MATHEMATICAL TECHNIQUES IN MOLECULAR CALCULATIONS USING SLATER ORBITALS

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Abstract
In this Review we show several mathematical techniques that can be used in molecular calculations using Slater orbitals, like the transformation of the Hamiltonian, derivatives of spherical harmonics with respect to the angles, and angular transformations. We treat several kinds of integrals in detail: the exchange, Coulomb and hybrid repulsion and exchange correlated integrals, and the three-center nuclear attraction ones. The Molecular Orbital (MO) wave function is compared with the elliptical one. It is discussed how MO wave functions using Slater orbitals can be extended to Configuration Interaction and Hylleraas-Configuration Interaction calculations. Finally, some CI calculations on Hydrogen molecule using these techniques are shown.

Keywords: Hylleraas type wave functions, Slater orbitals, MO

1. INTRODUCTION

Slater-type orbitals [1] (STOs) have the natural form of the solutions of the Schrödinger equation for the hydrogen atom. Since almost 80 years of STOs and the accurate Hylleraas calculation on the He atom, the predominancy of the use of Gaussian orbitals, which have the advantage of easier integration techniques, has relegated the use of the Slater ones. The development of the computer technology and the accuracy of the experiments have contributed in the last years to a renewed interest on more accurate approaches based on STOs. The lower number of integrals to be evaluated by using STOs in contrast to large Gaussian basis, as so as the possibility of achieving further than microhartree accuracy ($10^{-6}$ hartrees, in the order the wave number $1 \text{ cm}^{-1}$) when combined with correlation factors like Hylleraas did [2], make the STOs a topic of high importance for the development of new methods of computation. The applications of STOs to atomic and molecular systems have been somehow limited because the mathematical issues concerning the integral evaluation. In this review we go back to the earlier authors and will rescue some concepts from the so-called elliptical method, and will compare with the nowadays existing methods. In the next sections we treat some mathematical issues which are not trivial and may be of use for future workers in the field, like the treatment of charge distributions, angular integration, and other issues and techniques which may be of help in integral evaluation like
the transformation of the Hamiltonian, the derivatives of spherical harmonics and new coordinate transformations. We will treat in more detail the integrals of exchange, Coulomb and Hybrid ones, two-center correlated exchange, as so as one three-center integral. We will show some test calculations using these techniques on the hydrogen molecule. To pass review of all the contributions during the last years exceeds our task, we recall to the reader to see other Chapters in this Volume, as so as the Volume in Ref. [3] and the Reviews Refs. [4, 5]. We instead, after the look to the past, would like to give a look into the future and to call the attention about the performance of highly accurate integral evaluation on molecules, the extension to high precision arithmetic, and the introduction of correlation energy effects.

2. THE MOLECULAR ORBITAL METHOD

The Molecular Orbital method (MO) is the frame in which we propose that accurate molecular calculations can be made. The LCAO (linear combination of atomic orbitals) approximation introduced by Mulliken [6] gives the simplest wave function for a molecular system. As Coulson [7] discusses, the MO method permits the visualization of the electrons and the nuclei and the interpretation of the separate electrons, and gives also an explanation of the screening constants (orbital exponents), better than the wave functions written in elliptical coordinates, whereas these are known to lead to lower energy results. The wave functions in elliptical orbitals are the so-called James-Coodlige [8] wave functions (one-α), recently extended to two-α [9]), Kolos-Wolniewick [10, 11, 12] wave functions (with both orbitals exponents α, and β). Both are applied to the H₂ molecule. They have achieved results of the highest known accuracy in molecules (error of about 10⁻¹² hartree). Another fact is that these wave functions are the natural representation of a two-center problem. For three-center and larger molecules the MO method becomes necessary. Frost [13] used the MO method and the Correlated Molecular Method (CMO) in H₂ calculations. About the extension of the method he wrote: "The extension of CMO-type wave functions to more complex molecules does not seem feasible at the present time. The new integrals which will be introduced would involve more than two centers if more nuclei were involved and higher atomic orbitals than 1s if more electrons were considered, and their evaluation would be extremely difficult". Now the MO method has passed to be called Hartree-Fock if one configuration is involved, or Configuration Interaction (CI) if we have a sum of configurations. The CMO method with the explicit correlation factor is the Hylleraas method (Hy), see the Reviews [14], [15] and Hylleraas-Configuration Interaction method (Hy-CI) introduced by Sims and Hagstrom [16, 17], and independently by Woznicki [18] as Superposition of Correlated Configurations (SCC), which has been applied by Clary and Handy [19, 20] using elliptical STOs, and Clementi et al, this last using Gaussian orbitals [21]. Another type of explicitly correlated wave functions are the ones that use Gaussian orbitals. These are the Exponential Correlated Gaussians (ECG) [22], the interelectronic coordinates appear as exponentials and lead to comparable results to Hylleraas calculations, and the R12-wave function, see Reviews [23, 24, 25] which like Hylleraas-CI applied by Clementi use Gaussian orbitals uses up to one interelectronic coordinate per configuration performing a preliminary CI calculation. The R12 (or recently F12) method can achieve microhartree accurate energy results
for chemically interesting systems. For that, the three- and four-electron integrals are calculated approximately.

In the MO method, the following equation is a more general form of Frost equation, it is the equation for molecules used in Hy-CI calculations. For \( n \) electrons is:

\[
\Psi = \sum_{i=1}^{N} C_i \Phi_i, \quad \Phi_i = \hat{O}(L^2) \hat{A} \phi_i \chi_{ij}^\nu, \quad \nu = 0, 1
\]

where \( N \) is the number of basis functions, \( \hat{O} \) is an operator that projects over the correct space to ensure that the basis functions have the proper angular symmetry, and \( \hat{A} \) is the antisymmetrization operator:

\[
\hat{A} = \sum_{i} (-1)^i \hat{P}_i
\]

\( \chi \) is a spin eigenfunction:

\[
\chi = (\alpha(1)\beta(2) - \beta(1)\alpha(2)) (\alpha(3)\beta(4) - \beta(3)\alpha(4)) \cdots (\alpha(n-1)\beta(n) - \beta(n-1)\alpha(n))
\]

If \( \nu = 0 \) the wave function is a CI wave function. The spatial basis functions \( \phi_i \) are products of molecular orbitals of \( \sigma, \pi \) and \( \delta \) symmetry [26].

\[
\phi_i = \prod_{j=1}^{n} \sigma_j(j)
\]

The basis function \( \phi_0 \) is the ground configuration and corresponds to a Hartree-Fock wave function. If \( \sigma_j \) are equal within a shell, we have the "closed shell" method, if they are different analogously as when using Gaussian orbitals, the "open shell" method. Let us denote \( \sigma'_j \) stands for different exponents of electrons 1 and 2. The splitting of the shell is made with the aim to obtain electron correlation. From the variational principle:

\[
(H - E\Delta)C = 0
\]

the matrix elements are

\[
H_{kl} = \int \Phi_k \hat{H} \Phi_l d\tau, \quad \Delta_{kl} = \int \Phi_k \Phi_l d\tau
\]

with \( \Phi_k = \hat{A} \phi_k \chi \). The expression of the Hamiltonian in Hylleraas coordinates depends of the chosen wave function and will be discussed in a next section. Now let us pass to revise the different methods which can be used and how can look the plan of actual calculations: a \( \sigma \)-CI, \( \sigma, \pi \)-CI or \( \sigma, \pi, \delta \)-CI calculations, attending the type of angular orbitals included. As it is well known the CI wave function introduces \( r^2_{ij} \) implicitly [26]. As \( r^2_{ij} \) is known to be less important than \( r_{ij} \) concerning electron correlation, the CI wave function converges very slowly to the exact nonrelativistic energy. If \( r_{ij} \) is introduced explicitly into the wave function, we have methods which are post-CI. The convergence of the wave function to the exact nonrelativistic eigenvalue is therefore faster. There are two types of Hylleraas methods attending the orbitals used and the number of interelectronic coordinates per configuration. In the strictly Hylleraas method only s- (in atoms), \( \sigma \)-orbitals (in molecules) are used. Until now only S states have been calculated. The Hylleraas calculation of an atom or molecule of
ground state symmetry different of S would request angular orbitals, but in the strictly Hylleraas method no excited configurations are added, such a terms are described using several interelectronic coordinates per basis function. Therefore in the strictly Hylleraas method many-electron integrals have to be solved. Calculations using Hylleraas wave functions are done for \( \text{H}_2 [9] \), using the Iterative CI method [27, 28] which for \( \text{H}_2 \) is equivalent to the Hylleraas method including negative powers of the coordinates \( r_1, r_2 \), and \( \text{HeH}^+ \) and some species [29]. In the Hylleraas-CI method, configurations and excited configurations including up to one \( r_{ij} \) per configuration raised to the power 1, are added to a previous \( \sigma, \pi \)-CI or \( \sigma, \pi, \delta \)-CI wave function, in order to pick up in this way the correlation due to higher angular orbitals \( f, h, \cdots \), which are not explicitly present, as a result the convergence is accelerated. One has here to mention that only the odd powers of \( r_{ij} \) are important, the even powers can be represented as a product of spherical harmonics by the addition theorem. Higher odd powers can also be expressed as even powers times the power one. Therefore the use of only one \( r_{ij} \) per configuration does not suppose any restriction or limitation to the wave function. Because the Hy-CI uses up to one \( r_{ij} \) per configuration, the integrals that appear are up to four-electron ones for any system (atom or molecule). The three-electron and four-electron integrals are known and solved in the case of atoms, see King’s Chapter in this Volume, and in molecules by Budzinski et al, see the corresponding Chapter of this Volume. Actual calculations have been done only in the LiH molecule by Clary and Handy [20] using a basis of elliptical Slater orbitals. We are in our group calculating \( \text{H}_2 \) and larger molecules using this method. Another aspect of the method is the optimization of the orbital exponents and the calculation of the virial factor as a criterium of convergency of the energy [31]. Earlier authors have often used optimization of the orbital exponents [7], [10] in molecular calculations. The optimization may lead to a shorter wave function expansion. In the last section we will show the effect of the orbital optimization in the energy. The calculation only of the atomic and molecular energy it is not enough, it is necessary to calculate atomic and molecular properties, to consider relativistic effects at the same time that correlation for heavy atoms [32]-[34] which chemistry is dominated by the spin-orbit coupling effect, as the relativistic Hy-CI method, see the Chapter in this Volume. The methods using STOs have to be developed for the calculation of properties including expectation values of many simple operators, dipole, quadrupole moment operators, polarizabilities which are response properties linked to optical properties of matter, important in scattering processes and interatomic interactions. And these with high precision (in the calculation of properties one may obtain half of digits of precision than the obtained for the energy [10, 35]). There are some development in this respect, as for example the evaluation of electric field integrals [36], study of the density [37], the calculation of nuclear shielding tensors for Nuclear Magnetic Resonance (NMR) spectroscopy [38] and the calculation of higher electric multipole moments, see corresponding Chapter in this Volume. As the STOs describe the electron density at the nucleus better than Gaussian ones, a great improvement in the calculation of properties by the use of Slater orbitals is expected.

