶ Integral over ϕ has simple analytic solution
- ▶ $N_i^2 N_o^2$ Chebyshev nodes per expansion
- ▶ $N_i = N_o = 12$ gives $\sim 2 \times 10^4$ coefficients
i.e. **160 KiB per SW expansion.**

A rotation is required:

- ▶ ONETEP's SWs are aligned with z in the original Cartesian coordinate system
- ▶ Use Wigner D-matrices to express 2Dn-1Da SWs in terms of ONETEP SWs (a rotation)

$$\int_0^\pi d\theta \int_0^a dr r^2 \sin(\theta) f_{1,p}(r, \theta) g_{1,q}(r_B, \theta_B) \left\{ \int_0^{2\pi} d\phi [f_{2,p} g_{2,q}](\phi) \right\}$$

Some preliminary results

Full V-matrix evaluation for a H₂ molecule with typical size SW basis. . .

(I cheated a bit! No rotations are needed in this case: H₂ is aligned along Cartesian z axis.)

Numerical comparison of schemes:

- ▶ Comparison of full metric matrix
- ▶ **OT**: ONETEP implementation
- ▶ **SM**: Sage Math prototype

	Norm of diff.	Max abs. diff.
3Dc (OT) vs 2Dn-1Da (OT)	1.93×10^{-04}	4.12×10^{-05}
3Dc (OT) vs 2Dn-1Da (SM)	1.93×10^{-04}	4.12×10^{-05}
2Dn-1Da (OT) vs 2Dn-1Da (SM)	3.31×10^{-06}	5.27×10^{-07}

“[O]btaining the elements of V to an accuracy of the sixth decimal [is] sufficient for stable calculations”

J. Dzielicz *et al*, J. Chem. Phys., **139**, 214103 (2013)

	Min time over 3 repetitions / s	
	Total	Off-site blocks
PBE (no V-matrix)	0.85	-
PBE0 (new scheme)	8.24	0.46
PBE0 (old scheme)	141.07	133.11

Performance comparison of schemes:

- ▶ **Total**: time for fixed NGWF calculation (inner loop optimization only)
- ▶ **Off-site blocks**: time spent evaluating evaluating V-matrix blocks with $A \neq B$