COMPUTATION OF TWO-CENTER TWO-ELECTRON INTEGRALS FOR EXCITED-STATE CALCULATIONS

by

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ABSTRACT

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Four-orbital integrals containing the Coulomb kernel are computed to describe the interaction between two electrons as needed in most excited-state calculations. We outline their use in both time-dependent density-functional theory and Görling and Levy perturbation theory to find the excited-state properties of many-electron systems. The complete derivations are included to show how these six-dimensional integrals are simplified so that only three- or four-dimensional numerical integrations are required per integral. All numerical integrations are performed via the adaptive Simpson's rule. The integrals are computed and stored for use in the *ab initio* density-functional theory FIREBALL program. The integrals for each of the three distinct types of orbital arrangements are plotted for interactions between carbon and hydrogen atoms as a function of separation distance.

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Chapter 1

Introduction

1.1 Motivation

Many theoretical discoveries in physics are made through the study of optics. Two important examples in quantum mechanics are Bohr's model of the hydrogen atom and the explanation of the Zeeman effect. These theories were developed when the current models failed to explain the observed spectrum of hydrogen. Although the optical properties of hydrogen are now well understood, the optical properties of larger systems are much more difficult to model. Time-dependent density-functional theory (TDDFT) and Görling and Levy perturbation theory (GLPT) are two promising methods for obtaining these optical properties for many-body systems.

1.2 Approximate Solutions of the Schrödinger Equation

The Zeeman effect and other excited-state properties of hydrogen are all predicted by solutions to the Schrödinger equation [1]. Unfortunately, solving Schrödinger's equation exactly for the ground-state or excited-state properties of multielectron atoms is intractable. The complexity of Schrödinger's equation further increases when multiple atoms are considered as seen by writing out the complete time-independent, non-relativistic form of the equation in atomic units [2]:

$$\hat{H}\Psi_i\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N,\boldsymbol{R}_1,\ldots,\boldsymbol{R}_M\right)=E_i\Psi_i\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N,\boldsymbol{R}_1,\ldots,\boldsymbol{R}_M\right), \tag{1.1}$$

where $\hat{H}$ is the Hamilton operator:

$$\begin{aligned}\hat{H}=&-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2-\frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{|\boldsymbol{r}_i-\boldsymbol{R}_A|}\\&+\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}+\sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_AZ_B}{|\boldsymbol{R}_A-\boldsymbol{R}_B|}.\end{aligned} \tag{1.2}$$

In equations 1.1 and 1.2 capital letters refer to the M atoms, lowercase letters refer to the N electrons, M_A is the mass of nucleus A, Z_A is the charge of nucleus A, Ψ_i is the wave function describing the system, and E_i is the energy of the state Ψ_i.

1.2.1 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is usually the first approximation made to reduce the complexity of the Schrödinger equation. In this approximation Schrödinger's equation is solved first with the electronic Hamiltonian:

$$\hat{H}_{elec}=-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2-\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{|\boldsymbol{r}_i-\boldsymbol{R}_A|}+\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}, \tag{1.3}$$

in which the kinetic energy of the nuclei, $-\frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2$, is assumed to be zero and the repulsion between the nuclei, $\sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_AZ_B}{|\boldsymbol{R}_A-\boldsymbol{R}_B|}$, is assumed to be constant. The solution to Schrödinger's equation with the electronic Hamiltonian is called the electronic wave function, Ψ_{elec}, with corresponding electronic energy, E_{elec}, and both quantities depend parametrically on the nuclear coordinates. Once the electronic problem is solved, the Schrödinger equation is solved using the full Hamiltonian shown in 1.2 but this time with the electronic part of the Hamiltonian, H_{elec} replaced by E_{elec}. Thus the Born-Oppenheimer approximation solves the Schrödinger equation twice: the first time by treating the nuclei as fixed and the second time by averaging the electronic coordinates. This approximation is successful because the nuclei are much heavier than the electrons, (often 20,000 times or more for atoms like carbon [2]), and therefore move much slower than the electrons. For a qualitative introduction to the Born-Oppenheimer approximation see [3].

1.2.2 Hartree-Fock Approximation

Building off of the Born-Oppenheimer approximation, the Hartree-Fock approximation further simplifies the Schrödinger equation by making several additional assumptions. The main assumption is that the N-electron wave function can be approximated by a Slater determinant, which is an antisymmetric wave function composed of N one-electron wave functions [3]. The spin orbitals in each wave function of a Slater determinant are then varied so as to form new wave functions while maintaining their orthonormality. The expectation values of all of these possible Slater determinants are found using the full electronic Hamiltonian operator 1.3 and the one that yields the lowest energy is the closest approximation to the exact wave function according to the variation principle.

Although in principle the expectation value of each Slater determinant with the electronic Hamiltonian operator could be computed to find the wave function that produces the smallest energy, in practice a different procedure is used. This procedure involves solving a minimization problem using the nonlinear Hartree-Fock equations. Due to the nonlinearity of the equations they must be solved iteratively by the self-consistent-field method. If we closely examine the Hartree-Fock equations we find that the electron-electron interactions in the Hartree-Fock approximation involve an averaging, that is, each equation has a potential energy term formed by the interaction between one electron and the average of the other electrons. This averaging basically reduces the many-electron problem to a one-electron problem.

1.2.3 Density-functional Theory

Density-functional theory (DFT) also uses the Born-Oppenheimer approximation but differs from the Hartree-Fock approximation mainly in its focus and basic variables. In Hartree-Fock theory the N-electron wave function is the basic quantity being derived and it depends on 4N variables, (3N spatial variables and N spin variables), whereas the basic quantity for density-functional theory is the electron density, which depends only on three variables. The usefulness of this change of focus from the N-electron wave function to the electron density comes from the Hohenberg-Kohn theorems. These theorems state that a unique mapping exists, in principle, between the ground state density and the ground state energy of a given system [2].

Density-functional theory based on the Kohn-Sham approach is, in principle, exact. Unlike Hartree-Fock theory, which introduces an approximation right from the start by using Slater determinants as approximations to the N-electron wave function, density-functional theory only contains approximations in the exchange-correlation potential. This potential contains a portion of the kinetic energy that cannot be treated exactly and the non-classical exchange and correlation effects [2]. Many approximations to the exchange-correlation potential exist such as the local-density approximation (LDA) the generalized gradient approximation (GGA) etc. and their accuracy has the greatest influence on the quality of the density-functional approach.

The mathematical machinery used in DFT is very similar to that found in the Hartree-Fock method. In the Kohn-Sham formalism of DFT we again have a minimization problem of nonlinear equations which must be performed using the self-consistent-field method. These nonlinear equations are called the Kohn-Sham equations and the orbitals that yield the smallest energy in the minimization are termed the Kohn-Sham orbitals. Although Slater determinants of these orbitals do not produce the exact wave function of the system in question, they do prove to be very useful in excited-state calculations.

1.2.4 Time-dependent Density-functional Theory and Görling and Levy Perturbation Theory

The Kohn-Sham orbital energies found in DFT play a very important role in both time-dependent density-functional theory (TDDFT) and Görling and Levy perturbation theory (GLPT). Both TDDFT and GLPT use the Kohn-Sham eigenvalue differences as a starting point for finding the excitation energies of a given system. Both theories also need additional integrals containing the Coulomb interaction kernel in order to correct these eigenvalue diffences and find the true excitation energies.

The Kohn-Sham eigenvalue differences play a key role in GLPT. Görling shows in [4] that these differences are well-defined approximations of the excitation energies. This result is achieved through a combination of his Kohn-Sham formalism for excited states and the DFT perturbation theory first described in [5]. Based on this approach, which is exact in principle, the first order correction to the Kohn-Sham eigenvalue differences is:

$$ {}^{1}\Delta E\left(T, i \rightarrow v\right) = \left\langle \phi_\nu \middle| \hat{v}_x^{NL} - \hat{v}_x\left[n_0\right] \middle| \phi_\nu \right\rangle - \left\langle \phi_i \middle| \hat{v}_x\left[n_0\right] \middle| \phi_\nu \right\rangle - \left\langle \nu i \middle| \nu i \right\rangle , \tag{1.4} $$

for the triplet state and

$$ {}^{1}\Delta E\left(S, i \rightarrow v\right) = \left\langle \phi_\nu \middle| \hat{v}_x^{NL} - \hat{v}_x\left[n_0\right] \middle| \phi_\nu \right\rangle - \left\langle \phi_i \middle| \hat{v}_x^{NL} - \hat{v}_x\left[n_0\right] \middle| \phi_i \right\rangle - \left\langle \nu i \middle| \nu i \right\rangle + 2\left\langle \nu i \middle| i \nu \right\rangle , \tag{1.5} $$

for the singlet state [4]. In 1.5 and 1.4 $\hat{v}_x^{NL}$ is a nonlocal exchange operator, $\hat{v}_x\left[n_0\right]$ is the local density exchange potential, and

$$\langle ij|st\rangle = \int d\boldsymbol{r} \int d\boldsymbol{r}' \phi_i^*\left(\boldsymbol{r}\right)\phi_j^*\left(\boldsymbol{r}\right)\phi_s\left(\boldsymbol{r}'\right)\phi_t\left(\boldsymbol{r}'\right)/\left|\boldsymbol{r}-\boldsymbol{r}'\right|. \qquad (1.6)$$

In these transitions one electron is being excited from an occupied Kohn-Sham orbital ϕ_i to an unoccupied orbital ϕ_ν. It is important to note that none of the integrals in 1.5 and 1.4 involving the Coulomb interaction kernel, $1/\left|\boldsymbol{r}-\boldsymbol{r}'\right|$, are needed in DFT so incorporating GLPT in a normal DFT program requires the additional computation of these integrals.

TDDFT also uses the Kohn-Sham eigenvalue differences and two-electron integrals involving the Coulomb interaction kernel in its calculations of excited-state energies [6].

1.3 Additional Two-electron Integrals

Due to their common basis in density-functional theory (DFT), TDDFT and GLPT are particularly attractive theories for finding the optical properties of many-body systems. Unfortunately, both TDDFT and GLPT require additional two-electron integrals containing the Coulomb interaction kernel as shown in 1.2.4 and 1.2.4. The computation of these integrals for use in TDDFT and GLPT is the main focus of this paper.

Chapter 2

Computation of Coulomb and exchange integrals

The two-electron integrals that describe electron interactions for use in time-dependent density-functional theory, (TDDFT), and Görling and Levy perturbation theory, (GLPT), are challenging both theoretically and computationally. In this paper we show how to compute these two-electron integrals composed of the Coulomb operator and four fireball orbitals. By only considering two-center integrals and making other analytical considerations we significantly reduce the complexity of these integrals so as to effectively compute them for use in the FIREBALL program.

2.1 Orbital Composition

The atomic orbitals in our four-orbital integrals are slightly excited pseudo-atomic-orbitals commonly called fireballs. These orbitals are each composed of a radial wavefunction multiplied by a corresponding real spherical harmonic. The radial wavefunctions are created using a Herman-Skillman-like program [7] and are slightly excited

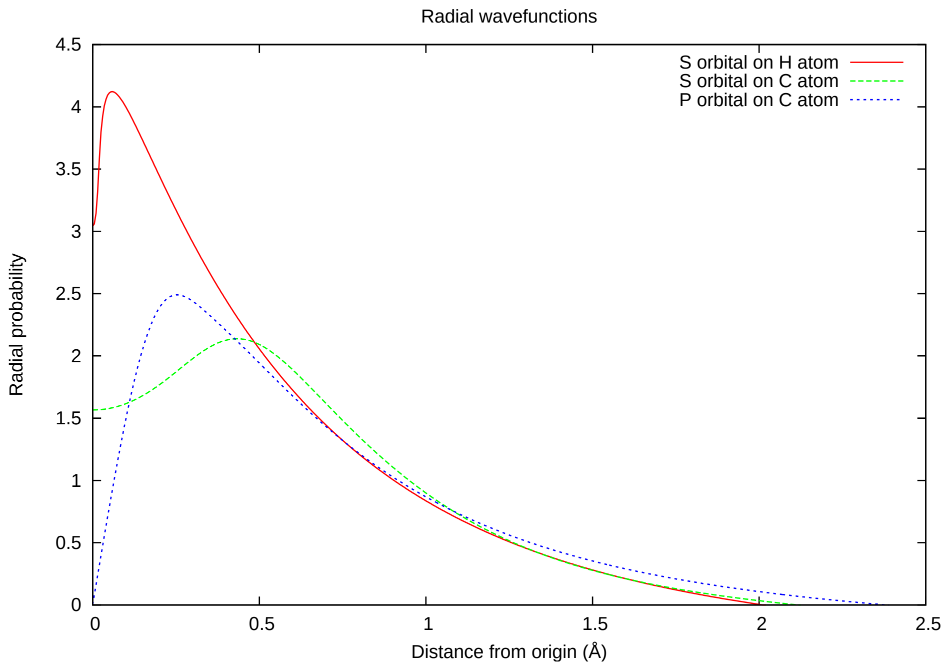

Figure 2.1 Radial fireball wavefunctions for hydrogen and carbon have finite cutoffs.

due to their finite cutoffs. (For more information on how the finite cutoffs are chosen see [8].) Although complex spherical harmonics are easier to work with theoretically we use real spherical harmonics (RSH) because the orbital rotations in the FIREBALL program are based on RSH. (It is possible to perform the integrations using complex spherical harmonics and then convert the answers to real spherical harmonics but this requires additional computational time and memory.) For other advantages to using RSH and to see their relationship to complex spherical harmonics see [9].

