Supporting Info: Radial overlap integrals

Radial STO

Double-zeta STOs

In[ ]:= $s[n\_, z\_] := (2 z)^{n} \sqrt{\frac{2 z}{(2 n)!}}\, r^{n-1}\, e^{-z*r}$

Spherical Bessel Functions

In[ ]:= $j_0 = \frac{\mathrm{Sin}[k*r]}{k*r}; \; j_1 = \frac{\mathrm{Sin}[k*r]}{(k*r)^2} - \frac{\mathrm{Cos}[k*r]}{k*r};$

$j_2 = \left(\frac{3}{(k*r)^2} - 1\right) \frac{\mathrm{Sin}[k\, r]}{k*r} - 3\, \frac{\mathrm{Cos}[k*r]}{(k*r)^2};$

Integral for the radial overlaps

s orbitals from n = 1 to n = 7

In[ ]:= $\int_0^\infty s[1, z] * j_0 * r^2 \, dr$

Out[ ]= $\frac{4 z^{5/2}}{(k^2 + z^2)^2}$ if Abs[Im[k]] < Re[z]

In[ ]:= $\int_0^\infty s[2, z] * j_0 * r^2 \, dr$

Out[ ]= $-\frac{4 z^{5/2} (k^2 - 3 z^2)}{\sqrt{3} (k^2 + z^2)^3}$ if Abs[Im[k]] < Re[z]

In[ ]:= $\int_0^\infty s[3, z] * j_0 * r^2 \, dr$

Out[ ]= $\frac{16 \sqrt{\frac{2}{5}} z^{9/2} (-k^2 + z^2)}{(k^2 + z^2)^4}$ if Abs[Im[k]] < Re[z]

In[ ]:= $\int_0^\infty s[4, z] * j_0 * r^2 \, dr$

Out[ ]= $\frac{16 z^{9/2} (k^4 - 10 k^2 z^2 + 5 z^4)}{\sqrt{35} (k^2 + z^2)^5}$ if Abs[Im[k]] < Re[z]

In[ ]:= $$\int_0^\infty s[5, z] * j_0 * r^2 \, dr$$

Out[ ]= $$\frac{32 \sqrt{\frac{2}{7}}\, z^{13/2} \left(3 k^4 - 10 k^2 z^2 + 3 z^4\right)}{3 \left(k^2 + z^2\right)^6} \text{ if } \mathrm{Abs}[\mathrm{Im}[k]] < \mathrm{Re}[z]$$

In[ ]:= $$\int_0^\infty s[6, z] * j_0 * r^2 \, dr$$

Out[ ]= $$-\frac{32 \sqrt{\frac{2}{231}}\, z^{13/2} \left(k^6 - 21 k^4 z^2 + 35 k^2 z^4 - 7 z^6\right)}{\left(k^2 + z^2\right)^7} \text{ if } \mathrm{Abs}[\mathrm{Im}[k]] < \mathrm{Re}[z]$$

In[ ]:= $$\int_0^\infty s[7, z] * j_0 * r^2 \, dr$$

Out[ ]= $$-\frac{512\, z^{17/2} \left(k^6 - 7 k^4 z^2 + 7 k^2 z^4 - z^6\right)}{\sqrt{429} \left(k^2 + z^2\right)^8} \text{ if } \mathrm{Abs}[\mathrm{Im}[k]] < \mathrm{Re}[z]$$

p orbitals from n = 2 to n = 6

In[ ]:= $$\int_0^\infty s[2, z] * j_1 * r^2 \, dr$$

Out[ ]= $$\frac{16\, k\, z^{7/2}}{\sqrt{3} \left(k^2 + z^2\right)^3} \text{ if } \mathrm{Abs}[\mathrm{Im}[k]] < \mathrm{Re}[z]$$

