Most quantum chemistry methods rely on expanding the electronic wavefunction or density in a basis of Gaussian functions. The quality of results thus depends strongly on the quality of the basis. Ideally, an arbitrarily large, near-complete set of functions would be used, but this is unfeasible. As such, robust optimisation methods are essential to select the best possible basis of a given size:

\[
\partial_\alpha E_{\text{HF}} \sim \text{Tr} \{ \partial_\alpha (H + F) + P \} - \partial_\alpha S \ast W \}
\]

Analytical derivatives of the Hartree-Fock (HF) and post-HF methods with respect to the exponent, \(\alpha\), require derivatives of the associated integrals:

\[
\partial_\alpha \phi \equiv -r^2 \phi
\]

These can be related to the already available derivatives with respect to nuclear coordinates:

\[
\nabla^2 \phi = \{4\alpha r^2 - 2\alpha(2\alpha + 3)\} \phi + K \phi_{l-2}
\]

Formulating in terms of existing quantities allows for very efficient evaluation of the derivatives for HF and second-order perturbation theory (MP2). The same information can be used to calculate both the nuclear and exponent Hessians, allowing for a true Newton-step optimisation.

For the helium trimer (marked by crosses), the best place to put the midbond functions is not obvious. The minimum is not in the centre of the bonds, but shifted towards the midpoint of the trimer. Both position and exponent need to be optimised.

Including functions in the centre of noncovalent interactions greatly improves their description. For the noble gas diatomics below, AVDZ plus a 2s2p set of midbond functions gives interaction energies closer to experiment than AVSZ. The previous sections show that this is a difficult problem, and the analytic method provides a robust way to systematically optimise these.