3. THE HAMILTONIAN IN HYLLERAAS COORDINATES

In the Molecular Orbital method (MO) the Slater orbitals are centered on the atoms, and therefore the wave function depends on the distances of the electrons to the centers \( r_{\alpha \nu} \), and the polar angles
of the electrons with respect to the nucleus \( \theta_{i\nu} \) and \( \phi_{i\nu} \), see Figure 1. In addition in Correlated MO (CMO) the wave function depends explicitly on the interelectronic coordinate \( r_{ij} \)

\[
\Psi = \Psi(r_{ij}, \theta_{i\nu}, \phi_{i\nu}) \tag{3.1}
\]

As in the atomic case, which has been studied independently by Ref. [40, 41], and [42, 43], it would be desirable to write the Hamiltonian into the same terms that the wave function because first, it gives us information about the exact wave function and second, it occurs a simplification and separation of the derivatives when calculating the kinetic energy. The derivatives of \( r_{ij} \) with respect to \( \theta_{i\nu} \) and \( \phi_{i\nu} \) (in the application of \( \hat{L}^2 \)) can be done without expanding \( r_{ij} \) by the Neumann expansion. This is because the chain rule of derivation has been used. The nonrelativistic Hamiltonian in the infinite nuclear mass and Born-Oppenheimer approximations for \( n \) electrons and \( N_\mu \) nuclei is (in Hartree atomic units):

\[
\hat{H} = -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \sum_{\mu=1}^{N_\mu} Z_{\nu} \frac{1}{r_{ij}} + \sum_{i<j}^{n} \sum_{\mu<\nu}^{N_\mu} \frac{Z_{\mu} Z_{\nu}}{R_{\mu\nu}} = \hat{H}_S + \hat{H}_L. \tag{3.2}
\]

The kinetic-energy operator is usually written in Cartesian coordinates. The derivatives of the wave function of Eq. (3.1) with respect to \( i.e. \), \( x_{i\nu} \) can be expressed as the sum of all derivatives of the wave function with respect to the Hylleraas coordinates \( r_{ij}, r_{ij}, \theta_{i\nu}, \phi_{i\nu} \) that depend on \( x_{i\nu} \):

\[
\frac{\partial \Psi}{\partial x_{i\nu}} = \sum_{\nu} \frac{\partial \Psi}{\partial r_{i\nu}} \frac{\partial r_{i\nu}}{\partial x_{i\nu}} + \sum_{j \neq i}^{n} \frac{\partial \Psi}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial x_{i\nu}} + \sum_{\nu} \frac{\partial \Psi}{\partial \theta_{i\nu}} \frac{\partial \theta_{i\nu}}{\partial x_{i\nu}} + \sum_{\nu} \frac{\partial \Psi}{\partial \phi_{j\nu}} \frac{\partial \phi_{j\nu}}{\partial x_{i\nu}} \tag{3.3}
\]

and \( \frac{\partial r_{i\mu}}{\partial x_{i\nu}}, \frac{\partial r_{i\mu}}{\partial x_{i\nu}}, \frac{\partial \theta_{i\nu}}{\partial x_{i\nu}} \) and \( \frac{\partial \phi_{j\nu}}{\partial x_{i\nu}} \) can be again written in Hylleraas coordinates. Doing this for \( y_{i\nu} \) and \( z_{i\nu} \) of all electrons and collecting the terms, one can finally extract the Hamiltonian from the eigenvalue equation. The straightforward derivation is given in [44]. The Hamiltonian can be separated into radial and angular part:

\[
\hat{H} = \hat{H}_S + \hat{H}_L \tag{3.4}
\]

where the radial part is equivalent to the atomic case:

\[
\hat{H}_S = -\sum_{i=1}^{n} \sum_{\mu}^{N_\mu} \left( \frac{1}{2} \frac{\partial^2}{\partial r_{i\mu}^2} + \frac{1}{r_{i\mu}} \frac{\partial}{\partial r_{i\mu}} + \frac{Z_{\mu}}{r_{i\mu}} \right) - \sum_{i<j}^{n} \sum_{\mu<\nu}^{N_\mu} \left( \frac{1}{2} \frac{\partial^2}{\partial r_{ij}^2} + \frac{1}{r_{ij}} \frac{\partial}{\partial r_{ij}} \right) + \sum_{i<j}^{n} \frac{1}{r_{ij}}
\]

\[
- \frac{1}{2} \sum_{i=1}^{n} \sum_{\mu<\nu}^{N_\mu} \frac{r_{i\mu}^2 + r_{i\nu}^2 - r_{\mu\nu}^2}{r_{i\mu} r_{i\nu}} \frac{\partial^2}{\partial r_{i\mu} \partial r_{i\nu}} - \frac{1}{2} \sum_{i<j}^{n} \sum_{\mu}^{N_\mu} \frac{r_{i\mu}^2 + r_{ij}^2 - r_{\mu ij}^2}{r_{i\mu} r_{ij}} \frac{\partial^2}{\partial r_{i\mu} \partial r_{ij}}
\]

\[
- \frac{1}{2} \sum_{i<j}^{n} \sum_{j<k}^{n} \frac{r_{ij}^2 + r_{ik}^2 - r_{jk}^2}{r_{ij} r_{ik}} \frac{\partial^2}{\partial r_{ij} \partial r_{ik}} + \sum_{\mu<\nu}^{N_\mu} \frac{Z_{\mu} Z_{\nu}}{R_{\mu\nu}} \tag{3.5}
\]

From the radial part we can extract some information about the wave function. First, the term \( -\frac{\partial^2}{\partial r_{i\mu} \partial r_{i\nu}} \) vanishes in MO wave functions. It will not vanish when \( r_{1a}, r_{1b} \) appear simultaneously in the same term of the wave function. This never occur in the MO method but it happens in the case of elliptical coordinate wave functions, one can see it by multiplying up \( \lambda_{ij}^2 \). This may be the reason why the elliptical wave functions (James-Coolidge and Kolos-Wolniewick) in the case of the
In the MO approximation the angular part of the Hamiltonian is greatly reduced:

$$\hat{H}^{\text{MO}}_{\text{S}} = - \sum_{i=1}^{n} \sum_{\mu}^{N_{\mu}} \left( \frac{1}{2} \frac{\partial^{2}}{\partial r_{ij}^{2}} + \frac{1}{r_{ij}} \frac{\partial}{\partial r_{ij}} + \frac{Z_{\mu}}{r_{ij}} \right) - \sum_{i<j}^{n} \left( \frac{1}{2} \frac{\partial^{2}}{\partial r_{ij}^{2}} + \frac{1}{r_{ij}} \frac{\partial}{\partial r_{ij}} + \frac{1}{r_{ij}} \right) + \sum_{i<j}^{n} \frac{1}{r_{ij}}$$

$$- \frac{1}{2} \sum_{i<j}^{n} \frac{n_{\mu}}{r_{i\mu} r_{j\mu}} \frac{\partial^{2}}{\partial r_{i\mu} \partial r_{j\mu}} - \frac{1}{2} \sum_{i<j}^{n} \sum_{j<k}^{n} \frac{r_{ij}^{2} + r_{jk}^{2} - r_{ik}^{2}}{r_{i\mu} r_{j\mu} r_{k\mu}} \frac{\partial^{2}}{\partial r_{i\mu} \partial r_{j\mu} \partial r_{k\mu}} + \sum_{\mu<\nu}^{N_{\mu} Z_{\mu} Z_{\nu}}$$

(3.6)