Using the radial wavefunctions and spherical harmonics described above we can

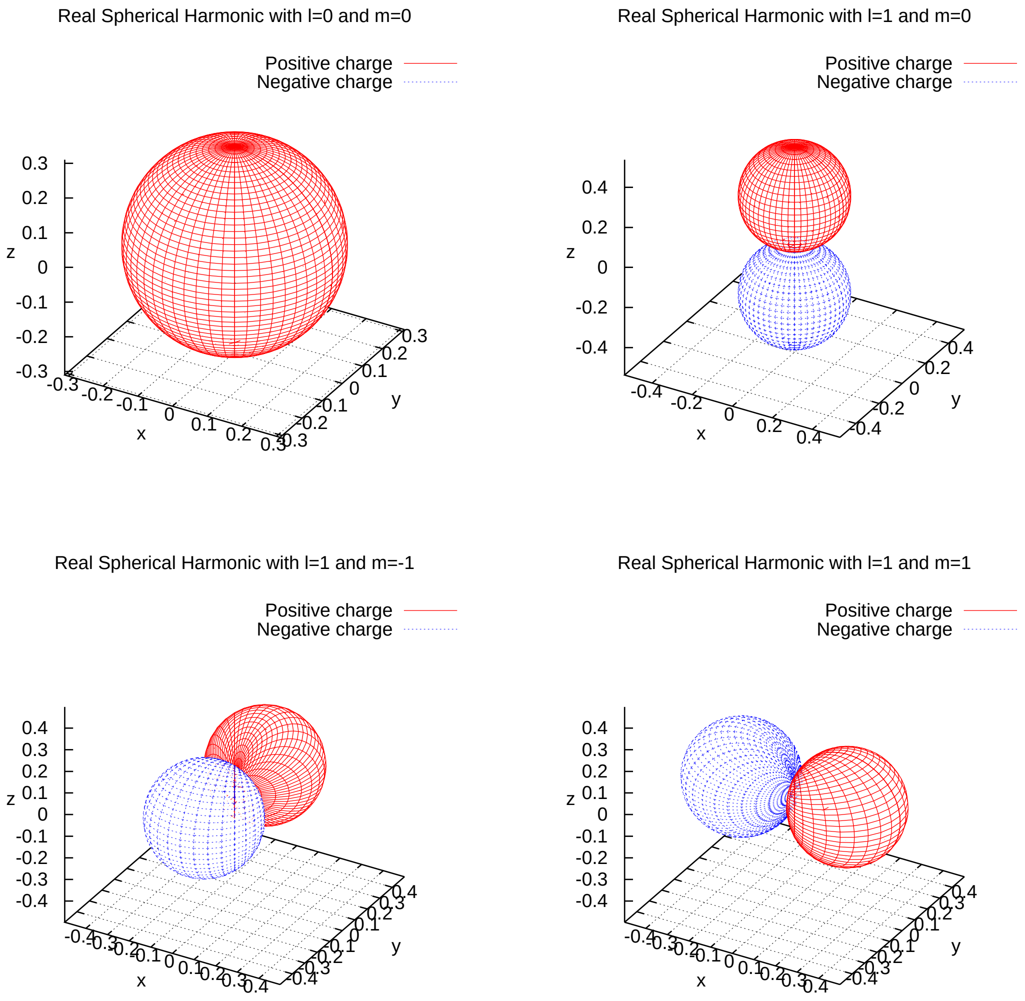

Figure 2.2 Plots of the $l = 0$ and $l = 1$ real spherical harmonics.

write a general fireball orbital ϕ centered at the origin as

$$\begin{aligned}\phi\left(\boldsymbol{r}\right) &= R\left(r\right)Y_{l,m}\left(\Omega\right)\\ &= R\left(r\right)\left[\frac{\left(2l+1\right)}{4\pi}\frac{\left(l-\left|m\right|\right)!}{\left(l+\left|m\right|\right)!}\right]^{\frac{1}{2}}P_{l,\left|m\right|}\left(\cos\theta\right)\begin{cases}\sqrt{2}\sin\left(\left|m\right|\phi\right)\text{ if } m<0\\ 1\text{ if } m=0\\ \sqrt{2}\cos\left(m\phi\right)\text{ if } m>0\end{cases}\end{aligned} \tag{2.1}$$

where $R\left(r\right)$ is the radial wavefunction, $P_{l,\left|m\right|}\left(\cos\theta\right)$ is the associated Legendre polynomial without the $\left(-1\right)^m$ Condon-Shortly factor, θ is the angle between the z-axis and the radial vector $\boldsymbol{r}$, and ϕ is the angle between the x-axis and the projection of the radial vector on the x-y plane. To help visualize these orbitals the radial wavefunctions for hydrogen and carbon are shown in Fig. 2.1 and their corresponding spherical harmonics are seen in Fig. 2.2.

2.2 Two-electron integrals

The two-electron integrals that we compute for excited-state calculations are composed of the product of four fireball orbitals and the Coulomb kernel all integrated over the spaces of both electrons. (For those readers familiar with Hartree-Fock theory, linear combinations of these integrals can be used to form the Hartree and exchange integrals.) The four fireball orbitals can be located on one, two, three, or four different atoms to form what are called, respectively, one-, two-, three-, or four-center integrals. At this point in time we restrict ourselves to the computation of one- and two- center integrals based on the assumption that the three- and four-center integrals are very small at normal molecular bonding distances.

In the FIREBALL program all integrals are precomputed on a numerical grid and stored in tables. When the integrals for specific geometries and configurations of atoms are needed their values are found by interpolation and rotation of the tabular values. Since we are only considering one- and two-center integrals we use a similar setup found in [7] for the kinetic and overlap matrix elements. In this setup the first atom lies at the origin and the second atom lies on the z-axis a positive distance d from the first atom. We are able to compute both the one- and two-center integrals with the same code because the two-center integrals are really one-center integrals when $d = 0$. With this arrangement of atoms we have three unique types of two-electron integrals to compute based on the position of the fireball orbitals. We call these three types of integrals no-overlap, one-overlap, and two-overlap integrals.

The no-overlap integrals have two orbitals centered on the first atom in the first coordinate system and two orbitals centered on the second atom in the second coordinate system. The one-overlap integrals have two orbitals centered on the first atom in the first coordinate system, one orbital centered on the first atom in the second coordinate system, and one orbital centered on the second atom in the second coordinate system. The two-overlap integrals have one orbital centered on the first atom in the first coordinate system, one orbital centered on the second atom in the first coordinate system, one orbital centered on the first atom in the second coordinate system, and one orbital centered on the second atom in the second coordinate system. Diagrams of these unique arrangements can be seen in Fig 2.3.

The ϕ integrations in both coordinate systems of all three integral types described above are performed analytically thus leaving at most four dimensions of these six-dimensional integrals to be integrated numerically. With the aid of Gaunt's formula [10] the θ integration in the first coordinate system of the no- and one-overlap integrals can also be performed analytically thus leaving three dimensions to be integrated numerically. These remaining numerical integrations are performed using an adaptive Simpson quadrature routine as described in [11] but with a recursive approach as opposed to the suggested stack approach. The complete integral derivations are

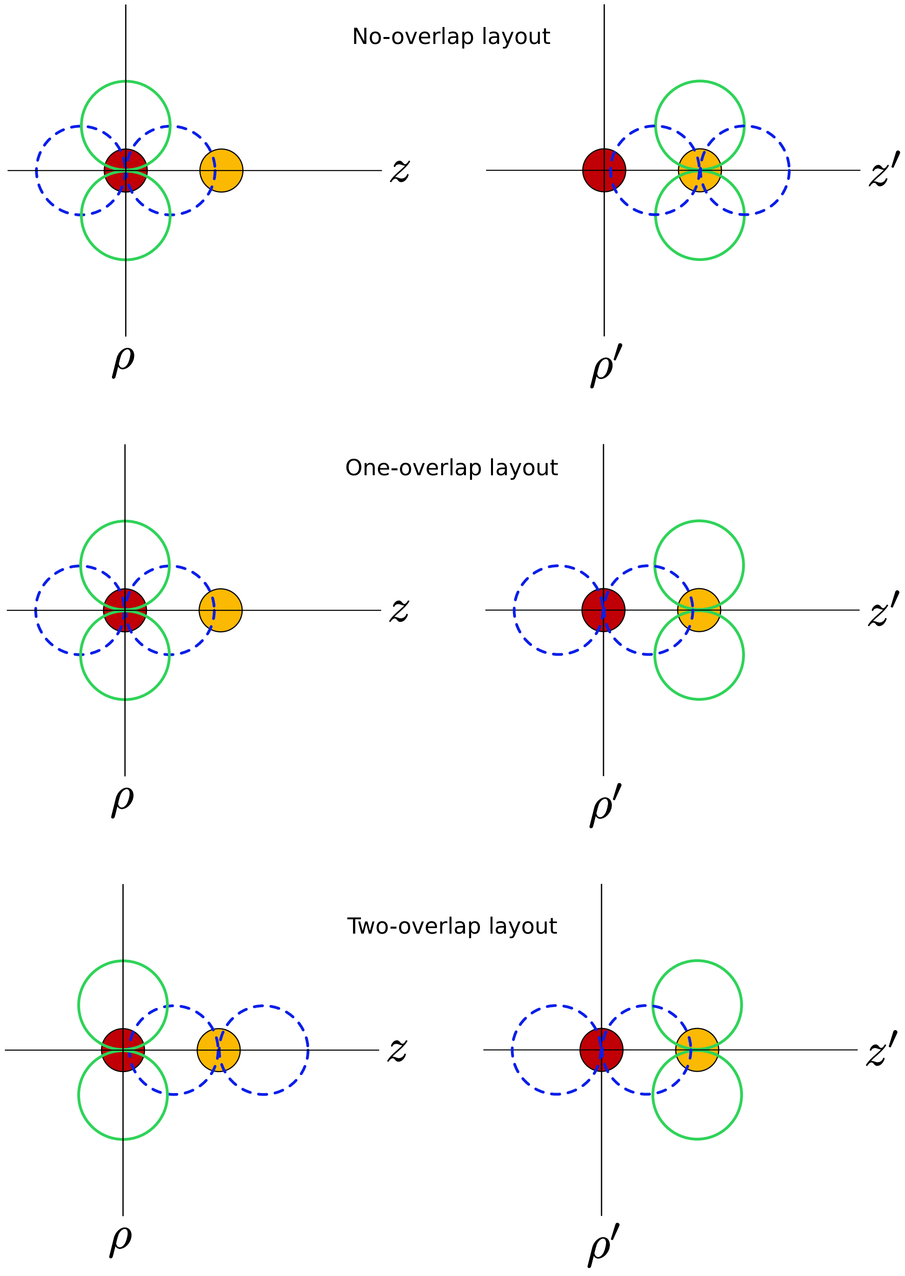

Figure 2.3 Placement of orbitals on different atoms to form two-, one-, and no-overlap integrals.

shown in Appendix A.

Chapter 3

Results and Conclusions

Plots of all unique two-center two-electron integrals needed for excited-state calculations are displayed below. Since all of these integrals contain the Coulomb operator as explained in chapter 2 we do no write it explicitly for each integral in order to save space. We use Dirac's notation to distinguish between integrals so that $\langle 100, 21-1 \| 210, 211 \rangle$ means that orbital A is a s orbital, orbital B is a p_y orbital, orbital C is a p_z orbital, and orbital D is a p_x orbital where orbitals A, B, C, and D appear in the same order as shown in the derivations of appendix A. The first number describing each orbital is the shell number while the second and third numbers are the l and m values respectively.

