**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 $\sim 1000$)
CCP9 flagship: Hybrid & range-separated (R-S) functionals

WP2 interacts with the other development work packages:

<table>
<thead>
<tr>
<th>WP1: Embedding methods</th>
<th>WP3: Excited state forces &amp; geometries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partition local orbitals into spatial regions:</td>
<td>Forces in LR-TDDFT calculations:</td>
</tr>
<tr>
<td>▶ Different levels of theory in different regions</td>
<td>▶ Geometry optimization and <em>ab initio</em> MD</td>
</tr>
<tr>
<td>▶ Embed excited state in ground state environment e.g. LR-TDDFT in ground state DFT</td>
<td>▶ Longer timescale excited state behaviour e.g. dissipation, reaction dynamics</td>
</tr>
</tbody>
</table>

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?

Hybrids include Hartree-Fock exchange:

\[
E_{x}^{\text{HF}}[n[\{\psi_{i}\}]] = - \sum_{i=1,j=1}^{N_{\text{occ}}} (\psi_{i}\psi_{j}|\psi_{j}\psi_{i})
\]

\[
\int \text{d}r \text{d}r' \psi_{i}^{*}(r)\psi_{j}^{*}(r') \frac{1}{|r - r'|} \psi_{j}(r)\psi_{i}(r')
\]

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

R-S hybrids partition Coulomb operator:

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

Hybrid functionals are (can be) more accurate!
Overview of linear-scaling Hartree-Fock exchange in ONETEP

HFX with SWRI

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

\[
E_{x}^{\text{HF}} = -K^\beta_\alpha (\varphi_\alpha \varphi_\delta | \varphi_\beta \varphi_\gamma) K^\delta_\gamma
\]

\[
E_{x}^{\text{SWRI}} = -K^\beta_\alpha (\varphi_\alpha \varphi_\delta | f_p) V^{pq} (f_q | \varphi_\beta \varphi_\gamma) K^\delta_\gamma
\]

Truncated SW basis

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

\[
f_p(r) = \begin{cases} 
  j_{l_p}(q_pr)Z_{l_p m_p}(\hat{r}) & r < a \\
  0 & r \geq a
\end{cases}
\]
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 ($V$)

My primary focus so far has been the development of new scheme for evaluating $V$...
Existing Coulomb metric evaluation scheme (3Dc)

\[ V_{A_p,B_q} = \int d\mathbf{r} f_p(\mathbf{r}_A)g_q(\mathbf{r}_B) \]

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

**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. \( 22 \text{ MiB per SW expansion} \).
- 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 \((r, \theta)\)- & \(\phi\)-dependent parts
- Integral over \(\phi\) has simple analytic solution
- \(N_i^2N_o^2\) 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)
Some preliminary results

Full V-matrix evaluation for a $\text{H}_2$ molecule with typical size SW basis. . .

(I cheated a bit! No rotations are needed in this case: $\text{H}_2$ is aligned along Cartesian $z$ axis.)

Numerical comparison of schemes:

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

<table>
<thead>
<tr>
<th></th>
<th>Min time over 3 repetitions / s</th>
<th>Norm of diff.</th>
<th>Max abs. diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE (no V-matrix)</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE0 (new scheme)</td>
<td>8.24</td>
<td>$1.93 \times 10^{-04}$</td>
<td>$4.12 \times 10^{-05}$</td>
</tr>
<tr>
<td>PBE0 (old scheme)</td>
<td>141.07</td>
<td>$3.31 \times 10^{-06}$</td>
<td>$5.27 \times 10^{-07}$</td>
</tr>
</tbody>
</table>

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


Performance comparison of schemes:

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