r12STOmolecular: Practical Analytic STO Two-Center Exchange Integrals

E. V. Rothstein Chan

evrothstein@gmail.com

The exchange integrals occur in solving for the quantum mechanical wave function using the Schroedinger equation. r12STOmolecular deals with interelectronic distances and STOs (Slater type orbitals), centered at various molecular origins. STOs have a radially dependent exponential term (multiplied by radial distance term to the power of principal quantum number n minus one) multiplied by a spherical harmonic with quantum numbers l and m. The small and large radial behavior differ from Gaussians. Ipython notebook with arbitrary precision for evaluation from analytic formula is presented. This work was undertaken to make accurate molecular computation more readily available to other researchers.

1. Spherical Harmonics

The spherical harmonics are the angular part of the solution to the hydrogenic wave function. the modulus squared of the solution is interpreted as the probability. Part of the importance of the spherical harmonics is that they form a complete orthonormal set and can be used as a basis for expansions of functions in spherical coordinate system. Clebsch-Gordon coefficients relate the spherical harmonics in different representations. In Mathematica program the spherical harmonics are implemented as SphericalHarmonicY[l,m,theta,phi]. In Matlab program they are not built in and were defined as complex functions and as real spherical harmonics squared. In the spherical coordinate system the polar or colatitudinal angle varies as 0 to pi and the azimuthal or longitudinal coordinate varies from 0 to 2*pi. In Matlab the angle instead of starting from the z axis and moving from 0 to pi, starts from the xy plane. This makes for some confusion! By replacing all sin(theta) by cos(theta) and cos(theta) by sin(theta) everything works out with theta varying from -pi/2 to pi/2 instead of the polar angle varying from 0 to pi. The representation of a complex function could be done by using different colors or by causing a rotation; the latter was chosen and rotation is represented by variation of light reflected off a rotating surface in the program[1] SHsquared.m . A video[2] was made from this showing that for m=0 the spherical harmonic is real and not rotating. Y(2,2) rotates twice as fast as Y(2,1). Y(1,-1) would rotate in the opposite direction to Y(1,1).
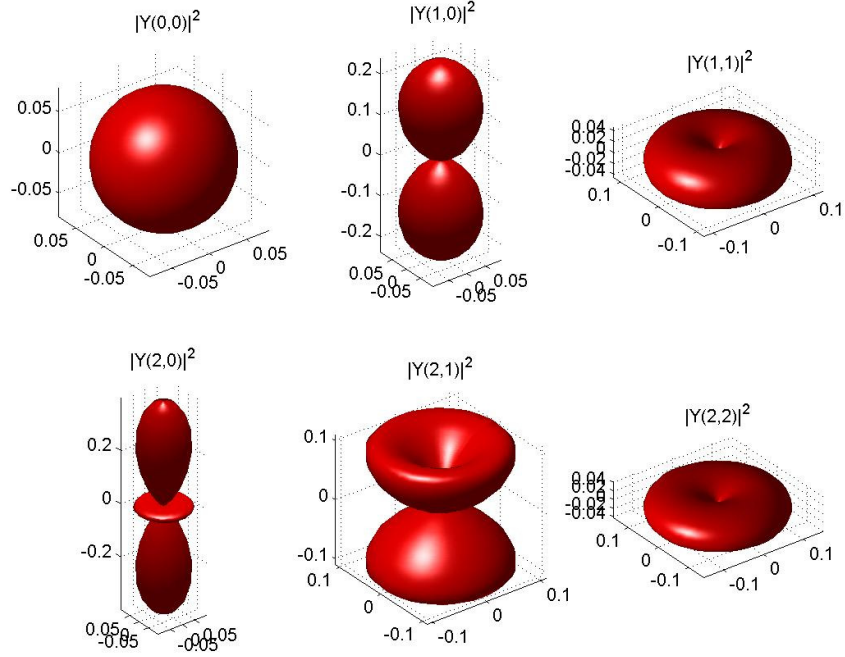
Fig. 1. The spherical harmonics squared are real Y(l,m) complex conjugate multiplied by Y(l,m) .