The angular part of the operator has more terms:

$$\hat{H}_{\text{L}} = \frac{1}{2} \sum_{i=1}^{n} \sum_{\mu}^{N_{\mu}} \frac{\hat{r}_{i\mu}^{2}}{r_{i\mu}^{2}} - \sum_{i<j}^{n} \sum_{\mu}^{N_{\mu}} \left( \frac{r_{ij} \cos \theta_{ij\mu}}{r_{ij} r_{i\mu} \sin \theta_{i\mu}} + \frac{1}{2} \cot \theta_{ij\mu} \frac{r_{ij}^{2} - r_{ij}^{2} - r_{ij}^{2}}{r_{ij} r_{i\mu} \sin \theta_{i\mu}} \right) \frac{\partial^{2}}{\partial r_{i\mu} \partial \theta_{i\mu}}$$

$$- \sum_{i<j}^{n} \sum_{\mu<\nu}^{N_{\mu}} \frac{r_{ij} \sin \theta_{ij\mu}}{r_{i\mu} r_{j\nu} \sin \theta_{i\nu}} \sin \left( \phi_{ij\mu} - \phi_{j\nu} \right) \frac{\partial^{2}}{\partial r_{i\mu} \partial \phi_{i\nu}}$$

$$- \sum_{i<j}^{n} \sum_{\mu<\nu}^{N_{\mu}} \left( \frac{1}{2} \cot \theta_{i\mu} \cos \theta_{i\nu} \frac{r_{ij}^{2} + r_{ij}^{2} - r_{ij}^{2}}{r_{ij}^{2} r_{i\mu}^{2} r_{i\nu}^{2}} - \frac{\cos^{2} \theta_{i\mu} + \cos^{2} \theta_{i\nu}}{r_{ij} r_{i\mu} \sin \theta_{i\mu} \sin \theta_{i\nu}} \right) \frac{\partial^{2}}{\partial \theta_{i\mu} \partial \theta_{i\nu}}$$

$$- \sum_{i<j}^{n} \sum_{\mu<\nu}^{N_{\mu}} \frac{\cos \left( \phi_{i\mu} - \phi_{i\nu} \right)}{r_{ij} r_{i\mu} \sin \theta_{i\nu} \sin \theta_{i\nu}} \frac{\partial^{2}}{\partial \phi_{i\mu} \partial \phi_{i\nu}}$$

$$- \sum_{i<j}^{n} \sum_{\mu<\nu}^{N_{\mu}} \frac{\cos \theta_{i\mu} \sin \left( \phi_{i\mu} - \phi_{i\nu} \right)}{r_{ij} r_{i\mu} \sin \theta_{i\nu} \sin \theta_{i\nu}} \frac{\partial^{2}}{\partial \theta_{i\mu} \partial \phi_{i\nu}}$$

(3.7)

where the angular momentum operator is:

$$\hat{L}_{ij\mu}^{2} = - \partial^{2}_{\theta_{ij\mu}^{2}} - \cot \theta_{ij\mu} \frac{\partial}{\partial \theta_{ij\mu}} - \frac{1}{\sin^{2} \theta_{ij\mu}} \frac{\partial^{2}}{\partial \phi_{ij\mu}^{2}}$$

(3.8)

and satisfy the eigenvalue equation:

$$\hat{L}^{2}\Phi = l(l + 1)\Phi$$

(3.9)

In the MO approximation the angular part of the Hamiltonian is greatly reduced:

$$\hat{H}^{\text{MO}}_{\text{S}} = \frac{1}{2} \sum_{i=1}^{n} \sum_{\mu}^{N_{\mu}} \hat{L}_{ij\mu}^{2} - \sum_{i<j}^{n} \sum_{\mu}^{N_{\mu}} \left( \frac{r_{ij} \cos \theta_{ij\mu}}{r_{ij} r_{i\mu} \sin \theta_{i\mu}} + \frac{1}{2} \cot \theta_{ij\mu} \frac{r_{ij}^{2} - r_{ij}^{2} - r_{ij}^{2}}{r_{ij} r_{i\mu} \sin \theta_{i\mu}} \right) \frac{\partial^{2}}{\partial r_{ij} \partial \theta_{ij\mu}}$$

$$- \sum_{i<j}^{n} \sum_{\mu}^{N_{\mu}} \frac{r_{ij} \sin \theta_{ij\mu}}{r_{ij} r_{i\mu} \sin \theta_{i\mu}} \sin \left( \phi_{ij\mu} - \phi_{j\mu} \right) \frac{\partial^{2}}{\partial r_{ij} \partial \phi_{ij\mu}}$$

(3.10)
The Hamiltonian can be considered a sum of one electron operators \( \sum_{i=1}^{n} \sum_{\mu} h_{i\mu} \). Also in the angular case we find that the terms which describe the interaction of the same electron over different centers vanish in the case of MO wave functions. The elliptical wave function of James-Coolidge is of radial form and was defined for the \( \text{H}_2 \) molecule. The Kolos-Wolniewicz wave function is elliptical and it has been extended to describe ground states with non-zero angular momentum [47], it takes implicitly into account the following terms of the Hamiltonian:

\[
- \frac{\partial^2}{\partial r_{i\mu} \partial \theta_{i\nu}}, \quad - \frac{\partial^2}{\partial r_{i\mu} \partial \phi_{i\nu}}, \quad - \frac{\partial^2}{\partial \theta_{i\mu} \partial \theta_{i\nu}}, \quad - \frac{\partial^2}{\partial \phi_{i\mu} \partial \phi_{i\nu}} \quad (3.11)
\]

But the Kolos-Wolniewicz wave function differs from the Hy-CI wave function in that the first has not the concept of including excitations to angular orbitals. These terms will not vanish in the case of elliptical angular wave functions. Clary and Handy used in their Hy-CI calculation of the LiH molecule elliptical orbitals. It seems that elliptical wave functions are the better choice for two-center molecules. Nevertheless to extend the use of elliptical wave functions to three-center molecules seems very complex. Finally for a HF and CI wave function the Hamiltonian reduces effectively to:

\[
\hat{H}^{CI} = - \sum_{i=1}^{n} \sum_{\mu} \left( \frac{1}{2} \frac{\partial^2}{\partial r_{i\mu}^2} + \frac{1}{r_{i\mu}} \frac{\partial}{\partial r_{i\mu}} + Z_{\mu} \frac{1}{r_{i\mu}} \right) + \sum_{i<j}^{n} \frac{1}{r_{ij}} + \sum_{\mu<\nu}^{N_{\mu}} \frac{Z_{\mu} Z_{\nu}}{R_{\mu\nu}} + \frac{1}{2} \sum_{i=1}^{n} \sum_{\mu}^{N_{\mu}} \hat{L}_{i\mu}^2 \quad (3.12)
\]

### 4. THE DERIVATIVES OF THE SPHERICAL HARMONICS WITH RESPECT TO THE ANGLES

The evaluation of the radial and angular operator terms of the Hamiltonian of Eq. (3.6) is easy. But to evaluate the angular part of the kinetic energy we need the derivatives of the spherical harmonics with respect to the angles. For that it is necessary the use of recursion relations between spherical harmonics. Let us define the Slater orbitals with an unnormalized radial part and orthonormal spherical harmonics as defined in Ref. [17].

\[
\begin{align*}
\phi^{a*}_{i\mu}(r) &= [n_{i\mu}, l_{i\mu}, m_{i\mu}]^* = r^{n_{i\mu}-1}_{i\mu} e^{-\alpha r_{i\mu}} Y^{m_{i\mu}*}_{l_{i\mu}}(\theta_{i\mu}, \phi_{i\mu}) \\
\phi^{l}_{i\mu}(r) &= [n'_{i\mu}, l'_{i\mu}, m'_{i\mu}] = r^{n'_{i\mu}-1}_{i\mu} e^{-\alpha' r_{i\mu}} Y^{m'_{i\mu}}_{l'_{i\mu}}(\theta_{i\mu}, \phi_{i\mu})
\end{align*}
\]

they are the spherical harmonics of an electron \( i \) with center in \( \mu \), for simplicity we omit the subindexes. The normalize spherical harmonics are defined:

\[
Y^m_l(\theta, \phi) = \left[ \frac{2l + 1}{4\pi} \frac{(l - m)!}{(l + m)!} \right]^{1/2} e^{im\phi} P^m_l(\cos \theta) \quad (4.2)
\]

where \( P^m_l(\cos \theta) \) are the usual Legendre functions, unnormalized. The derivatives of spherical harmonics expressed in terms of spherical harmonics are:

\[
\frac{\partial Y^m_l(\theta, \phi)}{\partial \theta} = m \cot \theta Y^m_l(\theta, \phi) + [(l - m)(l + m + 1)]^{1/2} e^{-i\phi} Y^{m+1}_l(\theta, \phi) \quad (4.3)
\]

\[
\frac{\partial Y^m_l(\theta, \phi)}{\partial \phi} = l \cot \theta Y^m_l(\theta, \phi) - \csc \theta [(l + m)(l - m)]^{1/2} Y^{m-1}_l(\theta, \phi) \quad (4.4)
\]
and a new relation can be obtained by combining Eq. (4.3) with the recursion relation containing the 
cot \theta. From Hobson [48], p. 107, Eq. (40):

$$-\cot(\theta)P_{l}^{m+1}(\cos \theta) = \frac{1}{2(m+1)} \left[ P_{l}^{m+2}(\cos \theta) + (l-m)(l+m+1)P_{l}^{m}(\cos \theta) \right] \quad (4.5)$$

written in terms of spherical harmonics:

$$-\cot \theta Y_{l}^{m+1}(\theta, \phi) = \frac{1}{2(m+1)} \left[ [(l+m+2)(l-m-1)]^{1/2}e^{-i\phi}Y_{l}^{m+2}(\theta, \phi) + [(l-m)(l+m+1)]^{1/2}e^{i\phi}Y_{l}^{m}(\theta, \phi) \right] \quad (4.6)$$

and its complex conjugate:

$$-\cot \theta Y_{l}^{m+1\ast}(\theta, \phi) = \frac{1}{2(m+1)} \left[ [(l+m+2)(l-m-1)]^{1/2}e^{i\phi}Y_{l}^{m+2\ast}(\theta, \phi) + [(l-m)(l+m+1)]^{1/2}e^{-i\phi}Y_{l}^{m\ast}(\theta, \phi) \right] \quad (4.7)$$

substituting Eq. (4.6) into Eq. (4.3), we get:

$$\frac{\partial Y_{l}^{m}(\theta, \phi)}{\partial \theta} = \frac{1}{2} [[(l+m+1)(l-m)]^{1/2}e^{-i\phi}Y_{l}^{m+1}(\theta, \phi) - \frac{1}{2} [[(l-m)(l+m+1)]^{1/2}e^{i\phi}Y_{l}^{m-1}(\theta, \phi) \quad (4.8)$$