In[ ]:= $\int_0^\infty s[3, z] * j_1 * r^2 \, dr$

Out[ ]= $-\frac{16 \sqrt{\frac{2}{5}} k z^{7/2} (k^2 - 5 z^2)}{3 (k^2 + z^2)^4}$ if Abs[Im[k]] < Re[z]

In[ ]:= $\int_0^\infty s[4, z] * j_1 * r^2 \, dr$

Out[ ]= $\frac{32 k z^{11/2} (-3 k^2 + 5 z^2)}{\sqrt{35} (k^2 + z^2)^5}$ if Abs[Im[k]] < Re[z]

In[ ]:= $\int_0^\infty s[5, z] * j_1 * r^2 \, dr$

Out[ ]= $\frac{32 \sqrt{\frac{2}{7}} k z^{11/2} (3 k^4 - 42 k^2 z^2 + 35 z^4)}{15 (k^2 + z^2)^6}$ if Abs[Im[k]] < Re[z]

In[ ]:= $\int_0^\infty s[6, z] * j_1 * r^2 \, dr$

Out[ ]= $\frac{256 \sqrt{\frac{2}{231}} k z^{15/2} (3 k^4 - 14 k^2 z^2 + 7 z^4)}{3 (k^2 + z^2)^7}$ if Abs[Im[k]] < Re[z]

Normalization constant for double-zeta *d* orbitals

Derivation of the normalization constant for double-zeta STOs for d-orbitals:

$$N = \frac{1}{\sqrt{c_1{}^2 + c_2{}^2 + 2 c_1 c_2 S_{AB}}}$$

where ψ is a single-zeta STO and

$$S_{AB} = \int_0^\infty \psi_A * \psi_B \, r^2 \, dr$$

Solving for S_{AB},

$$S_{AB} = \int_0^\infty \left((2\,z_1)^n \sqrt{\frac{2\,z_1}{(2\,n)!}}\; r^{n-1}\, e^{-z_1\,r}\right) * \left((2\,z_2)^n \sqrt{\frac{2\,z_2}{(2\,n)!}}\; r^{n-1}\, e^{-z_2\,r}\right) * r^2 \, dr$$

$$S_{AB} = \left((2\,z_1)^n \sqrt{\frac{2\,z_1}{(2\,n)!}}\;(2\,z_2)^n \sqrt{\frac{2\,z_2}{(2\,n)!}}\right) * \int_0^\infty \left(r^{2\,n}\, e^{-z_1 - z_2\,r}\right) dr$$

$$S_{AB} = \left(\frac{(4\,z_1\,z_2)^{n+1/2}}{(2\,n)!}\right) * \int_0^\infty \left(r^{2\,n}\, e^{-z_1 - z_2\,r}\right) dr$$

$$S_{AB} = \left(\frac{(4\,z_1\,z_2)^{n+1/2}}{(2\,n)!}\right) * (z_1 + z_2)^{-(2\,n+1)} * \Gamma(1+2\,n)$$

$$S_{AB} = \left(\frac{(4\,z_1\,z_2)^{n+1/2}}{(2\,n)!}\right) * (z_1 + z_2)^{-2\,(n+1/2)} * (2\,n)!$$

$$S_{AB} = \left(\frac{4\,z_1\,z_2}{(z_1+z_2)^2}\right)^{n+1/2}$$

This is confirmed through evaluation with Mathematica.

In[∘]:=
$$\int_0^\infty (s[n, z_1] * s[n, z_2]) * r^2 \, dr$$

Out[∘]=
$$2^{1+2\,n}\,\text{Gamma}[1+2\,n]\; z_1^n \sqrt{\frac{z_1}{(2\,n)\,!}}\; z_2^n \sqrt{\frac{z_2}{(2\,n)\,!}}\; (z_1+z_2)^{-1-2\,n} \quad \text{if } \text{Re}[n] > -\frac{1}{2} \,\&\&\, \text{Re}[z_1+z_2] > 0$$

Convert the Gamma function to a factorial.

https://en.wikipedia.org/wiki/Gamma_function

Γ(n) = (n-1)!

