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# Supplementary Material: Prescreening and efficiency in the evaluation of integrals over effective core potentials

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## PROOF OF UNIMODALITY OF THE INTEGRAND

Start by considering equation 17. Firstly, as $N \geq 2$ in all cases, $f(r) \sim r^N$ as $r \to 0$. Secondly, the enveloped Bessel functions are such that $0 \leq K_n(z) \leq 1$, such that $f(r) \sim \exp(-pr^2)$ as $r \to \infty$, with the exponential term dominating the power of $r$. Here we have defined $p = \eta + \alpha + \beta$, i.e. the 'total' exponent, a measure of the width of the distribution. In addition, we note that $K_n(0) = \delta_{n0}$, and that $K_n$ is unimodal. Therefore, as $r \in [0, \infty)$, $f(r) \geq 0$ for all possible $r$, and $f(r) \to 0$ as $r$ tends to zero or infinity. Moreover, the integrand contains no singularities, and thus is continuous and bounded on its entire domain. The extreme value theorem then implies that it has at least one maximum.

Differentiating equation 17 gives

$$\begin{aligned}\frac{f'(r;\rho,\kappa,N)}{f(r;\rho,\kappa,N)} =& \frac{N}{r} - 2pr + k_A + k_B \\ &+ k_A\frac{K'_\rho(k_A r)}{K_\rho(k_A r)} + k_B\frac{K'_\kappa(k_B r)}{K_\kappa(k_B r)}\end{aligned} \tag{S.1}$$

Given $f(r) > 0$ except at the boundaries, finding an extremum, $r_0$, is thus equivalent to determining when the right hand side above is zero. This can be reworked into the following transcendental equation:

$$2pr_0^2 = N + [k_A + k_B + k_A J_\rho(k_A r_0) + k_B J_\kappa(k_B r_0)]\, r_0 \tag{S.2}$$

where we have defined the ratio function $J_n(z) = K'_n(z)/K_n(z)$. We note that the exponentials implicit in the $K_n$ necessarily cancel out, such that $J_n(z) = M'_n(z)/M_n(z)$. Inserting equation 18 into equation 19 so as to eliminate $M_{n+1}$ then yields

$$M'_n(z) = M_{n-1}(z) - \frac{n+1}{z}M_n(z) \tag{S.3}$$

such that equation **??** can be transformed into the more useful form given in equation 20. We can then use the fact that $M_n(z)$ is monotonically increasing for all $n$, and $M_{n-1}(z) \geq M_n(z)$, such that their ratio is also monotonically increasing. The monotonicity of the left and right sides of equation 20 thus implies there can be at most one point at which they cross, i.e. at most one maximum of $f(r)$. This combined with the earlier determination that there is at least one maximum means that the integrand is necessarily unimodal. We denote this mode as $P$.

## DERIVATION OF BASE INTEGRALS

We first consider the integrals $F_N$, $G_N$, and $H_N$. Using the standard addition rules for the hyperbolic functions, all three integrals can be written in terms of the following:

$$\mathcal{I}_N^{\pm} = \int_0^{\infty} dr\ r^{N-2} \left\{ e^{-pr^2+2pPr} \pm e^{-pr^2-2pPr} \right\} \tag{S.4}$$

which upon completing the square and making the substitution $z_{\pm} = (r \pm P)$, becomes

$$\begin{aligned} e^{-pP^2} \mathcal{I}_N^{\pm} = &\int_{-P}^{\infty} dz\ (z+P)^{N-2} e^{-pz^2} \\ &\pm \int_{P}^{\infty} dZ\ (z-P)^{N-2} e^{-pz^2} \end{aligned} \tag{S.5}$$

Assuming that $N \geq 2$, the binomial expansion can be applied which then gives equation **??**:

$$\begin{aligned} \mathcal{I}_N^{\pm} = &\, e^{pP^2} \sum_{m=0}^{N-2} \binom{N-2}{m} P^m \\ &\times \left[ \int_{-P}^{\infty} \pm (-1)^m \int_{P}^{\infty} \right] z^{N-2-m} e^{-pz^2}\ dz \end{aligned} \tag{S.6}$$