In order to obtain recursion relations with \sin \theta, we substract Eq. (3) from Eq. (2) from Ref. [49],
and we obtain the recursion relation:

$$\frac{1}{\sin \theta}P_{l}^{m}(\cos \theta) = \frac{1}{2m} \left[ (l+m+2)(l-m+1)P_{l+1}^{m-1}(\theta) + P_{l+1}^{m+1}(\theta) \right], \quad m \neq 0 \quad (4.9)$$

written in terms of spherical harmonics:

$$\frac{Y_{l}^{m}(\theta, \phi)}{\sin \theta} = -\frac{1}{2m} \frac{2l+1}{(2l+3)} \left[ [(l+m+2)(l-m+1)]^{1/2}e^{i\phi}Y_{l+1}^{m-1}(\theta, \phi) + [(l+m+1)(l+m+2)]^{1/2}e^{-i\phi}Y_{l+1}^{m+1}(\theta, \phi) \right] \quad (4.10)$$

therefore

$$\frac{Y_{l}^{m+1}(\theta, \phi)}{\sin \theta} = \frac{1}{2(m+1)} \left[ [(l-m+1)(l-m)]^{1/2}e^{i\phi}Y_{l+1}^{m}(\theta, \phi) + [(l+m+2)(l+m+3)]^{1/2}e^{-i\phi}Y_{l+1}^{m+2}(\theta, \phi) \right] \quad (4.11)$$

Other recursion relations with the \sin \theta function:

$$\sin \theta Y_{l}^{m}(\theta, \phi) = \left[ \frac{(l+m+1)(l-m+2)}{(2l+3)(2l+1)} \right]^{1/2}e^{i\phi}Y_{l+1}^{m-1}(\theta, \phi) - \left[ \frac{(l-m)(l+m)}{(2l+1)(2l-1)} \right]^{1/2}e^{i\phi}Y_{l-1}^{m-1}(\theta, \phi) \quad (4.12)$$

$$\sin \theta \frac{\partial Y_{l}^{m}(\theta, \phi)}{\partial \theta} = l \cos \theta \partial_{\theta}Y_{l}^{m}(\theta, \phi) - [(l+m)(l-m)]^{1/2}Y_{l-1}^{m}(\theta, \phi) \quad (4.13)$$

Also we need the well-known recursion relation with the \cos(\theta):

$$\cos(\theta)P_{l}^{m}(\cos \theta) = \frac{1}{2(2l+1)} \left[ (l+m)P_{l+1}^{m-1}(\cos \theta) + (l-m+1)P_{l+1}^{m}(\cos \theta) \right] \quad (4.14)$$
written in terms of spherical harmonics:

\[
\cos \theta Y_l^m(\theta, \phi) = \left[ \frac{(l + m)(l - m)}{(2l + 1)(2l - 1)} \right]^{1/2} Y_{l-1}^m(\theta, \phi) + \left[ \frac{(l + m + 1)(l - m + 1)}{(2l + 1)(2l + 31)} \right]^{1/2} Y_{l+1}^m(\theta, \phi) \quad (4.15)
\]

The derivative of a spherical harmonic with respect to \(\phi\) is simple:

\[
\frac{\partial Y_l^m(\theta, \phi)}{\partial \phi} = imY_l^m(\theta, \phi) \quad (4.16)
\]

In the absence of decreasing recursion relations with the \(\sin \theta\), we obtained for the lowest \(l\) quantum numbers and \(m = 0\) the following relations:

\[
-\frac{1}{\sin(\theta)} \frac{\partial Y_l^0(\theta, \phi)}{\partial \theta} = \left[(2l+1)(2l-1)\right]^{1/2} Y_{l-1}^0(\theta, \phi) + \left[(2l+1)(2l-5)\right]^{1/2} Y_{l+3}^0(\theta, \phi) + \cdots \quad l \leq 4 \quad (4.17)
\]

for \(l \geq 5\) other terms appear, the derivation for those cases is straightforward. To evaluate the angular contributions to the kinetic energy for \(m \neq 0\) it is convenient to distinguish between the cases \(m > 0\) and \(m < 0\). For \(l \leq 2\) and some cases when \(l - m \leq 1\), we can write:

\[
\begin{align*}
\frac{1}{\sin(\theta)} Y_l^m &= -\left[ \frac{(2l-1)(2l+1)}{(l+m)(l+m-1)} \right]^{1/2} Y_{l-1}^{m-1}e^{i\phi}, \quad m > 0 \\
\frac{1}{\sin(\theta)} Y_l^m &= -\left[ \frac{(2l-1)(2l+1)}{(l+|m|)(l+|m|-1)} \right]^{1/2} Y_{l-1}^{m+1}e^{-i\phi}, \quad m < 0 \quad (4.18)
\end{align*}
\]

and their complex conjugate

\[
\begin{align*}
\frac{1}{\sin(\theta)} Y_l^{m*} &= -\left[ \frac{(2l-1)(2l+1)}{(l+m)(l+m-1)} \right]^{1/2} Y_{l-1}^{m-1*}e^{-i\phi}, \quad m > 0 \\
\frac{1}{\sin(\theta)} Y_l^{m*} &= -\left[ \frac{(2l-1)(2l+1)}{(l+|m|)(l+|m|-1)} \right]^{1/2} Y_{l-1}^{m+1*}e^{i\phi}, \quad m < 0 \quad (4.19)
\end{align*}
\]

Finally note that:

\[
\sin(\phi_1 - \phi_3) = e^{i\phi_1}e^{-i\phi_3} - e^{-i\phi_1}e^{i\phi_3} \quad (4.20)
\]

it can be written

\[
\sin \theta_3 e^{-i\phi_3} = \frac{\sqrt{8\pi}}{\sqrt{3}} Y_1^{-1}, \quad -\sin \theta_3 e^{i\phi_3} = \frac{\sqrt{8\pi}}{\sqrt{3}} Y_1^1 \quad (4.21)
\]

These relations have been used to calculate the kinetic energy of an electron using a Hylleraas-CI wave function [50].

### 5. Angular Integration of Spherical Harmonics

One method to perform angular integration using spherical harmonics in atoms is to write the integral in the Condon and Shortley form [17, 51]. This method can be transported to the case of molecules. The one-electron radial charge distributions are written like in Ref. [51] as an expansion of Slater orbitals:

\[
\Omega(r) = \chi^*(r)\chi'(r) = \sum_{L_i=|l_i-l_i'|}^{l_i+l_i'} (2L_i+1)^{1/2}C^{L_i}(l_i', m_i'; l_i, m_i)f_i(r) \quad (5.1)
\]
with

\[ f(r) = r^{N_i-1} e^{-\omega r} Y_L^{M_i}(\theta_i, \phi_i), \]  

(5.2)

where \( N_i = n_i + n_i' - 1 \), and the exponents \( \omega_i = \alpha_i + \alpha_i' \). \( L_i = |l_i - l_i'| + 2, \ldots, l_i + l_i' - 2, l_i + l_i' \) and \( M_i = m_i - m_i' \). The charge distributions have been written by expanding the products of spherical harmonics in Eq. (3) using the formula Eq. (12) of Ref. [17]:

\[ Y_{L_i}^{M_i} M_i = \sum_{L} \sum_{M} \frac{(2L + 1)^{1/2}}{(4\pi)^{1/2}} C^L(l', m'; l, m) Y_L^{m'-m}(\theta, \phi) \]  

(5.3)

where the Condon-Shortley [52] coefficients are defined by:

\[ C^L(l', m'; l, m) = \frac{(4\pi)^{1/2}}{(2L + 1)^{1/2}} \int Y_L^{m'-m}(\theta, \phi) Y_{L'}^{m'-m}(\theta, \phi) \sin \theta d\theta d\phi \]  

(5.4)

\( L_i \) satisfy the triangular condition \( |l_i - l_i'| \leq L \leq l_i + l_i' \) and the restriction \( L_i \leq |M_i| \). We solve as an example the angular integral which appears in the four-electron integrals of the Hy-CI method:

\[ I = \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_{L_3}^{M_3}(\theta_1, \phi_1) Y_{L_4}^{M_4}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \]  

(5.5)

using the property of the spherical harmonics:

\[ Y_{L_3}^{M_3}(\theta_1, \phi_1) = (-1)^{M_3} Y_{L_3}^{-M_3*}(\theta_1, \phi_1) \]  

(5.6)

and expanding the product of spherical harmonics using Eq. (5.3) we get:

\[ Y_{L_3}^{-M_3*}(\theta_1, \phi_1) Y_{L_4}^{M_4}(\theta_1, \phi_1) = \sum_{L = |L_3 - L_4|}^{L_3 + L_4} \frac{(2L + 1)^{1/2}}{(4\pi)^{1/2}} C^L(L_4, M_4; L_3, -M_3) Y_L^{M_3 + M_4}(\theta_1, \phi_1) \]  