In[ ]:= PowerExpand$\left[2^{1+2n}\,((1+2n)-1)!\,z_1^n\sqrt{\frac{z_1}{(2n)!}}\,z_2^n\sqrt{\frac{z_2}{(2n)!}}\,(z_1+z_2)^{-1-2n}\right]$

Out[ ]= $2^{1+2n}\,z_1^{\frac{1}{2}+n}\,z_2^{\frac{1}{2}+n}\,(z_1+z_2)^{-1-2n}$

Which is equivalent to the solution above.

In[ ]:= FullSimplify$\left[2^{1+2n}\,z_1^{\frac{1}{2}+n}\,z_2^{\frac{1}{2}+n}\,(z_1+z_2)^{-1-2n} == \left(\frac{4\,z_1\,z_2}{(z_1+z_2)^2}\right)^{n+1/2}\right]$

Out[ ]= $2^{1+2n}\left(-\left(\frac{z_1\,z_2}{(z_1+z_2)^2}\right)^{\frac{1}{2}+n}+z_1^{\frac{1}{2}+n}\,z_2^{\frac{1}{2}+n}\,(z_1+z_2)^{-1-2n}\right) == 0$

Evaluation of both expressions with Sc *d* orbitals.

In[ ]:= $2^{1+2n}\,z_1^{\frac{1}{2}+n}\,z_2^{\frac{1}{2}+n}\,(z_1+z_2)^{-1-2n}$ /. $\{z_1 \to 0.440416,\ z_2 \to 1.518473,\ n \to 3\}$

Out[ ]= 0.28287

In[ ]:= $\left(\frac{4\,z_1\,z_2}{(z_1+z_2)^2}\right)^{n+1/2}$ /. $\{z_1 \to 0.440416,\ z_2 \to 1.518473,\ n \to 3\}$

Out[ ]= 0.28287

d orbitals from n = 3 to n = 5 (without normalization constant)

In[ ]:= $\int_0^\infty (c_1 * s[3, z_1] + c_2 * s[3, z_2]) * j_2 * r^2 \, dr$

Out[ ]= $$\frac{32\sqrt{\frac{2}{5}}\,k^2\left(c_2\left(k^2+z_1^2\right)^4 z_2^{9/2}+c_1 z_1^{9/2}\left(k^2+z_2^2\right)^4\right)}{\left(k^2+z_1^2\right)^4\left(k^2+z_2^2\right)^4}$$ if Abs[Im[k]] < Re[z_1] && Abs[Im[k]] < Re[z_2]

In[ ]:= $\int_0^\infty (c_1 * s[4, z_1] + c_2 * s[4, z_2]) * j_2 * r^2 \, dr$

Out[ ]= $$-\frac{32\,k^2\left(\frac{c_1 z_1^{9/2}\left(k^2-7 z_1^2\right)}{\left(k^2+z_1^2\right)^5}+\frac{c_2 z_2^{9/2}\left(k^2-7 z_2^2\right)}{\left(k^2+z_2^2\right)^5}\right)}{\sqrt{35}}$$ if Abs[Im[k]] < Re[z_1] && Abs[Im[k]] < Re[z_2]

In[ ]:= $\int_0^\infty (c_1 * s[5, z_1] + c_2 * s[5, z_2]) * j_2 * r^2 \, dr$

Out[ ]= $$-\frac{256}{15}\sqrt{\frac{2}{7}}\,k^2\left(\frac{c_1 z_1^{13/2}\left(3k^2-7 z_1^2\right)}{\left(k^2+z_1^2\right)^6}+\frac{c_2 z_2^{13/2}\left(3k^2-7 z_2^2\right)}{\left(k^2+z_2^2\right)^6}\right)$$ if Abs[Im[k]] < Re[z_1] && Abs[Im[k]] < Re[z_2]