Integrals over effective core potentials

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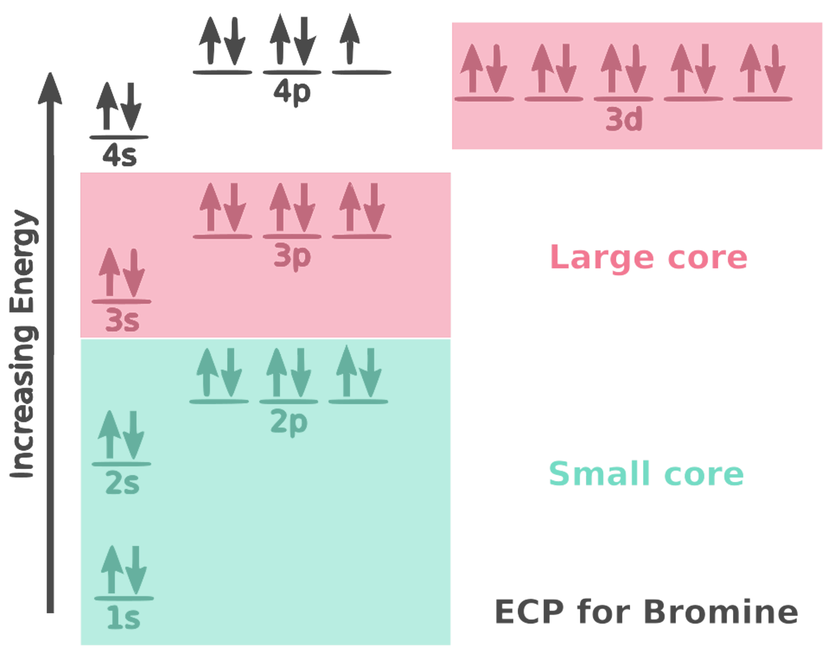
The innermost electrons in atoms are not strongly perturbed by the electrons on nearby atoms. They can therefore be approximated well by a fixed potential, called an effective core potential (ECP).

Depending on the number of electrons frozen, this can greatly increase the efficiency of quantum chemical calculations without significant loss in accuracy.[1] In fact, ECPs can be made to include relativistic effects. As these can be very important, especially for heavy atoms, they may even improve results. [2]



ECP for Bromine

The only cost is extra 3-centre integrals. The ECPs are fitted using gaussians and spherical-harmonics:

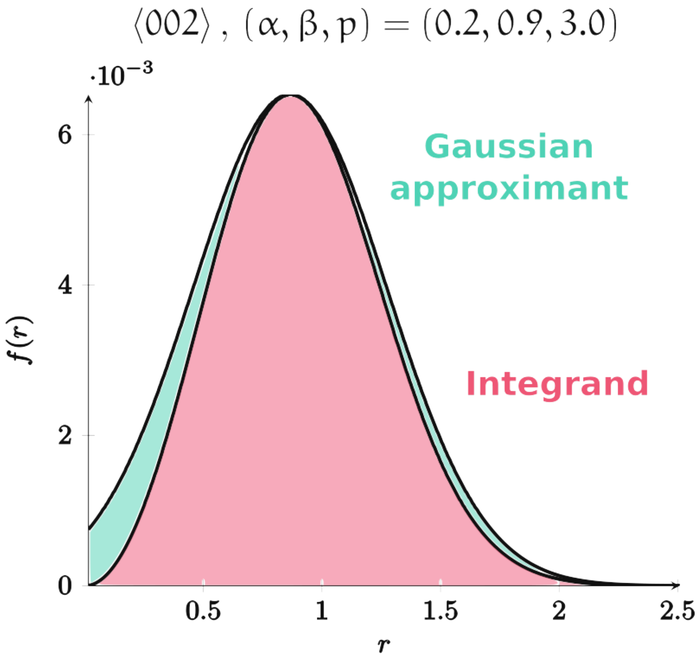
$$U(\mathbf{r}) = U_L(r) + \sum_{\lambda=0}^{L-1} \sum_{\mu=-\lambda}^{\lambda} |S_{\lambda\mu}\rangle\, U_\lambda(r)\, \langle S_{\lambda\mu}|$$

$$U_\lambda(r) = \sum_k d_{k\lambda} r^{n_{k\lambda}} \exp(-\zeta_{k\lambda} r^2)$$

This leads to difficult radial integrals over Bessel functions, usually evaluated by quadrature or a series expansion.[3, 4]

$$Q_{ijk}^{\alpha\beta p} = \langle ijk \rangle = \int_0^\infty dr\; r^k e^{-pr^2} M_i(2\alpha r) M_j(2\beta r)$$

We present a novel, efficient method for prescreening and computing these integrals.