(5.7)

the integral is then

\[
I = (-1)^{M_3} \sum_{L = |L_3 - L_4|}^{L_3 + L_4} \frac{(2L + 1)^{1/2}}{(4\pi)^{1/2}} C^L(L_4, M_4; L_3, -M_3) \]

\[
\times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_L^{M_3 + M_4}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1
\]  

(5.8)

making again

\[ Y_{L_1}^{M_1}(\theta_1, \phi_1) = (-1)^{M_1} Y_{L_1}^{-M_1*}(\theta_1, \phi_1) \]  

(5.9)

we have put it in the form that it can be evaluated using the Condon and Shortley coefficients definition of Eq. (5.4), as \( M_1 + M_2 + M_3 + M_4 = 0, M_3 + M_4 = -M_1 - M_2 \):

\[ \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_L^{M_3 + M_4}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \]

\[ = (-1)^{M_1} \int_0^\pi \int_0^{2\pi} Y_{L_1}^{-M_1*}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) Y_L^{-M_1 - M_2}(\theta_1, \phi_1) \sin(\theta_1) d\theta_1 d\phi_1 \]

\[ = (-1)^{M_1} \delta(M_1 + M_2 + M_3 + M_4, 0) C^L(L_1, -M_1; L_2, M_2) \frac{(2L + 1)^{1/2}}{(4\pi)^{1/2}} \]  

(5.10)
Finally substituting Eq. (5.10) into Eq. (5.8):

\[
I = (-1)^{M_1+M_3} \delta(M_1 + M_2 + M_3 + M_4, 0) \times \sum_{L=M_3}^{L_3+L_4} (2L+1)C^L(L_4; M_4; L_3, -M_3)C^L(L_1, -M_1; L_2, M_2)
\]

The integration of the angular part leads to an angular coefficient and radial four-electron integrals. Due to the \(\delta\)'s and the Condon and Sorthley coefficients many terms of the summation vanish.

Finally there are some integrals among spherical harmonics containing \(e^{2i\phi_1}\) and \(e^{-2i\phi_1}\) which deserve to be evaluated separately. Two examples are given:

\[
\int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-2}(\theta, \phi_1) Y_{L_2}^{M_2}(\theta, \phi_1) Y_{L_3}^{M_3}(\theta, \phi_1) e^{2i\phi_1} d\Omega_1 =
\]

\[
= \delta(M_1 + M_2 + M_3, 0)(-1)^{M_2} \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-2}(\theta, \phi_1) Y_{L_2}^{M_2}(\theta, \phi_1) Y_{L_3}^{M_3}(\theta, \phi_1) e^{2i\phi_1} d\Omega_1 =
\]

\[
= \delta(M_1 + M_2 + M_3, 0)(-1)^{M_2} \sum_{L=|L_2-L_3|}^{L_2+L_3} (2L+1)^{1/2}C^L(L_3, M_3; L_2, -M_2)
\]

\[
\times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-2}(\theta, \phi_1) Y_{L}^{M}(\theta, \phi_1) e^{2i\phi_1} d\Omega_1
\]

\[
= 2\pi \delta(M_1 + M_2 + M_3, 0)(-1)^{M_2} \sum_{L=|L_2-L_3|}^{L_2+L_3} \left(\frac{2L+1}{(4\pi)^{1/2}} C^L(L_3, M_3; L_2, -M_2)\right)
\]

\[
\left(\int_0^\pi P_{L_1}^{M_1-2} P_L^M \sin(\theta_1) d\theta_1\right)
\]

\[
\left(\int_0^\pi P_{L_1}^{M_1-2} P_L^M \sin(\theta_1) d\theta_1\right) = \delta(L, L_1) \delta(M_1 - 2, M) \left(\frac{(L+M)!}{(2L+1)(L-M)!}\right)
\]

\[
\text{with } M = M_2 + M_3 \text{ and }
\]

\[
\int_0^\pi P_{L_1}^{M_1-2} P_L^M \sin(\theta_1) d\theta_1 = \delta(L, L_1) \delta(M_1 - 2, M) \left(\frac{(L+M)!}{(2L+1)(L-M)!}\right)
\]

\[
\text{(5.13)}
\]

Similarly

\[
\int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1+2}(\theta, \phi_1) Y_{L_2}^{M_2}(\theta, \phi_1) Y_{L_3}^{M_3}(\theta, \phi_1) e^{-2i\phi_1} d\Omega_1
\]

\[
= \delta(M_1, -1) \delta(M_1 + M_2 + M_3, 0)(-1)^{M_2}(2L_1+1)^{1/2}C^{L_1}(L_3, M_3; L_2, -M_2)
\]

\[
\text{(5.14)}
\]

6. THE CONSTRUCTION OF ELLIPTICAL CHARGE DISTRIBUTIONS

We have discussed than in the MO method the orbitals are linear combinations of atomic ones. Once one has to evaluate an integral, a common procedure with the two-center integrals is to change the coordinates to elliptical ones. The great effort that is to write the charge distributions in elliptical
coordinates is usually overlooked. Here we will make some of this derivations following Roothaan et al [53] and Maslen and Trefry [54]. The normalize Legendre functions are defined:

\[ Y_l^m(\theta, \phi) = \mathcal{P}_l^m(\cos \theta) \Phi_m(\phi) \]  \hspace{1cm} (6.1)

\[ \mathcal{P}_l^m(\theta) = \left[ \frac{2l + 1}{4\pi} \frac{(l - m)!}{(l + m)!} \right]^{1/2} P_l^m(\cos \theta), \quad \Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \] \hspace{1cm} (6.2)

The normalize spherical harmonics are defined:

\[ Y_l^m(\theta, \phi) = \left[ \frac{2l + 1}{4\pi} \frac{(l - m)!}{(l + m)!} \right]^{1/2} e^{im\phi} P_l^m(\cos \theta) \] \hspace{1cm} (6.3)

where \( P_l^m(\cos \theta) \) are the usual Legendre functions. Let us take a two center system with elliptical \( \xi, \eta \) coordinates with \( a, b \) as centers with distance \( R \):

\[ r_a = \frac{(\xi + \eta)}{R}, \quad r_b = \frac{(\xi - \eta)}{R} \] \hspace{1cm} (6.4)

using the cosine theorem the angular functions can be expressed in elliptical coordinates, see Figure 2:

\[ r_a^2 = r_b^2 + R^2 - 2r_bR \cos(\theta_b) \] \hspace{1cm} (6.5)

\[ r_b^2 = r_a^2 + R^2 - 2r_aR \cos(\theta_a) \] \hspace{1cm} (6.6)

\[ \cos(\theta_a) = \frac{(1 + \xi \eta)}{(\xi + \eta)}, \quad \cos(\theta_b) = \frac{(1 - \xi \eta)}{(\xi - \eta)} \] \hspace{1cm} (6.7)

and using the sine theorem:

\[ \sin(\theta_a) = \left[ \frac{(\xi^2 - 1)(1 - \eta^2)}{(\xi + \eta)} \right]^{1/2}, \quad \sin(\theta_b) = \left[ \frac{(\xi^2 - 1)(1 - \eta^2)}{(\xi - \eta)} \right]^{1/2} \] \hspace{1cm} (6.8)

Roothaan et al [53] wrote the Slater orbitals in elliptical coordinates:

\[ \chi_a(\xi, \eta, \phi) = \frac{(2\xi)^{n+1/2}}{[(2n)!]^{1/2}} \left( \frac{R}{2} \right)^{n-1} (\xi + \eta)^{n-1} e^{-\frac{R}{2}(\xi+\eta)} \mathcal{P}_l^m \left( \frac{1 + \xi \eta}{\xi + \eta} \right) \Phi_m(\phi) \] \hspace{1cm} (6.9)

expanding the Legendre functions:

\[ \mathcal{P}_l^m(\cos \theta) = \left[ \frac{2l + 1}{4\pi} \frac{(l - m)!}{(l + m)!} \right]^{1/2} (-\sin \theta)^m \sum_{\nu=0}^{[(l-m)/2]} \omega_{\nu}^{lm} \cos \theta^{l-m-2\nu} \] \hspace{1cm} (6.10)

\[ \omega_{\nu}^{lm} = \frac{(-1)^\nu (2l - 2\nu)!}{2^{\nu}(l - m - 2\nu)!(l - \nu)!} \] \hspace{1cm} (6.11)