3.1 Results

The no-overlap integrals for the hydrogen-hydrogen, hydrogen-carbon, and carbon-carbon interactions are shown in figures 3.1, 3.2, and 3.3. All of these integrals have an absolute error of 10^{-4} and the grid between the two atoms has a spacing of 0.05 Å. Notice that the integrals with squared orbitals in both the bra and the ket follow

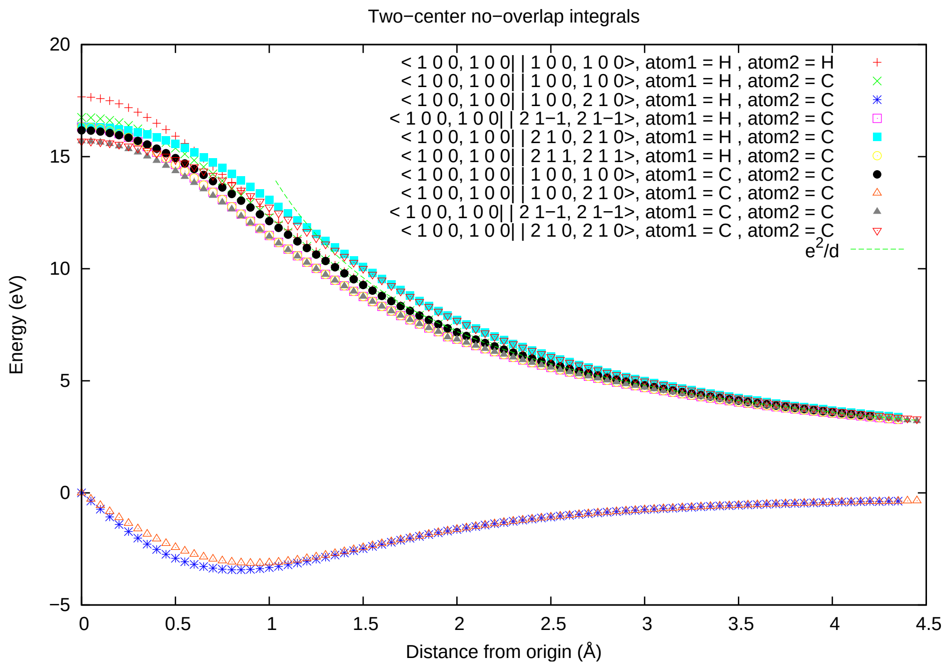

Figure 3.1 First plot of no-overlap integrals for hydrogen and carbon atoms.

a strict $1/d$ relationship after about 4 Å where d is the separation distance between the two atoms.

The one-overlap integrals for the hydrogen-hydrogen, hydrogen-carbon, and carbon-carbon interactions are shown in figures 3.4, 3.5, 3.6, 3.7, 3.8. All of these integrals have an absolute error of 10^{-4} and the grid between the two atoms has a spacing of 0.05 Å. Notice that at a 3.5 Å separation distance between the two atoms the absolute value of all of the one-overlap integrals is less than 0.12 eV.

The two-overlap integrals for the hydrogen-hydrogen, hydrogen-carbon, and carbon-carbon interactions are shown in figures 3.9, 3.10, and 3.11. All of these integrals have an absolute error of 10^{-4} and the grid between the two atoms has a spacing of 0.05 Å. Since the sum over l does not terminate for the two-overlap integrals, (see A.2), we stop the summation at $l = 4$, at which point the contributions to the integral are

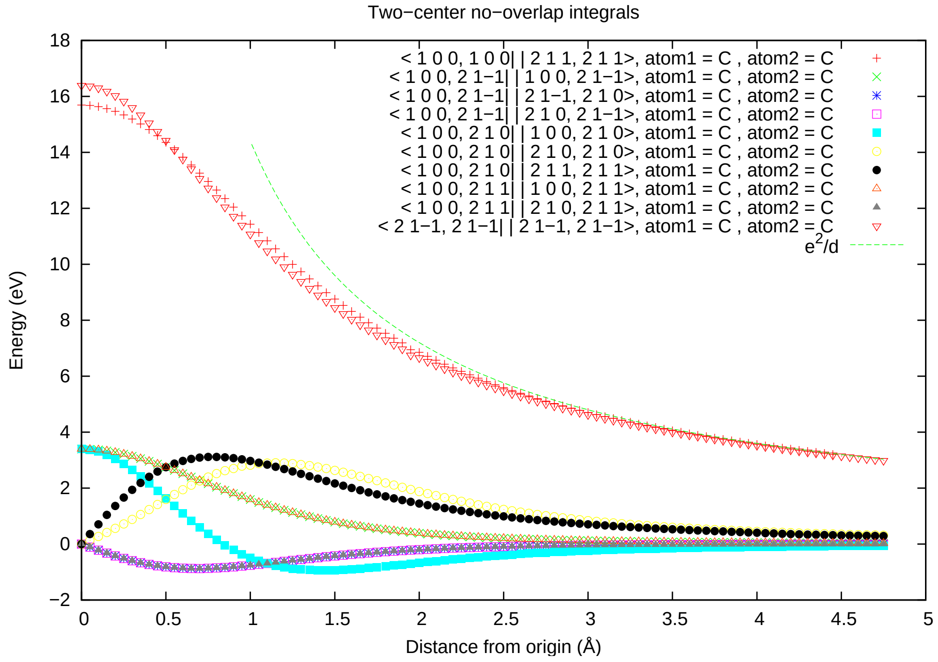

Figure 3.2 Second set of plots of no-overlap integrals for hydrogen and carbon atoms.

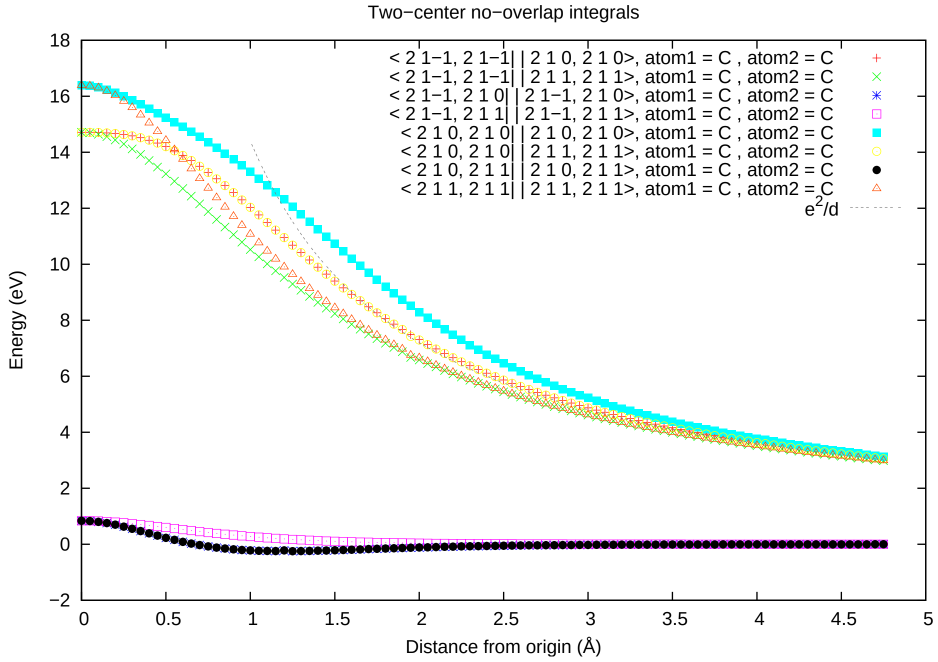

Figure 3.3 Third set of plots of no-overlap integrals for hydrogen and carbon atoms.

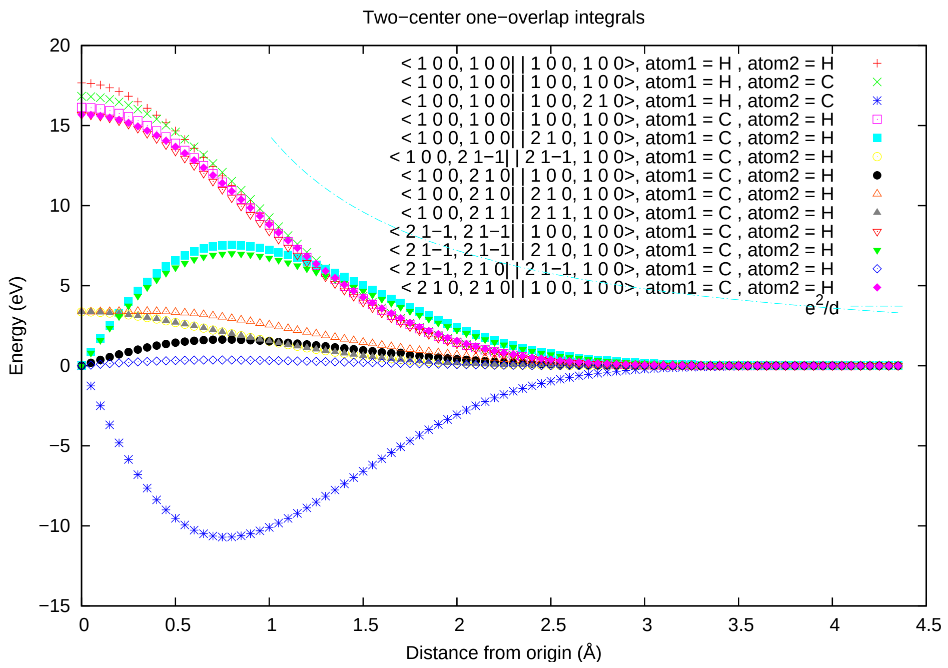

Figure 3.4 First set of plots of one-overlap integrals for hydrogen and carbon atoms.

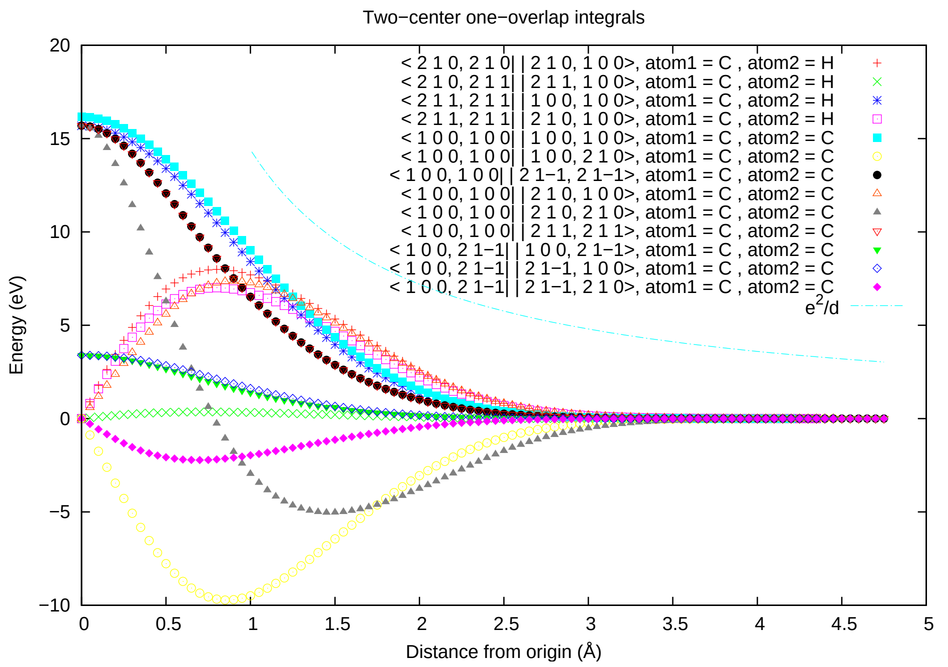

Figure 3.5 Second set of plots of one-overlap integrals for hydrogen and carbon atoms.

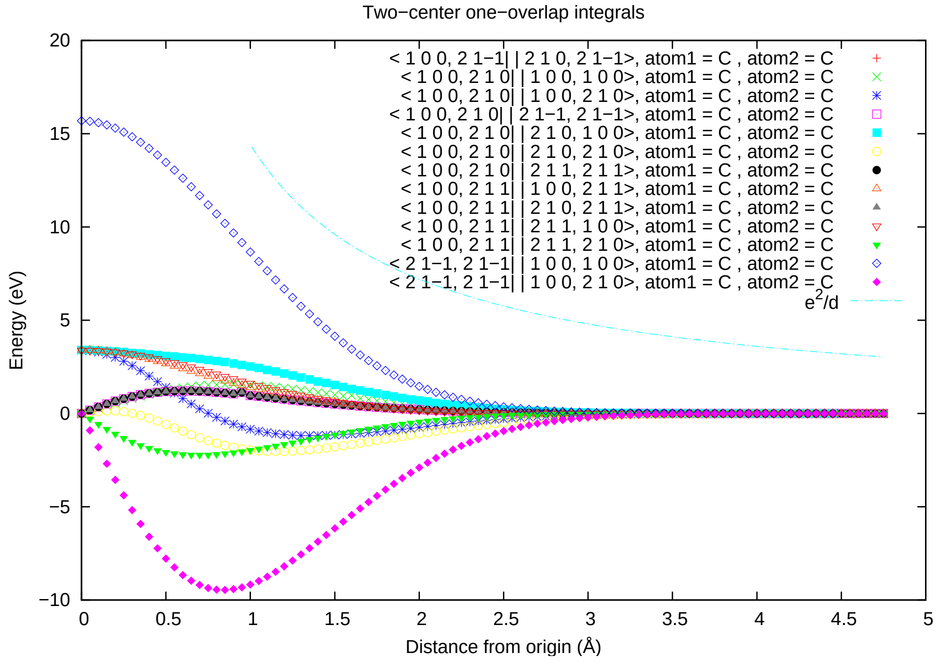

Figure 3.6 Third set of plots of one-overlap integrals for hydrogen and carbon atoms.