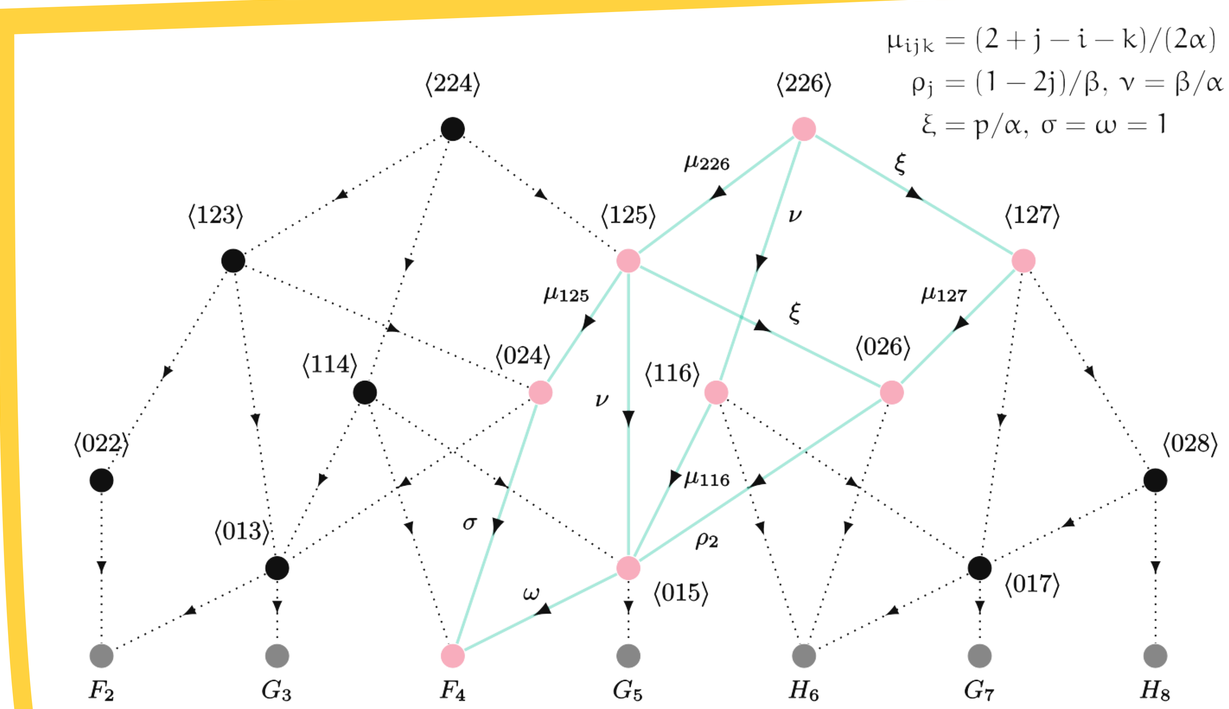


1.

The integrand will disappear for most combinations of the parameters, allowing many integrals to be avoided.

We have shown that it is rigorously enveloped by a spherical gaussian with exponent p, whose centre, r_0, is found by solving the equation below. In fact, it is accurate enough to be used to evaluate integrals below a given threshold.

$$2pr_0^2 = k - 2 + \left[\frac{1}{2\alpha} + \frac{1}{2\beta} + \frac{M_{i-1}(\alpha r_0)}{M_i(\alpha r_0)} + \frac{M_{j-1}(\beta r_0)}{M_j(\beta r_0)}\right] r_0$$



2.