At this point, it is prudent to split the term in brackets into integrals over $[0, \infty)$ and $[0, P]$, taking care to consider the parity of the integrand. This results in equation **??**:

$$\begin{aligned} \mathcal{I}_N^{\pm} = &\, \frac{1}{2} e^{pP^2} \sum_{m} \binom{N-2}{m} P^m p^{N_m/2} \\ &\times \left\{ r_m^{\pm} \Gamma\left(\frac{N_m}{2}\right) + s_{m,N}^{\pm} \gamma\left(\frac{N_m}{2}, \sqrt{p}P\right) \right\} \end{aligned} \tag{S.7}$$

where $\gamma(n, z)$ is the lower incomplete gamma function, $N_m = N - m - 1$, $r_m = 1 \pm (-1)^m$, and $s_{m,N}^{\pm} = (-1)^{N-m} \mp (-1)^m$. There are then eight possible cases, depending on the parities of both $N$ and $m$ and whether we are considering $\mathcal{I}^+$ or $\mathcal{I}^-$, determining if $r_m$ and $s_{m,N}$ are zero or two. For even $N$ in $\mathcal{I}_N^+$, all terms with odd $m$ are zero, while the incomplete gamma function also disappears for even $m$. This then leads to equation 34. The same happens for odd $N$ and $\mathcal{I}_N^-$, but with only odd $m$ terms being nonzero, leading to equation 35. For odd (even) $N$ in $\mathcal{I}_N^+$ ($\mathcal{I}_N^-$), the result is separate sums over odd and even $m$, as follows:

$$\begin{aligned} e^{-pP^2} \mathcal{I}_{2n+1}^{+} = &\sum_{m=0}^{n-1} \binom{2n-1}{2m} P^{2m} p^{n-m} \Gamma(n-m, \sqrt{p}P) \\ + &\sum_{m=0}^{n-1} \binom{2n-1}{2m+1} P^{2m+1} p^{-n_m} \gamma(n_m, \sqrt{p}P) \end{aligned} \tag{S.8}$$

where $\Gamma(n,z)$ is the upper incomplete gamma function, $n_m = n - m - 1/2$, and $\mathcal{I}^-_{2n+1}$ is the same as above, but with the upper and lower gamma functions swapped. The relevant odd and even, respectively, equivalents of equations 34 and 35 are thus given by:

$$I^{\pm}_{2n+1} = \frac{1}{4}\left\{\mathcal{I}^+_{2n+1}(p,P_+) \pm \mathcal{I}^+_{2n+1}(p,P_-)\right\}$$
$$G^B_{2n} = \frac{1}{4}\left\{\mathcal{I}^-_{2n}(p,P_+) - \mathcal{I}^-_{2n}(p,P_-)\right\}$$

We reiterate that $F_N = I^-_N$ and $H_N = I^+_N$, and $G^A_N$ can be found by simply exchanging $k_A$ and $k_B$.

As was noted earlier, the limitation for $N \geq 2$ is not sufficient, but this can be overcome via the relations in equations 37 – 39, with the exception of $N = 1$. To evaluate these, we note that the integrals in equation **??** can be rewritten, by substituting $z$ for $-z$ in the second term in the brackets, so as to get

$$\mathcal{I}^-_1 = e^{pP^2}\text{P. V.}\int_{-\infty}^{\infty} dz\ \frac{e^{-pz^2}}{z+P} \tag{S.9}$$

where we have taken the principal value integral. Writing $x = \sqrt{p}P$ and substituting $y = \sqrt{p}z$, this becomes

$$\mathcal{I}^-_1 = e^{x^2}\text{P. V.}\int_{-\infty}^{\infty} dy\ \frac{e^{-y^2}}{y+x} \tag{S.10}$$

This is simply the Hilbert transform of a Gaussian, and can be related to the Dawson function as $\mathcal{I}^-_1 = 2\sqrt{\pi}e^{x^2}D(x)$. This results in equation 40 for $G^B_1$. The case of $\mathcal{I}^+_1$ is similarly treated as

$$\mathcal{I}^+_1 = e^{x^2}\text{P. V.}\left\{\int_{-x}^{\infty} dy\ \frac{e^{-y^2}}{y+x} - \int_{-\infty}^{-x} dy\ \frac{e^{-y^2}}{y+x}\right\} \tag{S.11}$$

Using the Fourier representation of $1/(x+y)$ (treated here as a distribution), we get equation **??**:

$$\int_{-x}^{\infty} dy\ \frac{e^{-y^2}}{y+x} = \text{Im}\left\{\int_0^{\infty} dk\ \ \exp[-k^2/4 + ikx]\int_{-x}^{\infty} dy\ \ \exp[-(y-ik/2)^2]\right\} \tag{S.12}$$

The second integrand is an entire function, and thus we can translate the integral to the real axis, which then integrates to give $\sqrt{\pi}[1 + \text{erf}(-x - ik/2)]/2$. Completing the square and again translating to the real axis on the remaining integral then gives

$$\begin{aligned}&\sqrt{\pi}e^{-x^2}\text{Im}\int_{-x}^{\infty}du\ e^{-u^2}\left[1+\text{erf}(iu)\right]\\ =&\sqrt{\pi}e^{-x^2}\int_{-x}^{\infty}du\ e^{u^2}\text{erf}(u)\end{aligned}\tag{S.13}$$

Exactly the same process can be used to treat the second term in $\mathcal{I}_1^+$, such that the final integral becomes $\mathcal{I}_1^+ = 2\sqrt{\pi}e^{x^2}Dr(x)$, where $Dr(x)$ is the hybrid Dawson error function. The base integral is thus given by

$$I_1^{\pm} = \frac{\sqrt{\pi}}{2}\left\{e^{pP_+^2}Dr(\sqrt{p}P_+) \pm e^{pP_-^2}Dr(\sqrt{p}P_-)\right\}\tag{S.14}$$

with $F_1 = I_1^-$ and $H_1 = I_1^+$.