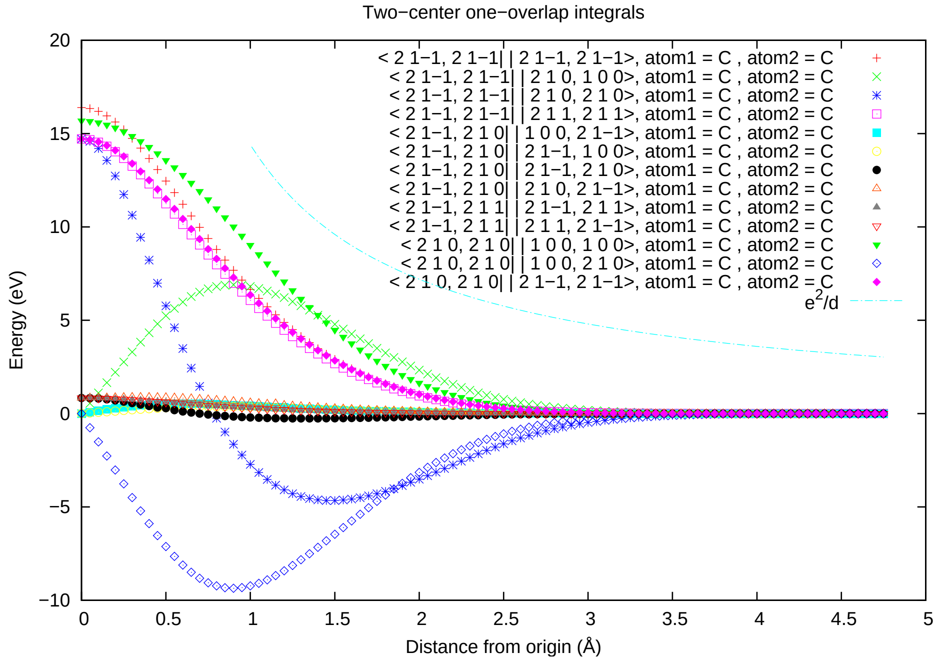

Figure 3.7 Fourth set of plots of one-overlap integrals for hydrogen and carbon atoms.

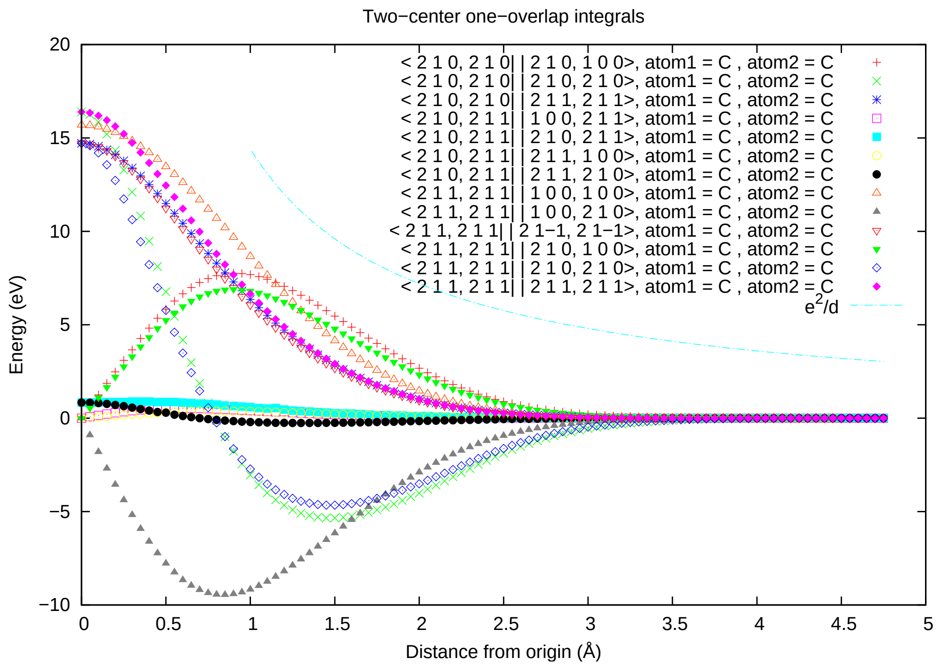

Figure 3.8 Fifth set of plots of one-overlap integrals for hydrogen and carbon atoms.

less than 10^{-3} eV. Notice that at a 2.75 Å separation distance between the two atoms the absolute value of all of the two-overlap integrals is less than 0.18 eV.

3.2 Conclusions

Although all three types of two-center two-electron integrals studied here make significant contributions to the integrals needed for excited-state calculations, it is obvious from our plots in 3.1 that the no-overlap integrals make the largest contribution. Furthermore, the no-overlap integrals with squared orbitals in both the bra and the ket make significant contributions even at large separation distances due to their $1/d$ relationship, where d is the separation distance between the two atoms. It is also apparent from the aforementioned plots that in general the one-overlap integrals are larger in magnitude than the two-overlap integrals.

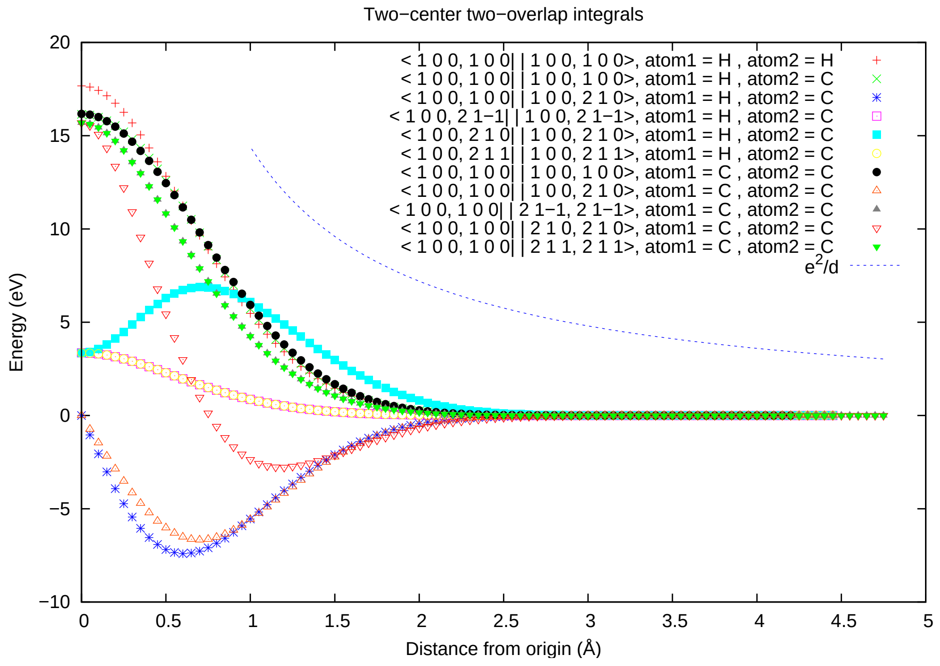

Figure 3.9 First set of plots of two-overlap integrals for hydrogen and carbon atoms.

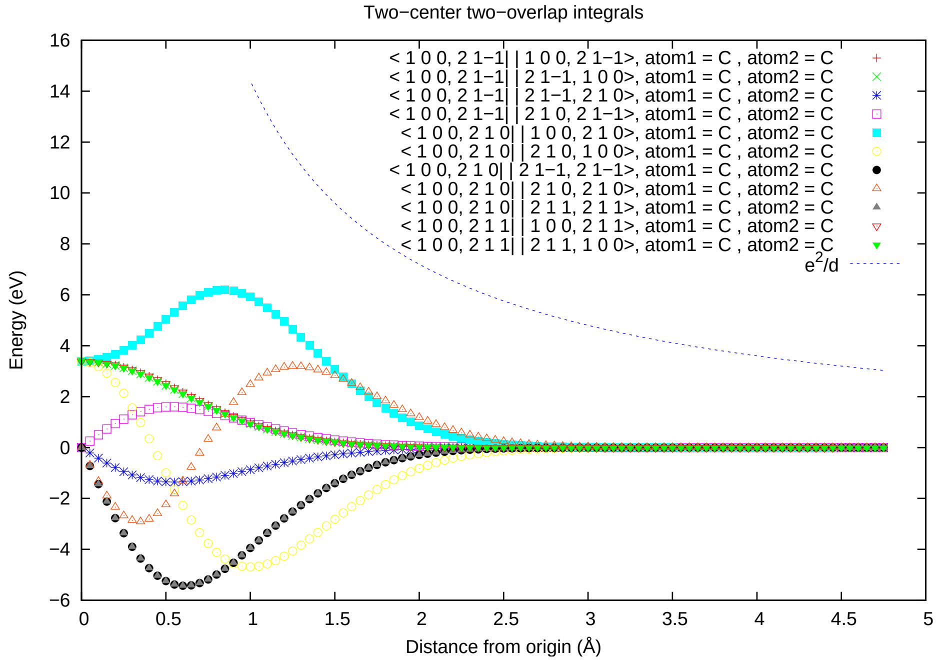

Figure 3.10 Second set of plots of two-overlap integrals for hydrogen and carbon atoms.

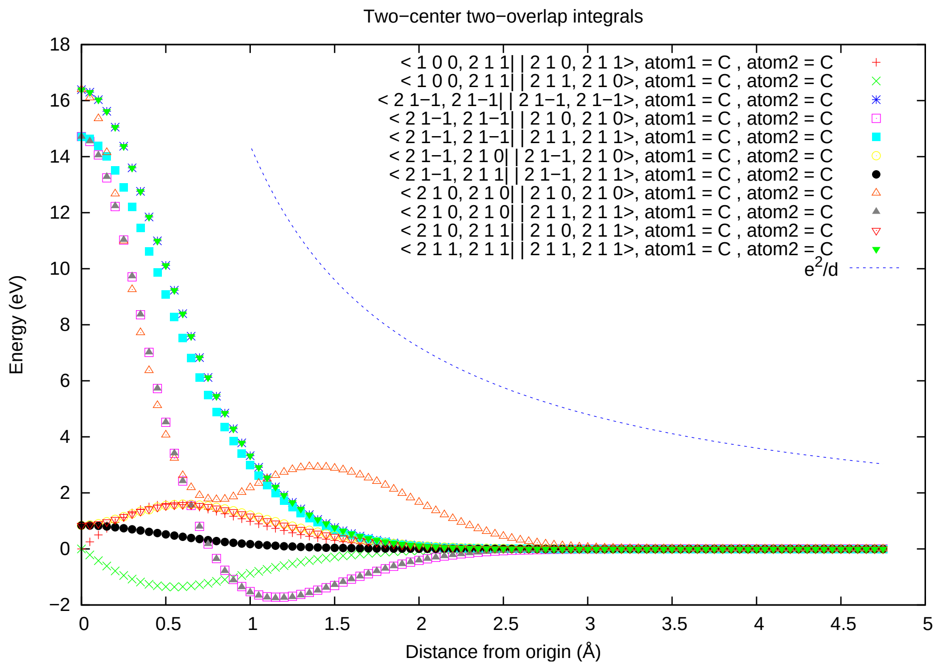

Figure 3.11 Third set of plots of two-overlap integrals for hydrogen and carbon atoms.

Our derivations of the two-, one-, and no-overlap integrals show that it is possible to perform two-center two-electron integrals with real spherical harmonics versus the more commonly used complex spherical harmonics. Instead of relying on the Clebsch-Gordon coefficients for the analytical evaluation of integrals with three complex spherical harmonics, we use Gaunt's formula to analytically integrate products of three associated Legendre functions. We also use a phase factor in the ϕ and ϕ' integrals to write all of the terms as cosine terms and analytically integrate their sum.

As efficient as our computations of the two-center two-electron integrals are, there are many improvements that could be made. Although our adaptive Simpson quadrature subroutine is much improved over the normal Simpson quadrature subroutines used throughout FIREBALL, there do exist more efficient quadrature algorithms such as Gauss-Kronrod and Clenshaw-Curtis quadrature. What's more, these other quadrature methods are much better at handling discontinuities such as those resulting from the Coulomb operator. We have also found that the Monte-Carlo based quadrature rules found in the Cuba library (see [12]) are very efficient at computing these two-electron integrals even when left as six-dimensional integrals. The ability to compute these six-dimensional integrals numerically may lead in the future to the inclusion of three- and four-center integrals.

Bibliography

[1] J. S. Townsend, *A Modern Approach to Quantum Mechanics* (University Science Books, California, 2000).

[2] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, 2nd ed. (Wiley-VCH, New York, 2001).

[3] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Macmillan, New York, 1982).

[4] A. Görling, "Density-functional theory for excited states," Phys. Rev. A **54,** 3912–3915 (1996).

[5] A. Görling and M. Levy, "Exact Kohn-Sham scheme based on perturbation theory," Phys. Rev. A **50,** 196–204 (1994).

[6] X. Gonze and M. Scheffler, "Exchange and Correlation Kernels at the Resonance Frequency: Implications for Excitation Energies in Density-Functional Theory," Phys. Rev. Lett. **82,** 4416–4419 (1999).

[7] O. F. Sankey and D. J. Niklewski, "Ab initio multicenter tight-binding model for molecular-dynamics simulations and other applications in covalent systems," Phys. Rev. B **40,** 3979–3995 (1989).