\([ (l-m)/2 ] \) means the integer part of \((l-m)/2 \). Substituting in Eq. (6.10)

\[ \mathcal{P}_l^m \left( \frac{(1 + \xi \eta)}{(\xi + \eta)} \right) = \left[ \frac{2l + 1}{4\pi} \frac{(l - m)!}{(l + m)!} \right]^{1/2} \left[ \frac{(\xi^2 - 1)(1 - \eta^2)}{(\xi - \eta)} \right]^{m/2} \]

\[ \times \sum_{\nu=0}^{[(l-m)/2]} (-1)^m \omega_{\nu}^{lm} (\xi + \eta)^{2\nu-l}(1 + \xi \eta)^{l-m-2\nu} \] \hspace{1cm} (6.12)
\( \omega_{\nu}^{lm} \) are called by Maslen and Trefry \( p_{\nu}^{lm} \). The charge distributions:

\[
\Omega_{ab}(\xi, \eta, \phi)(\xi^2 - \eta^2) \left( \frac{R}{2} \right)^3 = \left( \frac{R}{2} \right)^3 (\xi^2 - \eta^2)(\xi + \eta)^{n_a - 1}(\xi - \eta)^{n_b - 1}e^{-\alpha \xi e^{\beta \eta}}
\]

\[
\mathcal{P}_{l_a}^{m_a} \left( \frac{1 + \xi \eta}{(\xi + \eta)} \right) \mathcal{P}_{l_b}^{m_b} \left( \frac{(1 - \xi \eta)}{(\xi - \eta)} \right) \Phi_{m_a}^* (\phi) \Phi_{m_b} (\phi) \quad (6.13)
\]

defining

\[
K_{ab} = \left( \frac{R}{2} \right)^{n_a + n_b + 1} (-1)^{m_a + m_b} \left[ \frac{(2l_a + 1)(2l_b + 1)(l_a - m_a)!(l_b - m_b)!}{(l_a + m_a)!(l_b + m_b)!} \right]^{1/2} \quad (6.14)
\]

\[
\omega_{\xi, \eta} = (\xi^2 - \eta^2) \sum_{\nu=0}^{[(l_a - m_a)/2]} \sum_{\mu=0}^{[(l_b - m_b)/2]} \omega_{\nu}^{l_a} \omega_{\mu}^{l_b} (\xi + \eta)^{n_a + 2\nu - l_a - 1}(\xi - \eta)^{n_b + 2\mu - l_b - 1} \nonumber \times (1 + \xi \eta)^{l_a - m_a - 2\nu}(1 - \xi \eta)^{l_b - m_b - 2\mu} \quad (6.15)
\]

using the Binomial theorem in \( \alpha \), and \( \beta \) to combine terms in \( n_a, l_a, m_a \) and also in \( \gamma, \delta \) for \( n_b, l_b, m_b \), calling \( N = n_a + n_b \) and \( L = l_a + l_b \) and defining also

\[
d_{\alpha\beta\gamma}^{m_am_a} = \omega_{\nu}^{l_a} \omega_{\mu}^{l_b} \left( \sum_{\nu=0}^{n_a + 2\nu - l_a - 1} \sum_{\mu=0}^{n_b + 2\mu - l_b - 1} \right) \quad (6.16)
\]

\[
d_{\gamma\delta\mu}^{m_bm_b} = \omega_{\nu}^{l_a} \omega_{\mu}^{l_b} \left( \sum_{\gamma=0}^{n_a + 2\gamma - l_a - 1} \sum_{\delta=0}^{n_b + 2\delta - l_b - 1} \right) \quad (6.17)
\]

also \( p_{\nu}^{m} = \omega_{\nu}^{l_b} (-\gamma)^l \) in Maslen and Trefry [54]. Finally Yasui and Saika [56] gave the expression

\[
\omega_{\xi, \eta} = (\xi^2 - \eta^2) \sum_{\nu=0}^{[(l_a - m_a)/2]} \sum_{\mu=0}^{[(l_b - m_b)/2]} \sum_{\alpha=0}^{n_a + 2\nu - l_a - 1} \sum_{\beta=0}^{n_b + 2\mu - l_b - 1} \sum_{\gamma=0}^{N - L + 2\nu + 2\mu - 2 - \alpha - \gamma + \beta + \delta} \sum_{\delta=0}^{N - M + 2\nu + 2\mu - 2 - \alpha - \gamma + \beta + \delta} d_{\alpha\beta\gamma}^{m_am_a} d_{\gamma\delta\mu}^{m_bm_b} \nonumber \times \xi^{N - L + 2\nu + 2\mu - 2 - \alpha - \gamma + \beta + \delta} \eta^{\alpha + \beta + \gamma + \delta} \quad (6.18)
\]

this is the same than

\[
\omega(\xi, \eta) = \sum_{n=0}^{N-M} \sum_{j=0}^{N-M} \alpha_n - j - a_{nj} - 2 \quad (6.19)
\]

the coefficients \( C_{nj} \) are tabulated by Rüdenberg [55] for the exchange integral. And equal to \( \Xi \) from Maslen and Trefry [54]:

\[
C_{nj} = a_{n-2j} - a_{nj} - 2 \quad (6.20)
\]

where \( a_{n-2j} \) are the Roothaan coefficients. Finally

\[
\Omega_{ab}(\xi, \eta, \phi)(\xi^2 - \eta^2) \left( \frac{R}{2} \right)^3 = \left( \frac{R}{2} \right)^{n_a + n_b + 1} e^{-\alpha \xi e^{\beta \eta} K_{ab} [(\xi^2 - 1)(1 - \eta^2)]^{(m_a + m_b)/2} \omega_{\xi, \eta}^{f_{m_a}^* (\phi)} \Phi_{m_b} (\phi) \quad (6.21)
\]
7. THE COULOMB AND HYBRID INTEGRALS

The Coulomb \([aa, bb]\) and Hybrid \([aa, ab]\) two-electron repulsion integrals can be easily calculated by integrating over the coordinates of one electron. This electron is the one whose charge distribution is located at one center. Afterwards the charge distribution of the other electron is expressed in elliptical coordinates. This method of integration was shown by Slater [57].

The Coulomb integrals for the radial case are:

\[
[aa, bb] = \int dV_1 \int dV_2 \frac{1}{r_{12}^{12}} r_{1a}^{n_a} e^{-\rho_a r_{1a}} r_{2b}^{n_b} e^{-\rho_b r_{2b}}
\]  

(7.22)

which can be shortly written with \(n_a = n_1 + n_{1'}\), \(n_b = n_2 + n_{2'}\), \(p_a = p_1 + p_2\), \(p_b = q_1 + q_2\) as:

\[
[aa, bb] = \int dV_1 \int dV_2 \frac{1}{r_{12}^{12}} r_{1a}^{n_a} e^{-\rho_a r_{1a}} r_{2b}^{n_b} e^{-\rho_b r_{2b}}
\]  

(7.23)

First we integrate over the electron 1 in polar coordinates, for this we express \(\frac{1}{r_{12}}\) in polar coordinates also:

\[
\int dV_1 \frac{1}{r_{12}} r_{1a}^{n_a} e^{-\rho_a r_{1a}}
\]  

(7.24)

and the cosine theorem:

\[
r_{12}^{12} = r_{1a}^{2} + r_{2a}^{2} - 2r_{1a} r_{2a} \cos (\cos \theta_{12a})
\]  

(7.25)

\[
\frac{1}{r_{12}} = \sum_{q=0}^{s_{12a}} g_{12a}^{q+1} P_q (\cos \theta_{12a})
\]  

(7.26)

where here \(s_{12a}\) means the smaller from \(r_{1a}\) and \(r_{2a}\), and \(g_{12a}\) is the greater from \(r_{1a}\) and \(r_{2a}\). with

\[
\cos \theta_{12a} = \cos \theta_{1a} \cos \theta_{2a} + \sin \theta_{1a} \sin \theta_{2a} (\sin \phi_{1a} \sin \phi_{2a} + \cos \phi_{1a} \cos \phi_{2a})
\]  

(7.27)

The volume element is \(dV = r_{1a}^{2} \sin(\theta_{1a}) dr_{1a} d\theta_{1a} d\phi_{1a}\). The angular integration lead in this case to a factor \(4\pi\) for \(q = 0\):

\[
\int dV_1 \frac{1}{r_{12}} r_{1a}^{n_a} e^{-\rho_a r_{1a}} = 4\pi \int_{0}^{\infty} r_{1a}^{n_a + 1} e^{-\rho_a r_{1a}} \frac{1}{g_{12a}} r_{1a}^{2} dr_{1a}
\]  

(7.28)

substituting \(g_{12a}\) by \(r_{1a}\) or \(r_{2a}\) and rewriting the integration domains:

\[
4\pi \int_{0}^{\infty} r_{1a}^{n_a + 1} e^{-\rho_a r_{1a}} dr_{1a} = 4\pi \left( \int_{r_{2a}}^{\infty} r_{1a}^{n_a + 1} e^{-\rho_a r_{1a}} dr_{1a} + \int_{0}^{r_{2a}} r_{1a}^{n_a + 2} e^{-\rho_a r_{1a}} dr_{1a} \right)
\]  

(7.29)

using the integral expression

\[
\int t^{k} e^{-\alpha t} dt = -e^{-\alpha t} \sum_{k=0}^{\infty} \frac{k!}{(k-h)!} \alpha^{k-h}, \quad \text{for } k \geq 0
\]  

(7.30)

and considering that \(\int_{0}^{r_{1b}} dr_{2b} = \int_{0}^{\infty} dr_{2b} - \int_{r_{1b}}^{\infty} dr_{2b}\)

\[
\int dV_1 \frac{1}{r_{12}} r_{1a}^{n_a} e^{-\rho_a r_{1a}} = 4\pi \left\{ \sum_{k=0}^{n_a + 1} \frac{(n_a + 1)!}{(n_a + 1 - k)!} \frac{1}{p_a^{k+1}} r_{2a}^{n_a + 1-k} + A^0(n_a + 2; p_a) \right. \]

\[
- \sum_{k=0}^{n_a + 2} \frac{(n_a + 2)!}{(n_a + 2 - k)!} \frac{1}{p_a^{k+1}} r_{2a}^{n_a + 1-k} \right\}
\]  

(7.31)
Multipliying by $r_{2b}^{n_b} e^{-p_{r2b}}$, integrating and defining the basic one-electron elliptical integral [58]:

$$E(n_a, n_b; p_a, p_b) = \int r_a^{n_a} e^{-p_{r1a}} r_b^{n_b} e^{-p_{r2b}} d\tau$$

$$= \left(\frac{R}{2}\right)^{n_a+n_b+3} \int_0^{2\pi} \int_1^\infty \int_{-1}^{1} (\xi + \eta)^{n_a} (\xi - \eta)^{n_b} e^{-\alpha \xi} e^{-\beta \eta} d\xi d\eta d\phi$$

$$= 2\pi \left(\frac{R}{2}\right)^{n_a+n_b+3} \sum_{i=0}^{n_a+1} \sum_{j=0}^{n_b+1} (-1)^i \binom{n_a+1}{i} \binom{n_b+1}{j} A_{n_a+n_b+2-i-j} A_{i+j} B_{i+j}$$