## SPECIAL CASES OF THE INTEGRALS

Equations 28, 29, and 33 all involve factors of $1/A$ or $1/B$. In any typical chemical system, $A$ and $B$ will be sufficiently greater than zero for this not to cause numerical issues. It does, however, become a problem for the small subset of integrals where one or both of the basis functions is located on the same center as the ECP. The overall integral in equation 11 for these cases becomes simpler, such that it is worthwhile treating them separately. Direct integration in the case where $A = B = 0$ results in the following:

$$\begin{aligned}\chi_{ab}^{\lambda\mu}(A=B=0) = {}& 2\pi\Omega_{00,\lambda\mu}^{a_xa_ya_z}\Omega_{00,\lambda\mu}^{b_xb_yb_z}\\ &\times\sum_{ijk}d_{ia}d_{jb}d_{k\lambda}\Gamma\left(\frac{N_{abk}}{2}\right)p_{ijk}^{-N_{abk}/2}\end{aligned}\tag{S.15}$$

where $N_{abk} = 3+a+b+n_{k\lambda}$. This eliminates any potential numerical issues while also being trivial to compute.

In the second instance, where $A = 0$ but $B \neq 0$ (the reverse case is the same with the relevant parameters exchanged), we have

$$\begin{aligned}\chi_{ab}^{\lambda\mu}(A=0) = {}& 8\pi^{3/2}\Omega_{00,\lambda\mu}^{a_xa_ya_z}\\ &\times\sum_{pqr}D_{pqr}^{B}\sum_{\kappa\tau}S_{\kappa\tau}^{B}\Omega_{\kappa\tau,\lambda\mu}^{pqr}\mathcal{T}_{0\kappa\lambda}^{2+a+b_{pqr}+n_{k\lambda}}\end{aligned}\tag{S.16}$$

The remaining radial term then involves a special case of equation 13:

$$\mathcal{Q}_{0\kappa\lambda}^{N}(A=0) = \int_0^{\infty}dr\ r^N e^{-pr^2}M_\kappa(k_Br)\tag{S.17}$$

It is then possible to use the recurrence relation in equation 29, noting that this only includes a term in $1/B$, with no dependence on $A$. However, the base integrals that will be arrived at in this way will not be the same, and instead will be the following analogous ones:

$$F_N^0 = \int_0^\infty dr\ r^{N-1} e^{-pr^2} \sinh(k_B r) \tag{S.18}$$

$$G_N^0 = \int_0^\infty dr\ r^{N-1} e^{-pr^2} \cosh(k_B r) \tag{S.19}$$

These can be evaluated in much the same way as equations 30 – 32, and so are not considered here in any more detail.

## ADDITIONAL RESULTS

TABLE I. CCSD(T)/aVDZ-PP energies for small, closed-shell silver clusters, with absolute errors, $\Delta/\mathrm{E}_h$,[a] for energies calculated using the screened recursion and quadrature schemes for the ECP integrals. In addition, total ECP integration times relative to $Ag_2$ in the recursive scheme (0.07 seconds) are shown.

| **Cluster** | **Energy** | $\boldsymbol{\Delta}_{\mathrm{recur.}}$ | $\boldsymbol{\Delta}_{\mathrm{quad.}}$ | $\mathbf{t}_{\mathrm{recur.}}$ | $\mathbf{t}_{\mathrm{quad.}}$ |
|---|---|---|---|---|---|
| $Ag_2$ | −292.80912 | 0 | 0 | 1.0 | 29.6 |
| $Ag_3{}^+$ | −439.01167 | 0 | 0 | 3.64 | 132.1 |
| $Ag_3{}^-$ | −439.29308 | 0 | 0 | 3.64 | 114.5 |
| $Ag_4$ | −585.66013 | 0 | 0 | 14.29 | 613.7 |
| $Ag_5{}^+$ | −731.88243 | 0 | 0 | 16.11 | 707.9 |
| $Ag_5{}^-$ | −732.16323 | 0 | 0 | 15.8 | 651.4 |
| $Ag_6$ | −878.55067 | 0 | 0 | 25.9 | 1100.3 |

[a] These were zero to within the convergence threshold of $10^{-7}$.