[8] O. F. Sankey, A. A. Demkov, and W. Windl, “The application of approximate density functionals to complex systems,” International Journal of Quantum Chemistry **69,** 327–340 (1998).

[9] M. A. Blanco, M. Flórez, and M. Bermejo, “Evaluation of the rotation matrices in the basis of real spherical harmonics,” J. Mol. Struct. (Theochem) **419,** 19–27 (1997).

[10] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. I.

[11] M. J. Maron, *Numerical Analysis: A Practical Approach*, 2nd ed. (Macmillan, New York, 1987).

[12] T. Hahn, “Cuba–a library for multidimensional numerical integration,” Computer Physics Communications **168,** 78–95 (2005).

[13] J. D. Jackson, *Classical Electrodynamics*, 3rd ed. (John Wiley & Sons, New York, 1999), p. 23.

Appendix A

Two-electron integral derivations

In the following derivations number subscripts refer to atoms and letter subscripts refer to orbitals. All integrals without limits indicate integration over all space. Let $\boldsymbol{R}_i$ be a vector in the $\boldsymbol{r}$ coordinate system that gives the location of the ith atom and $\phi_\mu(\boldsymbol{r}) = R_\mu(r)\, Y_{l_\mu,m_\mu}(\theta,\varphi)$ be a specific type of orbital (i.e. $\phi_\mu(\boldsymbol{r})$ is a s orbital when $l_\mu = 0$ and $m_\mu = 0$). Each orbital consists of a radial wave function $R_\mu(r)$ and a real spherical harmonic $Y_{l_\mu,m_\mu}(\theta,\phi)$. Thus orbital μ located on atom i can be written as follows: (Diagram and further explanation of θ_i and ϕ_i. The associated Legendre polynomials do not contain the Condon-Shortley factor.)

$$\phi_\mu(\boldsymbol{r}-\boldsymbol{R}_i) = R_\mu(|\boldsymbol{r}-\boldsymbol{R}_i|)\, Y_{l_\mu,m_\mu}(\theta_i,\phi_i) = R_\mu(r_i)\, Y_{l_\mu,m_\mu}(\theta_i,\phi_i)$$

$$= R_\mu(r_i)\left[\frac{(2l_\mu+1)}{4\pi}\frac{(l_\mu-|m_\mu|)!}{(l_\mu+|m_\mu|)!}\right]^{\frac{1}{2}} P_{l_\mu,|m_\mu|}(\cos\theta_i)\begin{cases}\sqrt{2}\sin(|m_\mu|\,\phi_i)\text{ if }m_\mu<0\\ 1\text{ if }m_\mu=0\\ \sqrt{2}\cos(m_\mu\phi_i)\text{ if }m_\mu>0\end{cases}$$

With the above notation a general four-center two-electron integral with the Coulomb kernel can be written as

$$\int d\boldsymbol{r}\phi_A\left(\boldsymbol{r}-\boldsymbol{R}_1\right)\phi_B\left(\boldsymbol{r}-\boldsymbol{R}_2\right)\int d\boldsymbol{r}'\frac{e^2}{\left|\boldsymbol{r}-\boldsymbol{r}'\right|}\phi_C\left(\boldsymbol{r}'-\boldsymbol{R}_3\right)\phi_D\left(\boldsymbol{r}'-\boldsymbol{R}_4\right)$$

$$= e^2\int d\boldsymbol{r}\phi_A\left(\boldsymbol{r}-\boldsymbol{R}_1\right)\phi_B\left(\boldsymbol{r}-\boldsymbol{R}_2\right)$$

$$\int d\boldsymbol{r}'\sum_{l=0}^{\infty}\sum_{m=0}^{l}\left(2-\delta_{m,0}\right)\frac{(l-m)!}{(l+m)!}\left(\frac{r_{1<}^{l}}{r_{1>}^{l+1}}\right)P_l^m\left(\cos\theta\right)$$

$$P_{l,m}\left(\cos\theta'\right)\cos\left[m\left(\phi-\phi'\right)\right]\phi_C\left(\boldsymbol{r}'-\boldsymbol{R}_3\right)\phi_D\left(\boldsymbol{r}'-\boldsymbol{R}_4\right)$$

$$= e^2\sum_{l=0}^{\infty}\sum_{m=0}^{l}\frac{(l-m)!}{(l+m)!}\int d\boldsymbol{r}R_A\left(r_1\right)Y_{l_A,m_A}\left(\theta_1,\phi_1\right)$$

$$R_B\left(r_2\right)Y_{l_B,m_B}\left(\theta_2,\phi_2\right)P_{l,m}\left(\cos\theta\right)\int d\boldsymbol{r}'\left(\frac{r_{1<}^{l}}{r_{1>}^{l+1}}\right)P_{l,m}\left(\cos\theta'\right)$$

$$\left(2-\delta_{m,0}\right)\cos\left[m\left(\phi-\phi'\right)\right]R_C\left(r_3'\right)Y_{l_C,m_C}\left(\theta_3',\phi_3'\right)R_D\left(r_4'\right)Y_{l_D,m_D}\left(\theta_4',\phi_4'\right)$$

$$= e^2\sum_{l=0}^{\infty}\sum_{m=0}^{l}\frac{(l-m)!}{(l+m)!}\int\left(r_1\right)^2dr_1R_A\left(r_1\right)R_B\left(r_2\right)$$

$$\int d\Omega Y_{l_A,m_A}\left(\theta_1,\phi_1\right)Y_{l_B,m_B}\left(\theta_2,\phi_2\right)P_{l,m}\left(\cos\theta\right)$$

$$\int\left(r_1'\right)^2dr_1'\left(\frac{r_{1<}^{l}}{r_{1>}^{l+1}}\right)R_C\left(r_3'\right)R_D\left(r_4'\right)\int d\Omega' Y_{l_C,m_C}\left(\theta_3',\phi_3'\right)Y_{l_D,m_D}\left(\theta_4',\phi_4'\right)$$

$$P_{l,m}\left(\cos\theta'\right)\left(2-\delta_{m,0}\right)\cos\left[m\left(\phi-\phi'\right)\right],$$

where we have used the Addition Theorem for spherical harmonics to replace the $1/\left|\boldsymbol{r}-\boldsymbol{r}'\right|$ term with a double sum of associated legendre polynomials multiplied by cosine terms (see [13]).

A.1 Two-center integrals

Consider the cases where all orbitals are centered on only two atoms. These integrals are commonly known as two-center integrals. We place the center of the first atom at the origin and the center of the second atom a positive distance d from the first atom along the z-axis. One of the benefits of such an arrangement is that $\phi_1 = \phi_2$ and $\phi_1' = \phi_2'$ so we can let $\phi = \phi_1 = \phi_2$ and $\phi' = \phi_1' = \phi_2'$. We call the three unique cases that arise depending on which orbitals lie on which atoms the two-, one-, and no-overlap integrals. The general equation for these integrals is

$$\sum_{l=0}^{\infty}\sum_{m=0}^{l}\frac{(l-m)!}{(l+m)!}\int\left(r_1\right)^2 dr_1 R_A\left(r_1\right) R_B\left(r_{1\,\mathrm{or}\,2}\right)\int d\Omega Y_{l_A,m_A}\left(\theta_1,\phi\right) Y_{l_B,m_B}\left(\theta_{1\,\mathrm{or}\,2},\phi\right)$$
$$P_{l,m}\left(\cos\theta_1\right)\int\left(r_1'\right)^2 dr_1'\left(\frac{r_{1<}^{l}}{r_{1>}^{l+1}}\right) R_C\left(r'_{1\,\mathrm{or}\,2}\right) R_D\left(r_2'\right)\int d\Omega' Y_{l_C,m_C}\left(\theta'_{1\,\mathrm{or}\,2},\phi'\right)$$
$$Y_{l_D,m_D}\left(\theta_2',\phi'\right) P_{l,m}\left(\cos\theta_1'\right)\left(2-\delta_{m,0}\right)\cos\left[m\left(\phi-\phi'\right)\right].$$

Both the ϕ and the ϕ' integrals can be solved analytically after expanding the real spherical harmonics as follows:

$$= \sum_{l=0}^{\infty} \sum_{m=0}^{l} \frac{(l-m)!}{(l+m)!} \int (r_1)^2 \, dr_1 R_A (r_1) \, R_B (r_{1\,\mathrm{or}\,2}) \int d\Omega P_{l,m} (\cos\theta_1)$$

$$\left[\frac{(2l_A+1)}{4\pi} \frac{(l_A - |m_A|)!}{(l_A + |m_A|)!} \right]^{\frac{1}{2}} P_{l_A,|m_A|} (\cos\theta_1) \begin{pmatrix} \sqrt{2} \sin(|m_A| \, \phi) \text{ if } m_A < 0 \\ 1 \text{ if } m_A = 0 \\ \sqrt{2} \cos(m_A \phi) \text{ if } m_A > 0 \end{pmatrix}$$

$$\left[\frac{(2l_B+1)}{4\pi} \frac{(l_B - |m_B|)!}{(l_B + |m_B|)!} \right]^{\frac{1}{2}} P_{l_B,|m_B|} (\cos\theta_{1\,\mathrm{or}\,2}) \begin{pmatrix} \sqrt{2} \sin(|m_B| \, \phi) \text{ if } m_B < 0 \\ 1 \text{ if } m_B = 0 \\ \sqrt{2} \cos(m_B \phi) \text{ if } m_B > 0 \end{pmatrix}$$

$$\int (r_1')^2 \, dr_1' \left(\frac{r_{1<}^{l}}{r_{1>}^{l+1}} \right) R_C (r'_{1\,\mathrm{or}\,2}) \, R_D (r_2') \int d\Omega' P_{l,m} (\cos\theta_1') \, (2 - \delta_{m,0}) \cos[m(\phi - \phi')]$$

$$\left[\frac{(2l_C+1)}{4\pi} \frac{(l_C - |m_C|)!}{(l_C + |m_C|)!} \right]^{\frac{1}{2}} P_{l_C,|m_C|} (\cos\theta'_{1\,\mathrm{or}\,2}) \begin{pmatrix} \sqrt{2} \sin(|m_C| \, \phi') \text{ if } m_C < 0 \\ 1 \text{ if } m_C = 0 \\ \sqrt{2} \cos(m_C \phi') \text{ if } m_C > 0 \end{pmatrix}$$

$$\left[\frac{(2l_D+1)}{4\pi} \frac{(l_D - |m_D|)!}{(l_D + |m_D|)!} \right]^{\frac{1}{2}} P_{l_D,|m_D|} (\cos\theta_2') \begin{pmatrix} \sqrt{2} \sin(|m_D| \, \phi') \text{ if } m_D < 0 \\ 1 \text{ if } m_D = 0 \\ \sqrt{2} \cos(m_D \phi') \text{ if } m_D > 0 \end{pmatrix}$$

$$= \frac{1}{16\pi^2} \sum_{l=0}^{\infty} \sum_{m=0}^{l} \frac{(l-m)!}{(l+m)!} \left[(2l_A+1)\frac{(l_A-|m_A|)!}{(l_A+|m_A|)!}\right]^{\frac{1}{2}} \left[(2l_B+1)\frac{(l_B-|m_B|)!}{(l_B+|m_B|)!}\right]^{\frac{1}{2}}$$

$$\left[(2l_C+1)\frac{(l_C-|m_C|)!}{(l_C+|m_C|)!}\right]^{\frac{1}{2}} \left[(2l_D+1)\frac{(l_D-|m_D|)!}{(l_D+|m_D|)!}\right]^{\frac{1}{2}} \int (r_1)^2\, dr_1 R_A(r_1)\, R_B(r_{1\,\mathrm{or}\,2})$$

$$\int d\Omega P_{l,m}(\cos\theta_1)\, P_{l_A,|m_A|}(\cos\theta_1)\, P_{l_B,|m_B|}(\cos\theta_{1\,\mathrm{or}\,2}) \begin{pmatrix} \sqrt{2}\sin(|m_A|\,\phi)\ \mathrm{if}\ m_A<0 \\ 1\ \mathrm{if}\ m_A=0 \\ \sqrt{2}\cos(m_A\phi)\ \mathrm{if}\ m_A>0 \end{pmatrix}$$

$$\begin{pmatrix} \sqrt{2}\sin(|m_B|\,\phi)\ \mathrm{if}\ m_B<0 \\ 1\ \mathrm{if}\ m_B=0 \\ \sqrt{2}\cos(m_B\phi)\ \mathrm{if}\ m_B>0 \end{pmatrix} \int (r_1')^2\, dr_1' \left(\frac{r_{1<}^{l}}{r_{1>}^{l+1}}\right) R_C(r'_{1\,\mathrm{or}\,2})\, R_D(r_2')$$

$$\int d\Omega' P_{l,m}(\cos\theta_1')\, P_{l_C,|m_C|}(\cos\theta'_{1\,\mathrm{or}\,2})\, P_{l_D,|m_D|}(\cos\theta_2')\,(2-\delta_{m,0})\cos[m(\phi-\phi')]$$