(7.32)

where $\alpha = \frac{R}{2}(p_a + p_b)$, $\beta = \frac{R}{2}(p_a + p_b)$, $n_a, n_b \geq -1$ and the auxiliary integrals:

$$A_n(\alpha) = \int_1^\infty \xi^n e^{-\alpha \xi} d\xi$$

$$B_n(\beta) = \int_{-1}^{1} e^{-\beta \eta} \eta^n d\eta$$

(7.33)

finally the Coulomb integral is

$$[aa, bb] = 4\pi \left\{ \sum_{k=0}^{n_a+1} \frac{(n_a+1)!}{(n_a+1-k)!} \frac{1}{p_a^{k+1}} E(n_a+1-k, n_b; p_a, p_b) 
+ A^0(n_a+2; p_a) E(-1, n_b; 0, p_b) 
- \sum_{k=0}^{n_a+2} \frac{(n_a+2)!}{(n_a+2-k)!} \frac{1}{p_a^{k+1}} E(n_a+1-k, n_b; p_a, p_b) \right\}$$

(7.34)

The Hybrid integral for radial distributions is:

$$[aa, ab] = \int dV_1 \int dV_2 \frac{1}{r_{12}} r_{1a}^{n_1} e^{-p_{r1a}} r_{1a}^{n_1'} e^{-p_{2r1a}} r_{2a}^{n_2} e^{-q_{1r2a}} r_{2b}^{n_2'} e^{-q_{2r2b}}$$

(7.35)

with $n_a = n_1 + n_1'$,

$$[aa, ab] = \int dV_1 \int dV_2 \frac{1}{r_{12}} r_{1a}^{n_a} e^{-p_{r1a}} r_{2a}^{n_2} e^{-q_{1r2a}} r_{2b}^{n_2'} e^{-q_{2r2b}}$$

(7.36)

the integration over electron 1 leads to the same expression than in the case of the Coulomb integral Eq. (7.31) in terms of the coordinate $r_{2a}$, multipliying by the charge distribution of electron 2 and using the basic elliptical integral Eq. (7.32) we get:

$$[aa, ab] = 4\pi \left\{ \sum_{k=0}^{n_a+1} \frac{(n_a+1)!}{(n_a+1-k)!} \frac{1}{p_a^{k+1}} E(n_a+n_2+1-k, n'_2; p_a+q_1, q_2) 
+ A^0(n_a+2; p_a) E(n_2-1, n'_2; q_1, q_2) 
- \sum_{k=0}^{n_a+2} \frac{(n_a+2)!}{(n_a+2-k)!} \frac{1}{p_a^{k+1}} E(n_a+n_2+1-k, n'_2; p_a+q_1, q_2) \right\}$$

(7.37)

These expressions are programmed and lead to highly accurate Coulomb and Hybrid integrals using quadruple precision.
8. THE EXCHANGE INTEGRAL

The first bottle-neck in molecular calculations is the exchange integral, which is very difficult to be calculate with great accuracy. In case of open shell, the exponents of charge distributions are not equal one has to deal with two elliptical exponents \( \alpha, \beta \), and the Neumann expansion does not collapse, it is an infinite expansion. The first important work was the well-known of Rüdenberg [55], but some of the integrals have to be calculated numerically, therefore we return to the elliptical coordinate methods. At the moment the best procedure seems to be the "Ellipsoidal coordinate method" by Fernández-Rico et al [59]. Here we review the treatment which Slater did in his book Ref. [57] and we also apply the earlier methods of James [60], Kotani [61], as so as the more recent of Yasui and Saika [56], Maslen and Trefry [54] and Harris [62]. Our method agrees with the Ellipsoidal coordinate method for \( M=0 \). We will show some results which agree with the ones of Fernández Rico et al method. We illustrate the method in the case of 1s Slater orbitals \( a = \exp(-pr) \), where \( p \) is a non-linear variational parameter. Assume we have two charge distributions \( \Omega \) and \( \Omega' \), and the centers \( a, b \). the exchange integral is \([ab, ab]\):

\[
I = \int dV_1 \int dV_2 \frac{1}{r_{12}} \Omega(1)\Omega'(2) = [\Omega(1)|\Omega'(2)] = [ab, ab] \tag{8.1}
\]

our integral:

\[
I = \int dV_1 \int dV_2 \frac{1}{r_{12}} e^{-p_1r_1a} e^{-p_2r_1b} e^{-q_1r_2a} e^{-q_2r_2b} \tag{8.2}
\]
we transform the coordinates into elliptical ones, see Figure 2:

\[
\begin{align*}
\Omega(1) &= e^{-\alpha_1\xi_1} e^{\beta_1\mu_1}, \quad \alpha_1 = \frac{R}{2}(p_1 + p_2), \quad \beta_1 = \frac{R}{2}(p_1 - p_2) \\
\Omega(2) &= e^{-\alpha_2\xi_2} e^{\beta_2\mu_2}, \quad \alpha_2 = \frac{R}{2}(q_1 + q_2), \quad \beta_2 = \frac{R}{2}(q_1 - q_2)
\end{align*} \tag{8.3}
\]

and the volume element as \( dV = \frac{R^3}{8} (\xi^2 - \mu^2) d\xi d\mu d\phi \). The integral:

\[
[ab, ab] = \frac{R^6}{8^2} \int \int \int \int \int e^{-\alpha_1\xi_1} e^{\beta_1\mu_1}(\xi_1^2 - \mu_1^2) \frac{1}{r_{12}} e^{-\alpha_2\xi_2} e^{\beta_2\mu_2}(\xi_2^2 - \mu_2^2) d\xi_1 d\xi_2 d\mu_1 d\mu_2 d\phi_1 d\phi_2 \tag{8.5}
\]

The Neumann expansion [63]:

\[
\frac{1}{r_{12}} = \frac{2}{R} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-1)^m (2l + 1) \left[ \frac{(l - m)!}{(l + m)!} \right]^2 P_l^m(\xi_1) Q_l^m(\xi_2) P_l^m(\mu_1) P_l^m(\mu_2)e^{im(\phi_1 - \phi_2)} \tag{8.6}
\]
where \( P_l^m \) and \( Q_l^m \) are the Associate Legendre Polynomials of 1. and 2. Kind. \( \xi_1 \) means the smaller of \( \xi_1 \) and \( \xi_2 \), and \( \xi_2 \) the greater of \( \xi_1 \) and \( \xi_2 \). We integrate over \( \phi \), the charge distribution does not depend on the elliptical angle \( \phi \).

\[
\int f(\xi, \mu)e^{im\phi_1} e^{-im\phi_2} d\phi_1 = f(\xi, \mu) e^{-im\phi_2} \int e^{im\phi_1} d\phi_1 = \frac{1}{im} e^{im\phi_1} \bigg|^2_{0} = \frac{1}{im} [e^{2\pi} - 1] = \frac{1}{im} [1 - 1] = 0 \tag{8.7}
\]
only for \( m = 0 \), it leads to a factor \( 2\pi \), and the integral does not vanishes. The same for \( \phi_2 \). For \( m = 0 \) the Neumann expansion for elliptic orbitals is reduced to:

\[
\frac{1}{r_{12}} = 4\pi^2 \frac{2}{R} \sum_{l=0}^{\infty} (-1)^m (2l + 1) P_l(\xi_1) Q_l(\xi_2) P_l(\mu_1) P_l(\mu_2) \tag{8.8}
\]
substituting into the integral equation and reorganizing the terms according to the six-fold integration, we find a linear combination using auxiliary one and two-electron integrals, which will be given in next paragraphs. We have the same two exponents for the both electrons. Therefore the result is an infinite sum.

\[
[1s_a1s_b|1s_a1s_b] = \frac{\pi^2 R^5}{8} \sum_{k=0}^{\infty} (2k+1) \left[ W_k(2,2,\alpha)G^0_k(\beta)^2 - 2W_k(2,0,\alpha)G^0_k(\beta)G^2_k(\beta) \right] + W_k(0,0,\alpha)G^2_k(\beta)^2 \]  

(8.9)

To check this expression we have calculated this integral with four different exponents and compared with Ref. [64]. They agree in 11 decimal digits. For example, our integral \([1s_a1s_b|1s_a1s_b]\) for \(p_{1a} = 0.5, p_{1b} = 1.5, p'_{1a} = 0.8\) and \(p'_{1b} = 1.2\) and \(R = 2.0\) a.u. leads to 0.13529 47202 02196. We use unnormalized orbitals. For equal exponents the equation is still simpler:

\[
[1s_a1s_b|1s_a1s_b] = \frac{\pi^2 R^5}{8} \left[ 4W_0(2,2,\alpha) - \frac{8}{3}W_0(2,0,\alpha) + \frac{4}{9}W_0(0,0,\alpha) \right] + 5W_2(0,0,\alpha)R^2 R^2 \]  

(8.10)

For example for \(\alpha = 2.0 = pR\) we obtain 0.18415 64571 32219 which agrees with Budzinski [64] in 12 decimal figures. A general expression for different s-orbitals with different exponents of given quantum numbers \(n_1, n_2, m_1, m_2\) has been found by Peuker [58]:

\[
[n_1s_am_1s_b|n_2s_am_2s_b] = 4\Pi^2 \left( \frac{R_{ab}}{2} \right)^{n_1+m_1+n_2+m_2+1} \sum_{l=0}^{\infty} (2l+1) \times \\
\times \sum_{k_1=0}^{n_1} \sum_{h_1=0}^{m_1} \sum_{k_2=0}^{n_2} \sum_{h_2=0}^{m_2} \left( \begin{array}{c} n_1 \\ k_1 \end{array} \right) \left( \begin{array}{c} m_1 \\ h_1 \end{array} \right) \left( \begin{array}{c} n_2 \\ k_2 \end{array} \right) \left( \begin{array}{c} m_2 \\ h_2 \end{array} \right) (-1)^{h_1+h_2} \\
\times W_l(n_1+m_1-k_1-h_1, \alpha_1, n_2+m_2-k_2-h_2, \alpha_2)G^{k_1+h_1}(\beta_1)G^{k_2+h_2}(\beta_2) \]  

(8.11)

The first summation is infinite because all exponents are different. Now we pass to discuss the auxiliary functions. In Table 1 we give some values of exchange integrals for different orbital exponents, we have fully reproduced the Table I of Ref. [59].