2. Two Center Exchange Integral

Integral is called exchange because electron 1 is in a product of orbitals centered on both nucleus a and nucleus b; the same for electron 2. The Heisenberg exchange integral is a special case of the quantum mechanical exchange integral.

$$\Phi_c = (-)^{(m-|m|)/2}(2\delta)^{n+\frac{1}{2}}\left[\frac{(2l+1)(l-|m|)!}{4\pi(2n)!(l+|m|)!}\right]^{\frac{1}{2}}$$
$$\times e^{im\phi}r_c^{n-1}e^{-\delta r_c}P_l^{|m|}(cos\theta_c)$$

Φ_c is a normalized Slater orbital in spherical coordinates centered on center a or center b with quantum numbers (n, l, m) and screening constant δ (not the usual Kronecker delta function).

Exchange integral = I = $\int\int d\tau_1 d\tau_2 \Phi_{1a}(1)\Phi_{3b}(1)\frac{1}{r_{12}}\Phi_{2a}(2)\Phi_{4b}(2)$

The integral was evaluated for various values of principal quantum numbers, screening constants and distances between the two centers. The results, Figure 2, subplots one and two, agree with previous Fortran calculations[3].
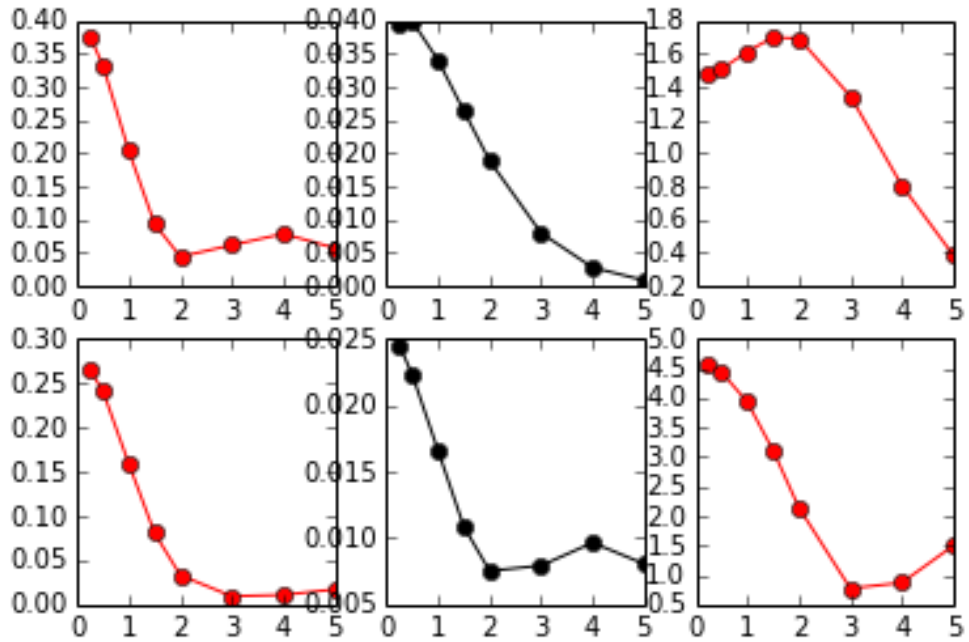
Fig. 2. I =EXCHEQ/dt1 versus R=alf1=alf2; all bet1=bet2=0, dt1 is screening constant for orbital 1 is unity Top Row all n=2, l=1, m=0; all n=2, l=1, m1=m3=-1,m2=m4=+1; all n=2, l=1, m1= -1=m4,m3=+1=m2 Bottom Row all n=3, l=2, m=0; all n=3, l=2, m1=m3= -1,m2=m4=+1; all n=3,l=2, m1= -1=m4, m3=+1=m2 .

3. IPython Notebook

4

Fig. 3. fragment of EXCHEQ .

Figure 3 is a fragment of EXCHEQ function $=$ I ,which is Equation (1) from the derivation[4] , The entire Ipython notebook can be viewed[5].

The function FIN in the program is Equation (2) in Reference 4

The function INT3EQ is equation (3) of Reference 4

References

1. https://drive.google.com/file/d/
   0B5WiToDBlNanSHdGbVJ4a0p6WUE/view?usp=sharing

2. https://drive.google.com/file/d/
   0B5WiToDBlNanNWRTajRjZEVfR1E/view?usp=sharing
3. E.R. Chan,Analytic Two-Center Exchange Integrals *Chem. Phys. Lett.* **23**, 99 (1973).
4. E.V. Rothstein,Derivation of Unified Analytic Electron Interaction Integrals over Slater Orbitals for Diatomic Molecules *ArXiv:1207.5866* .
5. https://drive.google.com/file/d/
   0B5WiToDBlNanVjhQbnJacENBZ2M.view?usp=sharing