$$\begin{pmatrix} \sqrt{2}\sin(|m_C|\,\phi')\ \mathrm{if}\ m_C<0 \\ 1\ \mathrm{if}\ m_C=0 \\ \sqrt{2}\cos(m_C\phi')\ \mathrm{if}\ m_C>0 \end{pmatrix} \begin{pmatrix} \sqrt{2}\sin(|m_D|\,\phi')\ \mathrm{if}\ m_D<0 \\ 1\ \mathrm{if}\ m_D=0 \\ \sqrt{2}\cos(m_D\phi')\ \mathrm{if}\ m_D>0 \end{pmatrix}$$

$$= \frac{1}{16\pi^2}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{(l-m)!}{(l+m)!}c_{l_A,m_A}c_{l_B,m_B}c_{l_C,m_C}c_{l_D,m_D}\int_0^{\infty}(r_1)^2\,dr_1R_A(r_1)\,R_B(r_{1\,\mathrm{or}\,2})$$

$$\int_0^{\pi}\sin\theta_1 d\theta_1 P_{l,m}(\cos\theta_1)\,P_{l_A,|m_A|}(\cos\theta_1)\,P_{l_B,|m_B|}(\cos\theta_{1\,\mathrm{or}\,2})$$

$$\int_0^{\infty}(r_1')^2\,dr_1'\left(\frac{r_{1<}^{l}}{r_{1>}^{l+1}}\right)R_C(r'_{1\,\mathrm{or}\,2})\,R_D(r_2')$$

$$\int_0^{\pi}\sin\theta_1 d\theta_1' P_{l,m}(\cos\theta_1')\,P_{l_C,|m_C|}(\cos\theta'_{1\,\mathrm{or}\,2})\,P_{l_D,|m_D|}(\cos\theta_2')$$

$$\frac{\pi^2}{\pi^2}\int_0^{2\pi}d\phi_1\begin{pmatrix}\sqrt{2}\sin(|m_A|\,\phi)\,\mathrm{if}\,m_A<0\\ 1\,\mathrm{if}\,m_A=0\\ \sqrt{2}\cos(m_A\phi)\,\mathrm{if}\,m_A>0\end{pmatrix}\begin{pmatrix}\sqrt{2}\sin(|m_B|\,\phi)\,\mathrm{if}\,m_B<0\\ 1\,\mathrm{if}\,m_B=0\\ \sqrt{2}\cos(m_B\phi)\,\mathrm{if}\,m_B>0\end{pmatrix}$$

$$\int_0^{2\pi}d\phi_1'\,(2-\delta_{m,0})\cos\left[m\left(\phi-\phi'\right)\right]$$

$$\begin{pmatrix}\sqrt{2}\sin(|m_C|\,\phi')\,\mathrm{if}\,m_C<0\\ 1\,\mathrm{if}\,m_C=0\\ \sqrt{2}\cos(m_C\phi')\,\mathrm{if}\,m_C>0\end{pmatrix}\begin{pmatrix}\sqrt{2}\sin(|m_D|\,\phi')\,\mathrm{if}\,m_D<0\\ 1\,\mathrm{if}\,m_D=0\\ \sqrt{2}\cos(m_D\phi')\,\mathrm{if}\,m_D>0\end{pmatrix}$$

$$= \frac{1}{16\pi^2}\sum_{l=0}^{\infty}\sum_{m=\mathrm{mmin}}^{\mathrm{mmax}}\frac{(l-m)!}{(l+m)!}c_{l_A,m_A}c_{l_B,m_B}c_{l_C,m_C}c_{l_D,m_D}\int_0^{\infty}(r_1)^2\,dr_1R_A(r_1)\,R_B(r_{1\,\mathrm{or}\,2})$$

$$\int_0^{\pi}\sin\theta_1 d\theta_1 P_{l,m}(\cos\theta_1)\,P_{l_A,|m_A|}(\cos\theta_1)\,P_{l_B,|m_B|}(\cos\theta_{1\,\mathrm{or}\,2})\int_0^{\infty}(r_1')^2\,dr_1'\left(\frac{r_{1<}^{l}}{r_{1>}^{l+1}}\right)$$

$$R_C(r'_{1\,\mathrm{or}\,2})\,R_D(r_2')\int_0^{\pi}\sin\theta_1' d\theta_1' P_{l,m}(\cos\theta_1')\,P_{l_C,|m_C|}(\cos\theta'_{1\,\mathrm{or}\,2})\,P_{l_D,|m_D|}(\cos\theta_2')$$

$$\pi^2\cdot\mathrm{phiphip}\left(m,m_A,m_B,m_C,m_D\right)$$

where we have let

$$c_{l_\mu,m_\mu} = \left[(2l_\mu + 1)\frac{(l_\mu - |m_\mu|)!}{(l_\mu + |m_\mu|)!}\right]^{\frac{1}{2}},$$

$$\text{mmin} = \max\left(||m_A| - |m_B||, ||m_C| - |m_D||\right),$$

$$\text{mmax} = \min\left(||m_A| + |m_B||, ||m_C| + |m_D||, l\right), \text{and}$$

$$\text{phiphip}\left(m, m_{\mu 1}, m_{\mu 2}, m_{\mu 3}, m_{\mu 4}\right) = \frac{1}{\pi^2}\int_0^{2\pi} d\phi \begin{pmatrix} \sqrt{2}\sin\left(|m_{\mu 1}|\,\phi\right) \text{if } m_{\mu 1} < 0 \\ 1 \text{ if } m_{\mu 1} = 0 \\ \sqrt{2}\cos\left(m_{\mu 1}\phi\right) \text{if } m_{\mu 1} > 0 \end{pmatrix}$$

$$\begin{pmatrix} \sqrt{2}\sin\left(|m_{\mu 2}|\,\phi\right) \text{if } m_{\mu 2} < 0 \\ 1 \text{ if } m_{\mu 2} = 0 \\ \sqrt{2}\cos\left(m_{\mu 2}\phi\right) \text{if } m_{\mu 2} > 0 \end{pmatrix} \int_0^{2\pi} d\phi_1'\left(2 - \delta_{m,0}\right)\cos\left[m\left(\phi - \phi'\right)\right]$$

$$\begin{pmatrix} \sqrt{2}\sin\left(|m_{\mu 3}|\,\phi_1'\right) \text{if } m_{\mu 3} < 0 \\ 1 \text{ if } m_{\mu 3} = 0 \\ \sqrt{2}\cos\left(m_{\mu 3}\phi_1'\right) \text{if } m_{\mu 3} > 0 \end{pmatrix} \begin{pmatrix} \sqrt{2}\sin\left(|m_{\mu 4}|\,\phi_1'\right) \text{if } m_{\mu 4} < 0 \\ 1 \text{ if } m_{\mu 4} = 0 \\ \sqrt{2}\cos\left(m_{\mu 4}\phi_1'\right) \text{if } m_{\mu 4} > 0 \end{pmatrix}.$$

For a complete derivation of the phiphip integral see A.4.

$$= \frac{1}{16}\sum_{l=0}^{\infty}\sum_{m=\text{mmin}}^{\text{mmax}} \frac{(l-m)!}{(l+m)!} c_{l_A,m_A} c_{l_B,m_B} c_{l_C,m_C} c_{l_D,m_D}\, \text{phiphip}\left(m, m_A, m_B, m_C, m_D\right)$$
$$\int_0^\infty \left(r_1\right)^2 dr_1 R_A\left(r_1\right) R_B\left(r_{1\,\text{or}\,2}\right) \int_0^\pi \sin\theta_1 d\theta_1 P_l^m\left(\cos\theta_1\right) P_{l_A}^{|m_A|}\left(\cos\theta_1\right)$$
$$P_{l_B}^{|m_B|}\left(\cos\theta_{1\,\text{or}\,2}\right) \int_0^\infty \left(r_1'\right)^2 dr_1' \left(\frac{r_{1<}^l}{r_{1>}^{l+1}}\right) R_C\left(r'_{1\,\text{or}\,2}\right) R_D\left(r_2'\right)$$
$$\int_0^\pi \sin\theta_1' d\theta_1' P_l^m\left(\cos\theta_1'\right) P_{l_C}^{|m_C|}\left(\cos\theta'_{1\,\text{or}\,2}\right) P_{l_D}^{|m_D|}\left(\cos\theta_2'\right) \tag{A.1}$$

A.2 Two-overlap integrals

In our canonical ordering for the two-overlap integrals we place orbitals A and C on atom 1 and orbitals B and D on atom 2. Applying this definition to A.1 allows us to write the general two-overlap integral as

$$
\begin{aligned}
&= \frac{1}{16}\sum_{l=0}^{\infty}\sum_{m=\mathrm{mmin}}^{\mathrm{mmax}}\frac{(l-m)!}{(l+m)!}c_{l_A,m_A}c_{l_B,m_B}c_{l_C,m_C}c_{l_D,m_D}\,\mathrm{phiphip}\left(m,m_A,m_B,m_C,m_D\right)\\
&\int_0^\infty \left(r_1\right)^2 dr_1 R_A\left(r_1\right)R_B\left(r_2\right)\int_0^\pi \sin\theta_1 d\theta_1 P_l^m\left(\cos\theta_1\right)P_{l_A}^{|m_A|}\left(\cos\theta_1\right)\\
&P_{l_B}^{|m_B|}\left(\cos\theta_2\right)\int_0^\infty \left(r_1'\right)^2 dr_1'\left(\frac{r_{1<}^l}{r_{1>}^{l+1}}\right)R_C\left(r_1'\right)R_D\left(r_2'\right)\\
&\int_0^\pi \sin\theta_1' d\theta_1' P_l^m\left(\cos\theta_1'\right)P_{l_C}^{|m_C|}\left(\cos\theta_1'\right)P_{l_D}^{|m_D|}\left(\cos\theta_2'\right).
\end{aligned}
$$

Since the ϕ integrals have already been computed we are only left with integrals in r and θ, which can easily be arranged into polar coordinates:

$$
\begin{aligned}
&= \frac{1}{16}\sum_{l=0}^{\infty}\sum_{m=\mathrm{mmin}}^{\mathrm{mmax}}\frac{(l-m)!}{(l+m)!}c_{l_A,m_A}c_{l_B,m_B}c_{l_C,m_C}c_{l_D,m_D}\,\mathrm{phiphip}\left(m,m_A,m_B,m_C,m_D\right)\\
&\int_0^\infty r_1 dr_1\int_0^\pi d\theta_1 r_1\sin\theta_1 R_A\left(r_1\right)R_B\left(r_2\right)P_l^m\left(\cos\theta_1\right)P_{l_A}^{|m_A|}\left(\cos\theta_1\right)P_{l_B}^{|m_B|}\left(\cos\theta_2\right)\\
&\int_0^\infty r_1' dr_1'\int_0^\pi d\theta_1' r_1'\sin\theta_1'\left(\frac{r_{1<}^l}{r_{1>}^{l+1}}\right)R_C\left(r_1'\right)R_D\left(r_2'\right)\\
&P_l^m\left(\cos\theta_1'\right)P_{l_C}^{|m_C|}\left(\cos\theta_1'\right)P_{l_D}^{|m_D|}\left(\cos\theta_2'\right)
\end{aligned}
$$

Now we switch from polar coordinates to cartesian coordinates: $\rho = r\sin\theta$, $z = r\cos\theta$, $\tan\theta = \frac{\rho}{z}$, $r = \sqrt{\rho^2+z^2}$, $\int_0^\infty rdr\int_0^\pi d\theta_1 = \int_{-\infty}^\infty dz\int_0^\infty d\rho$. To shorten the derivation we continue to use the r variable but with the understanding that it is now a function of z and ρ: $r_1\left(z,\rho\right) = \sqrt{z^2+\rho^2}$, $r_2\left(z,\rho\right) = \sqrt{\left(z-d\right)^2+\rho^2}$. With this notation we can write $\sin\theta_1 = \rho/r_1$, $\cos\theta_1 = z/r_1$, and $\cos\theta_2 = \left(z-d\right)/r_2$. Since $\rho_1 = \rho_2$ we let $\rho = \rho_1 = \rho_2$ so that the two-overlap equation becomes:

$$
\begin{aligned}
&= \frac{1}{16}\sum_{l=0}^{\infty}\sum_{m=\mathrm{mmin}}^{\mathrm{mmax}}\frac{(l-m)!}{(l+m)!}c_{l_A,m_A}c_{l_B,m_B}c_{l_C,m_C}c_{l_D,m_D}\,\mathrm{phiphip}\left(m,m_A,m_B,m_C,m_D\right)\\
&\int_{-\infty}^\infty dz_1\int_0^\infty d\rho r_1\frac{\rho}{r_1}R_A\left(r_1\right)R_B\left(r_2\right)P_l^{|m|}\left(\frac{z_1}{r_1}\right)P_{l_A}^{|m_A|}\left(\frac{z_1}{r_1}\right)P_{l_B}^{|m_B|}\left(\frac{z_2}{r_2}\right)\\
&\int_{-\infty}^\infty dz_1'\int_0^\infty d\rho' r_1'\frac{\rho'}{r_1'}\left(\frac{r_{1<}^l}{r_{1>}^{l+1}}\right)R_C\left(r_1'\right)R_D\left(r_2'\right)P_l^{|m|}\left(\frac{z_1'}{r_1'}\right)P_{l_C}^{|m_C|}\left(\frac{z_1'}{r_1'}\right)P_{l_D}^{|m_D|}\left(\frac{z_2'}{r_2'}\right)
\end{aligned}
$$

