Some Helium Coulomb Integrals by James Pate Williams, Jr.

The Coulomb integral is a measure of the electron-electron repulsion in an atom. Take for example the helium atom (atomic number 2). The approximate wave function of the two-electron helium is given by the equations [1] [2] [3]:

$$\Psi_{100}(r_1,r_2) = \psi_{100}(r_1)\psi_{100}(r_2) = \frac{1}{\pi}{\zeta_1}^{3/2}e^{-\zeta_1 r_1}{\zeta_2}^{3/2}e^{-\zeta_2 r_2}$$

$$\psi_{100}(r) = R_{10}(r)Y_{00}(\vartheta,\varphi) = 2\zeta^{3/2}e^{-\zeta r}\frac{1}{2\sqrt{\pi}} = \frac{1}{\sqrt{\pi}}\zeta^{3/2}e^{-\zeta r}$$

The wave function can be expressed in Dirac's Bra-Ket notation as:

$$|1s(1)1s(2)\rangle = |1s(1)\rangle|1s(2)\rangle$$

The Coulomb integral in mathematically verbose format is [1] [2]:

$$J(r_1,r_2) = \int_0^\infty\int_0^\pi\int_0^{2\pi}\int_0^\infty\int_0^\pi\int_0^{2\pi} \Psi(r_1,r_2)\frac{1}{r_{12}}\Psi(r_1,r_2)r_1^2r_2^2\sin\vartheta_1\sin\vartheta_2 dr_1dr_2d\vartheta_1d\vartheta_2d\varphi_1d\varphi_2$$

A similar formulation is given in Dirac's notation [1] [4]:

$$J(r_1,r_2) = \left\langle 1s(1)1s(2)\middle|\frac{1}{r_{12}}\middle|1s(1)1s(2)\right\rangle$$

In some cases, the Coulomb integral can be reduced to a double integral over two radial wavefunctions. For now, we numerically evaluate the six integral interactions. The results for 1s to 5s orbitals are as follows [4]:

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desired relative error 1e-08
f#      integral        epsilon         number  err code
1       +3.401593e+01   4.790309e+00    257     0
2       +1.147305e+01   1.948449e+00    257     0
3       +5.443569e+00   3.039712e+00    257     0
4       +3.136499e+00   2.001779e+00    257     0
5       +2.040218e+00   1.493084e+00    257     0
f#      abs error       percent error
1       +1.685950e-03   +4.956598e-03
2       +5.731374e-02   +5.020592e-01
3       +3.207963e-02   +5.928059e-01
4       +1.217805e-02   +3.867670e-01
5       +5.041759e-04   +2.470576e-02
f# Coulomb Integral Legend:
f1 <1s(1)1s(2)|1/r_12|1s(1)1s(2)>
f2 <1s(1)2s(2)|1/r_12|1s(1)2s(2)>
f3 <1s(1)3s(2)|1/r_12|1s(1)3s(2)>
f4 <1s(1)4s(2)|1/r_12|1s(1)4s(2)>
f5 <1s(1)5s(2)|1/r_12|1s(1)5s(2)>
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References

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