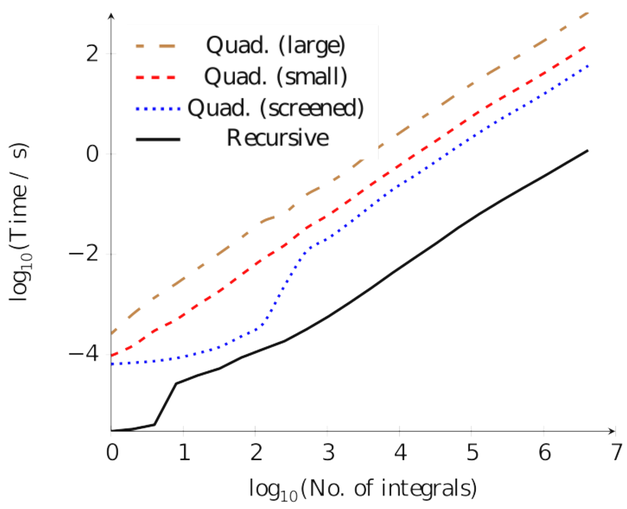
The integrals can be reduced to recursion on three soluble base integrals. This can then be unrolled *a priori* by a combinatorial search over a network.

$$F_N = \int_0^\infty dr\; r^{N-2} e^{-pr^2} \sinh(2\alpha r) \sinh(2\beta r)$$

$$G_N = \int_0^\infty dr\; r^{N-2} e^{-pr^2} \sinh(2\alpha r) \cosh(2\beta r)$$

$$H_N = \int_0^\infty dr\; r^{N-2} e^{-pr^2} \cosh(2\alpha r) \cosh(2\beta r)$$

1. Prescreening
2. Recursion
3. Code generation
4. Calculation



Calculations are about 40 times faster than conventional algorithms. Both the prefactor and exponent of the scaling with system size are reduced.

3.

This can then be used in combination with an algebraic simplifier, leaving a minimal number of arithmetic operations on known quantities. Optimised code can then be generated for all integrals up to a given total angular momentum.

For example, from the network above, we get the algebraic expression

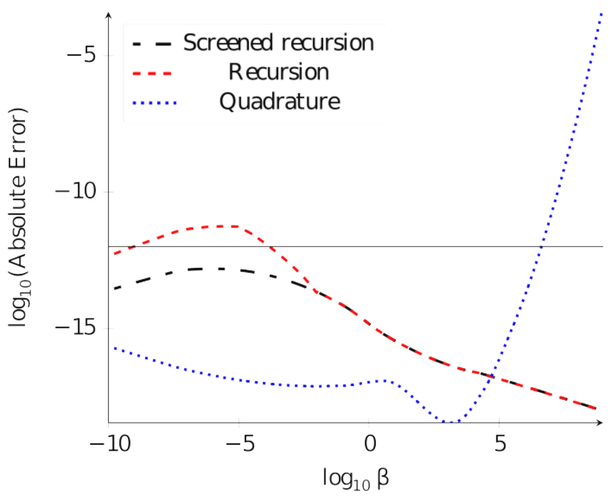
$$\langle 125 \rangle = [\mu\rho\omega] H_2 + [\mu\rho\nu] G_3 + \{[\mu\sigma] + [\nu\omega] + [\zeta\rho\omega]\} H_4 + \{[\nu\upsilon] + [\zeta\rho\upsilon]\} G_5 + [\xi\sigma] H_6$$

which simplifies to give the following:

```
double F125(double p, double alpha, double beta) {
        double *values = compute_base_integrals(2, 6, p, alpha, beta);
        double oalpha = 1.0 / alpha;
        double o2beta = 0.5 / beta;
        double value = 3.0 * o2beta * ( values[1] - o2beta * values[0]);
        value += (3.0 * p * o2beta * o2beta - 0.5) * values[2];
        value -= (beta + 3.0 * p * o2beta) * values[3];
        value += p * values[4];
        return oalpha * value;
}
```

4.

The resulting algorithm is numerically stable across all arguments, due to the tightness of the prescreening bound. Importantly, a single approach is used for all arguments.



References

[1] L. R. Kahn and W. A. Goddard, J. Chem. Phys. 56 (1972), 2685
[2] P. Pyykkö, Chem. Rev. 112 (2012), 371
[3] L. R. McMurchie and E. R. Davidson, J. Comput. Phys. 44 (1981), 289
[4] R. Flores-Moreno et al., J. Comput. Chem. 27 (2006), 1009

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