Since our orbitals are FIREBALL orbitals (see [7]) they have finite radial cutoffs that we will write as rc_A, rc_B, rc_C, and rc_D. These finite cutoffs affect the limits of integration as follows: (see diagrams for more info)

$$= \frac{1}{16} \sum_{l=0}^{\infty} \sum_{m=\mathrm{mmin}}^{\mathrm{mmax}} \frac{(l-m)!}{(l+m)!} c_{l_A,m_A} c_{l_B,m_B} c_{l_C,m_C} c_{l_D,m_D} \,\mathrm{phiphip}\,(m, m_A, m_B, m_C, m_D)$$

$$\int_{\max(-\mathrm{rc}_A, d-\mathrm{rc}_B)}^{\min(\mathrm{rc}_A, d+\mathrm{rc}_B)} dz_1 \int_0^{\min\left(\sqrt{\mathrm{rc}_A^2 - z_1^2}, \sqrt{\mathrm{rc}_B^2 - z_2^2}\right)} d\rho_1 \rho_1 R_A(r_1) R_B(r_2) P_l^m\left(\frac{z_1}{r_1}\right)$$

$$P_{l_A}^{|m_A|}\left(\frac{z_1}{r_1}\right) P_{l_B}^{|m_B|}\left(\frac{z_2}{r_2}\right) \int_{\max(-\mathrm{rc}_C, d-\mathrm{rc}_D)}^{\min(\mathrm{rc}_C, d+\mathrm{rc}_D)} dz_1' \int_0^{\min\left(\sqrt{\mathrm{rc}_C^2 - \left(z_1'\right)^2}, \sqrt{\mathrm{rc}_D^2 - \left(z_2'\right)^2}\right)} d\rho_1'$$

$$\rho_1' \left(\frac{r_{1<}^l}{r_{1>}^{l+1}}\right) R_C(r_1') R_D(r_2') P_l^m\left(\frac{z_1'}{r_1'}\right) P_{l_C}^{|m_C|}\left(\frac{z_1'}{r_1'}\right) P_{l_D}^{|m_D|}\left(\frac{z_2'}{r_2'}\right)$$

A.3 One- and no-overlap integrals

Now we consider the cases where both orbitals A and B are on atom 1 and therefore are centered at the origin.

$$= \frac{1}{16} \sum_{l=0}^{\infty} \sum_{m=\mathrm{mmin}}^{\mathrm{mmax}} \frac{(l-m)!}{(l+m)!} c_{l_A,m_A} c_{l_B,m_B} c_{l_C,m_C} c_{l_D,m_D} \,\mathrm{phiphip}\,(m, m_A, m_B, m_C, m_D)$$

$$\int_0^{\infty} (r_1)^2 dr_1 R_A(r_1) R_B(r_1) \int_0^{\pi} \sin\theta_1 d\theta_1 P_l^m(\cos\theta_1) P_{l_A}^{|m_A|}(\cos\theta_1) P_{l_B}^{|m_B|}(\cos\theta_1)$$

$$\int_0^{\infty} (r_1')^2 dr_1' \left(\frac{r_{1<}^l}{r_{1>}^{l+1}}\right) R_C\left(r'_{1\,\mathrm{or}\,2}\right) R_D(r_2') \int_0^{\pi} \sin\theta_1' d\theta_1'$$

$$P_l^m(\cos\theta_1') P_{l_C}^{|m_C|}\left(\cos\theta'_{1\,\mathrm{or}\,2}\right) P_{l_D}^{|m_D|}(\cos\theta_2')$$

Since the $\mathrm{phiphip}\,(m, m_A, m_B, m_C, m_D)$ function must have $m = |m_A| + |m_B|$ or $|m_A| = m + |m_B|$ or $|m_B| = m + |m_A|$ to be nonzero we can apply Gaunt's formula to the θ_1 integral after a simple change of variables ($u = \cos\theta_1$) and multiplication by $2 \cdot \frac{1}{2} = 1$:

$$= \frac{1}{16} \sum_{l=0}^{\infty} \sum_{m=\mathrm{mmin}}^{\mathrm{mmax}} \frac{(l-m)!}{(l+m)!} c_{l_A,m_A} c_{l_B,m_B} c_{l_C,m_C} c_{l_D,m_D} \,\mathrm{phiphip}\,(m, m_A, m_B, m_C, m_D)$$
$$\int_0^{\infty} (r_1)^2 \, dr_1 R_A(r_1) R_B(r_1) (2) \left(\frac{1}{2} \int_{-1}^{1} du P_l^m(u) P_{l_A}^{|m_A|}(u) P_{l_B}^{|m_B|}(u) \right)$$
$$\int_0^{\infty} (r_1')^2 \, dr_1' \left(\frac{r_{1<}^l}{r_{1>}^{l+1}} \right) R_C(r_{1\,\mathrm{or}\,2}') R_D(r_2') \int_0^{\pi} \sin\theta_1' d\theta_1' P_l^m(\cos\theta_1')$$
$$P_{l_C}^{|m_C|}(\cos\theta_{1\,\mathrm{or}\,2}') P_{l_D}^{|m_D|}(\cos\theta_2')$$

$$= \frac{1}{8} \sum_{l=\mathrm{lmin}}^{\mathrm{lmax}} \sum_{m=\mathrm{mmin}}^{\mathrm{mmax}} \frac{(l-m)!}{(l+m)!} c_{l_A,m_A} c_{l_B,m_B} c_{l_C,m_C} c_{l_D,m_D} \,\mathrm{phiphip}\,(m, m_A, m_B, m_C, m_D)$$
$$\mathrm{gaunt}\,(l, m, l_A, m_A, l_B, m_B) \int_0^{\min(\mathrm{rc}_A,\mathrm{rc}_B)} (r_1)^2 \, dr_1 R_A(r_1) R_B(r_1) \int_0^{\infty} (r_1')^2 \, dr_1'$$
$$\left(\frac{r_{1<}^l}{r_{1>}^{l+1}} \right) R_C(r_{1\,\mathrm{or}\,2}') R_D(r_2') \int_0^{\pi} \sin\theta_1' d\theta_1' P_l^m(\cos\theta_1') P_{l_C}^{|m_C|}(\cos\theta_{1\,\mathrm{or}\,2}') P_{l_D}^{|m_D|}(\cos\theta_2')$$

$$= \frac{1}{8} \sum_{l=\mathrm{lmin}}^{\mathrm{lmax}} \sum_{m=\mathrm{mmin}}^{\mathrm{mmax}} \frac{(l-m)!}{(l+m)!} c_{l_A,m_A} c_{l_B,m_B} c_{l_C,m_C} c_{l_D,m_D} \,\mathrm{phiphip}\,(m, m_A, m_B, m_C, m_D)$$
$$\mathrm{gaunt}\,(l, m, l_A, m_A, l_B, m_B) \int_0^{\infty} (r_1')^2 \, dr_1' R_C(r_{1\,\mathrm{or}\,2}') R_D(r_2') \int_0^{\pi} \sin\theta_1' d\theta_1'$$
$$P_l^m(\cos\theta_1') P_{l_C}^{|m_C|}(\cos\theta_{1\,\mathrm{or}\,2}') P_{l_D}^{|m_D|}(\cos\theta_2')$$
$$\int_0^{\min(\mathrm{rc}_A,\mathrm{rc}_B)} (r_1)^2 \, dr_1 \left(\frac{r_{1<}^l}{r_{1>}^{l+1}} \right) R_A(r_1) R_B(r_1),$$

where we have let lmin and lmax be as defined by the triangular condition given in [10].

Since the r_1 integral has no dependence on d we can compute it once for all d and then store it as a function of r_1':

$$\mathrm{r1\,integral}_{A,B}(r_1') = \int_0^{\min(\mathrm{rc}_A,\mathrm{rc}_B)} (r_1)^2 \, dr_1 \left(r_{1<}^l / r_{1>}^{l+1} \right) R_A(r_1) R_B(r_1),$$

for each pair of orbitals A and B. Since we only store the integral for discrete values of r_1' we must interpolate when using this function in the remaining integrals. Using this function we can once again simplify the one- and no-overlap integrals:

$$= \frac{1}{8}\sum_{l=\mathrm{lmin}}^{\mathrm{lmax}}\sum_{m=\mathrm{mmin}}^{\mathrm{mmax}}\frac{(l-m)!}{(l+m)!}c_{l_A,m_A}c_{l_B,m_B}c_{l_C,m_C}c_{l_D,m_D}\,\mathrm{phiphip}\left(m,m_A,m_B,m_C,m_D\right)$$

$$\mathrm{gaunt}\left(l,m,l_A,m_A,l_B,m_B\right)\int_0^\infty \left(r_1'\right)^2 dr_1' R_C\left(r_{1\,\mathrm{or}\,2}'\right) R_D\left(r_2'\right)$$

$$\int_0^\pi \sin\theta_1' d\theta_1' P_l^{|m|}\left(\cos\theta_1'\right) P_{l_C}^{|m_C|}\left(\cos\theta_{1\,\mathrm{or}\,2}'\right) P_{l_D}^{|m_D|}\left(\cos\theta_2'\right) \mathrm{r1\,integral}_{A,B}\left(r_1'\right).$$

As in the two-overlap case we convert the remaining integrals to cartesian coordinates:

$$= \frac{1}{8}\sum_{l=\mathrm{lmin}}^{\mathrm{lmax}}\sum_{m=\mathrm{mmin}}^{\mathrm{mmax}}\frac{(l-|m|)!}{(l+|m|)!}c_{l_A,m_A}c_{l_B,m_B}c_{l_C,m_C}c_{l_D,m_D}\,\mathrm{phiphip}\left(m,m_A,m_B,m_C,m_D\right)$$

$$\mathrm{gaunt}\left(l,m,l_A,m_A,l_B,m_B\right)\int_{-\infty}^\infty dz_1' \int_0^\infty d\rho_1' r_1' \frac{\rho_1'}{r_1'} R_C\left(r_{1\,\mathrm{or}\,2}'\right) R_D\left(r_2'\right)$$

$$P_l^m\left(\frac{z_1'}{r_1'}\right) P_{l_C}^{|m_C|}\left(\frac{z_1'}{r_1'}\ \mathrm{or}\ \frac{z_2'}{r_2'}\right) P_{l_D}^{|m_D|}\left(\frac{z_2'}{r_2'}\right) \mathrm{r1\,integral}_{A,B}\left(r_1'\right)$$

A.3.1 One-overlap integrals

We call the integrals with orbital C on atom one the one-overlap integrals so their general formula is

$$\frac{1}{8}\sum_{l=\mathrm{lmin}}^{\mathrm{lmax}}\sum_{m=\mathrm{mmin}}^{\mathrm{mmax}}\frac{(l-|m|)!}{(l+|m|)!}c_{l_A,m_A}c_{l_B,m_B}c_{l_C,m_C}c_{l_D,m_D}\,\mathrm{phiphip}\left(m,m_A,m_B,m_C,m_D\right)$$

$$\mathrm{gaunt}\left(l,m,l_A,m_A,l_B,m_B\right)\int_{-\infty}^\infty dz_1' \int_0^\infty d\rho_1' \rho_1' R_C\left(r_1'\right) R_D\left(r_2'\right)$$

$$P_l^m\left(\frac{z_1'}{r_1'}\right) P_{l_C}^{|m_C|}\left(\frac{z_1'}{r_1'}\right) P_{l_D}^{|m_D|}\left(\frac{z_2'}{r_2'}\right) \mathrm{r1\,integral}_{A,B}\left(r_1'\right)$$

$$= \frac{1}{8}\sum_{l=\mathrm{lmin}}^{\mathrm{lmax}}\sum_{m=\mathrm{mmin}}^{\mathrm{mmax}}\frac{(l-|m|)!}{(l+|m|)!}c_{l_A,m_A}c_{l_B,m_B}c_{l_C,m_C}c_{l_D,m_D}\,\mathrm{phiphip}\left(m,m_A,m_B,m_C,m_D\right)$$

$$\mathrm{gaunt}\left(l,m,l_A,m_A,l_B,m_B\right)\int_{\max(-\,\mathrm{rc}_C,d-\mathrm{rc}_D)}^{\min(\mathrm{rc}_C,d+\mathrm{rc}_D)} dz_1' \int_0^{\min\left(\sqrt{\mathrm{rc}_C^2-z_1^2},\sqrt{\mathrm{rc}_D^2-z_2^2}\right)} d\rho_1'$$

$$\rho_1'\left(\frac{r_{1<}^l}{r_{1>}^{l+1}}\right) R_C\left(r_1'\right) R_D\left(r_2'\right) P_l^m\left(\frac{z_1'}{r_1'}\right) P_{l_C}^{|m_C|}\left(\frac{z_1'}{r_1'}\right) P_{l_D}^{|m_D|}\left(\frac{z_2'}{r_2'}\right) \mathrm{r1\,integral}_{A,B}\left(r_1'\right).$$

A.3.2 No-overlap integrals

We call the integrals with orbital C on atom 2 the no-overlap integrals so their general formula is

$$\frac{1}{8}\sum_{l=\mathrm{lmin}}^{\mathrm{lmax}}\sum_{m=\mathrm{mmin}}^{\mathrm{mmax}}\frac{(l-m)!}{(l+m)!}c_{l_A,m_A}c_{l_B,m_B}c_{l_C,m_C}c_{l_D,m_D}\,\mathrm{phiphip}\left(m,m_A,m_B,m_C,m_D\right)$$
$$\mathrm{gaunt}\left(l,m,l_A,m_A,l_B,m_B\right)\int_{-\infty}^{\infty}dz_1'\int_0^{\infty}d\rho_1'\rho_1'\left(\frac{r_{1<}^{l}}{r_{1>}^{l+1}}\right)$$
$$R_C\left(r_2'\right)R_D\left(r_2'\right)P_l^m\left(\frac{z_1'}{r_1'}\right)P_{l_C}^{|m_C|}\left(\frac{z_2'}{r_2'}\right)P_{l_D}^{|m_D|}\left(\frac{z_2'}{r_2'}\right)\mathrm{r1\,integral}_{A,B}\left(r_1'\right)$$

$$=\frac{1}{8}\sum_{l=\mathrm{lmin}}^{\mathrm{lmax}}\sum_{m=\mathrm{mmin}}^{\mathrm{mmax}}\frac{(l-m)!}{(l+m)!}c_{l_A,m_A}c_{l_B,m_B}c_{l_C,m_C}c_{l_D,m_D}\,\mathrm{phiphip}\left(m,m_A,m_B,m_C,m_D\right)$$
$$\mathrm{gaunt}\left(l,m,l_A,m_A,l_B,m_B\right)\int_{\max(d-\mathrm{rc}_C,d-\mathrm{rc}_D)}^{\min(d+\mathrm{rc}_C,d+\mathrm{rc}_D)}dz_1'\int_0^{\min\left(\sqrt{\mathrm{rc}_C^2-\left(z_2'\right)^2},\sqrt{\mathrm{rc}_D^2-\left(z_2'\right)^2}\right)}d\rho_1'$$
$$\rho_1'\left(\frac{r_{1<}^{l}}{r_{1>}^{l+1}}\right)R_C\left(r_2'\right)R_D\left(r_2'\right)P_l^m\left(\frac{z_1'}{r_1'}\right)P_{l_C}^{|m_C|}\left(\frac{z_2'}{r_2'}\right)P_{l_D}^{|m_D|}\left(\frac{z_2'}{r_2'}\right)\mathrm{r1\,integral}_{A,B}\left(r_1'\right).$$

A.4 Phi and phi prime integral

The combined ϕ, ϕ' integral is used in all of our two-center integrals. We only consider $m \geqslant 0$ and $m, m_1, m_2, m_3, m_4 \in \mathbb{I}$ since the loop over m is nonnegative and all of the m values must be integers. The derivation proceeds as follows:

$$\begin{aligned}
&\operatorname{phiphip}(m, m_1, m_2, m_3, m_4) \\
&= \frac{1}{\pi^2}\int_0^{2\pi} d\phi \begin{pmatrix} \sqrt{2}\sin(|m_1|\,\phi) \text{ if } m_1 < 0 \\ 1 \text{ if } m_1 = 0 \\ \sqrt{2}\cos(m_1\phi) \text{ if } m_1 > 0 \end{pmatrix} \begin{pmatrix} \sqrt{2}\sin(|m_2|\,\phi) \text{ if } m_2 < 0 \\ 1 \text{ if } m_2 = 0 \\ \sqrt{2}\cos(m_2\phi) \text{ if } m_2 > 0 \end{pmatrix} \\
&\quad \int_0^{2\pi} d\phi_1'\,(2-\delta_{m,0})\cos\left[m\left(\phi-\phi'\right)\right] \\
&\quad \begin{pmatrix} \sqrt{2}\sin(|m_3|\,\phi_1') \text{ if } m_3 < 0 \\ 1 \text{ if } m_3 = 0 \\ \sqrt{2}\cos(m_3\phi_1') \text{ if } m_3 > 0 \end{pmatrix} \begin{pmatrix} \sqrt{2}\sin(|m_4|\,\phi_1') \text{ if } m_4 < 0 \\ 1 \text{ if } m_4 = 0 \\ \sqrt{2}\cos(m_4\phi_1') \text{ if } m_4 > 0 \end{pmatrix}
\end{aligned}$$

$$\begin{aligned}
&= \frac{\text{factor}_{m,m_1,m_2,m_3,m_4}}{\pi^2}\int_0^{2\pi} d\phi \begin{pmatrix} \sin(|m_1|\,\phi) \text{ if } m_1 < 0 \\ \cos(m_1\phi) \text{ if } m_1 \geqslant 0 \end{pmatrix} \begin{pmatrix} \sin(|m_2|\,\phi) \text{ if } m_2 < 0 \\ \cos(m_2\phi) \text{ if } m_2 \geqslant 0 \end{pmatrix} \\
&\quad \int_0^{2\pi} d\phi_1'\cos\left[m\left(\phi-\phi'\right)\right] \begin{pmatrix} \sin(|m_3|\,\phi_1') \text{ if } m_3 < 0 \\ \cos(m_3\phi_1') \text{ if } m_3 \geqslant 0 \end{pmatrix} \begin{pmatrix} \sin(|m_4|\,\phi_1') \text{ if } m_4 < 0 \\ \cos(m_4\phi_1') \text{ if } m_4 \geqslant 0 \end{pmatrix}
\end{aligned}$$

where

$$\begin{aligned}
&\text{factor}_{m,m_1,m_2,m_3,m_4} = \begin{pmatrix} 1 \text{ if } m = 0 \\ 2 \text{ if } m \neq 0 \end{pmatrix} \begin{pmatrix} 1 \text{ if } m_1 = 0 \\ \sqrt{2} \text{ if } m_1 \neq 0 \end{pmatrix} \begin{pmatrix} 1 \text{ if } m_2 = 0 \\ \sqrt{2} \text{ if } m_2 \neq 0 \end{pmatrix} \\
&\quad \begin{pmatrix} 1 \text{ if } m_3 = 0 \\ \sqrt{2} \text{ if } m_3 \neq 0 \end{pmatrix} \begin{pmatrix} 1 \text{ if } m_4 = 0 \\ \sqrt{2} \text{ if } m_4 \neq 0 \end{pmatrix}.
\end{aligned}$$

Now we convert the sine terms into cosine terms using the $\sin(\theta) = \cos\left(\theta - \frac{\pi}{2}\right)$ identity:

$$\begin{aligned}
&= \frac{\text{factor}_{m,m_1,m_2,m_3,m_4}}{\pi^2}\int_0^{2\pi} d\phi\cos\left(|m_1|\,\phi + \gamma_1\frac{\pi}{2}\right)\cos\left(|m_2|\,\phi + \gamma_2\frac{\pi}{2}\right) \\
&\quad \int_0^{2\pi} d\phi_1'\cos\left[m\left(\phi-\phi'\right)\right]\cos\left(|m_3|\,\phi + \gamma_3\frac{\pi}{2}\right)\cos\left(|m_4|\,\phi + \gamma_4\frac{\pi}{2}\right)
\end{aligned}$$

where $\gamma_a = \begin{cases} -1\,\text{if}\, m_a < 0 \\ 0\,\text{if}\, m_a \geqslant 0 \end{cases}$ for $a = 1, 2, 3, 4$. Applying the trigonometric identity,

$$\cos\theta\cos\phi = \frac{1}{2}\left[\cos\left(\theta-\phi\right)+\cos\left(\theta+\phi\right)\right],$$

repeatedly until the integrand becomes just a sum of cosine terms gives us:

$$\begin{aligned}
&= \frac{\text{factor}_{m,m_1,m_2,m_3,m_4}}{\pi^2}\int_0^{2\pi}d\phi\int_0^{2\pi}d\phi'_1\frac{1}{16}\sum_{i_1,i_2,i_3,i_4=0}^{1}\cos\{\\
&\quad\left[(-1)^{i_1}|m_1|+(-1)^{i_2}|m_2|-m\right]\phi+\left[(-1)^{i_3}|m_3|+(-1)^{i_4}|m_4|+m\right]\phi'\\
&\quad+\left[(-1)^{i_1}\gamma_1+(-1)^{i_2}\gamma_2+(-1)^{i_3}\gamma_3+(-1)^{i_4}\gamma_4\right]\frac{\pi}{2}\}\\
&= \frac{\text{factor}_{m,m_1,m_2,m_3,m_4}}{16\pi^2}\sum_{i_1,i_2,i_3,i_4=0}^{1}\int_0^{2\pi}d\phi\int_0^{2\pi}d\phi'_1\cos\{\\
&\quad\left[(-1)^{i1}|m_1|+(-1)^{i2}|m_2|-m\right]\phi+\left[(-1)^{i3}|m_3|+(-1)^{i4}|m_4|+m\right]\phi'\\
&\quad+\frac{\pi}{2}\sum_{j=1}^{4}(-1)^{i_j}\gamma_j\Bigg\}
\end{aligned}$$

The $\frac{\pi}{2}\sum_{j=1}^{4}(-1)^{i_j}\gamma_j$ term is the phase and in this particular sum it can take on the values $\frac{m\pi}{2}$ where m ranges from $-4\,\text{to}\,4$. If m is odd then the integrand becomes a $\pm$ sine term and if m is even then the integrand becomes a $\pm$ cosine term. Since $\int_0^{2\pi}d\phi\int_0^{2\pi}d\phi'_1\sin\left[a\phi+b\phi'\right]=0$ and $\int_0^{2\pi}d\phi\int_0^{2\pi}d\phi'_1\cos\left[a\phi+b\phi'\right]=4\pi^2\cdot\delta_{a,0}\cdot\delta_{b,0}$ for all $a, b \in \mathbb{I}$ we have the integral simplifies to:

$$\frac{\text{factor}_{m,m_1,m_2,m_3,m_4}}{16\pi^2} \sum_{i_1,i_2,i_3,i_4=0}^{1} \text{phasefactor}_{\sum_{j=1}^{4}(-1)^{i_j}\gamma_j} \int_0^{2\pi} d\phi \int_0^{2\pi} d\phi_1'$$

$$\cos\left\{\left[(-1)^{i1}|m_1| + (-1)^{i2}|m_2| - m\right]\phi + \left[(-1)^{i3}|m_3| + (-1)^{i4}|m_4| + m\right]\phi'\right\}$$

$$= \frac{\text{factor}_{m,m_1,m_2,m_3,m_4}}{16\pi^2} \sum_{i_1,i_2,i_3,i_4=0}^{1}$$

$$\text{phasefactor}_{\sum_{j=1}^{4}(-1)^{i_j}\gamma_j} \cdot 4\pi^2 \cdot \delta_{(-1)^{i1}|m_1|+(-1)^{i2}|m_2|-m,0} \cdot \delta_{(-1)^{i3}|m_3|+(-1)^{i4}|m_4|+m}$$

$$= \frac{\text{factor}_{m,m_1,m_2,m_3,m_4}}{4} \sum_{i_1,i_2,i_3,i_4=0}^{1}$$

$$\text{phasefactor}_{\sum_{j=1}^{4}(-1)^{i_j}\gamma_j} \cdot \delta_{(-1)^{i1}|m_1|+(-1)^{i2}|m_2|-m,0} \cdot \delta_{(-1)^{i3}|m_3|+(-1)^{i4}|m_4|+m,0}$$

where $\text{phasefactor}_k = \begin{cases} 0 \text{ if } k \text{ is odd} \\ 1 \text{ if } |k| = 0 \text{ or } 4 \\ -1 \text{ if } |k| = 2 \end{cases}$ since $\cos\left(\theta + \frac{0\pi}{2}\right) = \cos(\theta)$, $\cos\left(\theta \pm \frac{\pi}{2}\right) = \mp\sin(\theta)$, $\cos\left(\theta \pm \frac{2\pi}{2}\right) = -\cos(\theta)$, $\cos\left(\theta \pm \frac{3\pi}{2}\right) = \pm\sin(\theta)$, and $\cos\left(\theta \pm \frac{4\pi}{2}\right) = \cos(\theta)$.

Notice that since $m1, m2, m3,$ and $m4$ are all fixed in the delta functions above only a certain range of m values can possibly result in a nonzero integral. Remembering that m can only take on positive values the only values we need consider must be in the interval from $\max(||m_1| - |m_2||, |m_3| - |m_4||)$ to $\min(||m_1| + |m_2||, |m_3| + |m_4||)$.

Note: rather than combine all of the terms into a sum of cosine terms it is also possible to consider the different cases that arise from the product of the four sine or cosine terms (the $\cos[m(\phi - \phi')]$ doesn't change). Six unique cases arise after ordering the numbered m values.

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