Now we pass to discuss the auxiliary functions. The accuracy of this method depends on the accuracy with which these auxiliary functions are calculated. We use quadruple precision for all
Table 1: Exchange integrals \([1s_a(1)1s_b(1)|1s_a(2)1s_b(2)]\) with \(p_1 = p_2 = p\) and \(q_1 = q_2 = q\). R=1 a.u. Calculated using quadruple precision.

<table>
<thead>
<tr>
<th>p</th>
<th>q</th>
<th>p q value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.05</td>
<td>0.03121 87817 80736 28752</td>
</tr>
<tr>
<td>0.05</td>
<td>0.10</td>
<td>0.04064 37758 11483 51371</td>
</tr>
<tr>
<td>0.10</td>
<td>0.20</td>
<td>0.08071 15756 75244 29622</td>
</tr>
<tr>
<td>0.10</td>
<td>1.00</td>
<td>0.08414 48845 94643 50994</td>
</tr>
<tr>
<td>0.20</td>
<td>0.50</td>
<td>0.16321 13342 80925 29751</td>
</tr>
<tr>
<td>0.50</td>
<td>5.00</td>
<td>0.04385 00814 31561 14989</td>
</tr>
</tbody>
</table>

integrals, that means real*16. We use the auxiliary integrals defined by James [60] and Kotani [61].

\[
A_n(\alpha) = \int_{1}^{\infty} \xi^n e^{-\alpha \xi} d\xi
\]

\[
B_n(\beta) = \int_{-1}^{+1} e^{-\beta \eta} \eta^n d\eta
\]

\[
R^n_T = \int_{-1}^{+1} P_T(\eta) \eta^n d\eta
\]

\[
G^n_T(\beta) = \int_{-1}^{+1} P_T(\eta) \eta^n e^{-\beta \eta} d\eta
\]

\[
W_{\tau}(m, \alpha_1, n, \alpha_2) = \int_{1}^{\infty} d\xi_1 \int_{1}^{\infty} d\xi_2 Q_0(\frac{\xi_1}{\xi_2}) P_T(\frac{\xi_2}{\xi_1}) \xi_1^m \xi_2^n e^{-\alpha_1 \xi_1 - \alpha_2 \xi_2} \frac{\xi_1 > \xi_2}{\xi_2 > \xi_1}
\]

The integral \(W\) is related to the Rüdenberg’s \(\phi\)-function. A general formula of \(W_{\tau}(m, \alpha_1, n, \alpha_2)\) which James calls \(H(m, \alpha_1, n, \alpha_2)\) is Eq. (49) in Ref. [60]. Denoting \(W_k(m, n, \alpha) = W_{\tau}(m, \alpha_1, n, \alpha_2)\) when \(\alpha = \alpha_1 = \alpha_2\). For the case of equal exponents the corresponding definitions are given by Rosen [65].

\[
W_0(m, \alpha_1, n, \alpha_2) = F_m(\alpha_1) A_n(\alpha_2) + F_m(\alpha_2) B_n(\alpha_1) - T(m, \alpha_1, n, \alpha_2) - T(n, \alpha_2, m, \alpha_1)
\]

\[
W_1(m, \alpha_1, n, \alpha_2) = W_0(m + 1, \alpha_1, n + 1, \alpha_2) - S(m, \alpha_1, n + 1, \alpha_2) - S(n, \alpha_2, m + 1, \alpha_1)
\]

with

\[
F_n(\alpha) = \int_{1}^{\infty} \xi^n e^{-\alpha \xi} Q_0(\xi) d\xi
\]

\[
S(m, \alpha_1, n, \alpha_2) = \int_{1}^{\infty} \xi_1^m e^{-\alpha_1 \xi_1} d\xi_1 \int_{1}^{\xi_1} \xi_2^n e^{-\alpha_2 \xi_2} d\xi_2
\]

\[
T(m, \alpha_1, n, \alpha_2) = \int_{1}^{\infty} \xi_1^m e^{-\alpha_1 \xi_1} Q_0(\xi_1) d\xi_1 \int_{\xi_1}^{\infty} \xi_2^n e^{-\alpha_2 \xi_2} d\xi_2
\]
These can be evaluated through the recurrence relations:

\[
S(m, \alpha_1, n, \alpha_2) = \frac{1}{\alpha_1} [mS(m-1, \alpha_1, n, \alpha_2) + A_{m+n}(\alpha_1 + \alpha_2)]
\] (8.22)

\[
S(0, \alpha_1, n, \alpha_2) = \frac{1}{\alpha_1}A_n(\alpha_1 + \alpha_2)
\] (8.23)

\[
T(m, \alpha_1, n, \alpha_2) = \frac{1}{\alpha_2} [nT(m, \alpha_1, n-1, \alpha_2) + F_{m+n}(\alpha_1 + \alpha_2)]
\] (8.24)

\[
T(m, \alpha_1, 0, \alpha_2) = \frac{1}{\alpha_2}F_m(\alpha_1 + \alpha_2)
\] (8.25)

\[
F_n(\alpha) = F_{n-2}(\alpha) + \frac{1}{\alpha}[nF_{n-1}(\alpha) - (n-2)F_{n-3}(\alpha - A_{n-2}(\alpha)]
\] (8.26)

and the fundamental, see demonstration in Slater book [57]:

\[
F_0(\alpha) = \frac{1}{2} [(\ln 2\alpha + C)(e^{-\alpha}/\alpha) - Ei(-2\alpha)(e^{\alpha}/\alpha)]
\] (8.27)

this expression is also given in detail by Slater book [57], and it can be calculated with the desired accuracy with Maple. Rosen in pag. 2108 of Ref. [65] has an error in Eqs. A9 and A9a instead of \(\ln(2)\) should be \(\ln(2\alpha)\). In Ref. [60] it is correct. Where \(C\) is the Euler constant which we use with the value \(C = 0.57721 56649 01532 86110 65120 90082\). The Euler constant is the value at the limit

\[
\lim \delta \rightarrow 1 \{2Ei(-\alpha R(\sigma - 1)) - Ei(-2\alpha R(\sigma - 1)) - \ln(\sigma - 1)\} = C + \ln(\alpha R) - \ln 2
\] (8.28)

Higher W's are constructed using the recursion relations given by James in Ref. [60]. The first recursion relations are (now with the W notations):

\[
W_1(m, \alpha_1, n, \alpha_2) = 2W_1(m + 1, \alpha_1, n + 1, \alpha_2) - S(m, \alpha_1, n + 1, \alpha_2) - S(n, \alpha_2, m, \alpha_2)
\] (8.29)

\[
W_2(m, \alpha_1, n, \alpha_2) = \frac{1}{4} [9W_1(m + 1, \alpha_1, n + 1, \alpha_2) + W_0(m, \alpha_1, n, \alpha_2) - 3[W_0(m + 2, \alpha_1, n, \alpha_2)
+ W_0(m, \alpha_1, n + 2, \alpha_2) - S(m + 1, \alpha_1, n, \alpha_2) - S(n + 1, \alpha_2, m, \alpha_1)]]
\] (8.30)

Further recursion relations and a general formula can be found in the paper of James Ref. [60]. Yasui and Saika [56] generalized the method to angular orbitals and gave the following recursion relation:

\[
W_i^m(n_1, n_2, \alpha_1, \alpha_2) = (l + 1 - m) \left[ \frac{(l + 2 - m)^2}{2l + 1}W_{l+1}^{m-1}(n_1, n_2, \alpha_1, \alpha_2)
- (l - m)W_i^{m-1}(n_1 + 1, n_2 + 1, \alpha_1, \alpha_2) \right]
+ \frac{(l + m - 1)^2}{2l + 1}(l + m)W_{l-1}^{m-1}(n_1, n_2, \alpha_1, \alpha_2)
\] (8.31)

Further results are given in our paper Ref. [66]. We have tested our exchange integral program with the program DERIC by Hagstrom [67], and also the program of Fernández Rico et al, Ref. [68], see the Chapter in this Volume.

9. THE THREE-CENTER NUCLEAR ATTRACTION INTEGRAL

The three-center nuclear attraction integral has been extensively investigated in the past [72, 73], and in the last years [69, 70, 71]. Our method is based in Hoyland’s method [73], who finally integrated
numerically, we use instead analytical integration [74]. In Figure 3 the conformation of the centers is given. We evaluate the integral for different exponents and arbitrary conformation of the centers. We distinguish two kinds of three-center nuclear attraction integral.

\[
K_{a,n'_ia,n_{ic}s_c} = \int \frac{n'_ia's_b(i) n_{ic}s_c(i)}{r_{ia}} dr_i,
\]

(9.1)

\[
K_{c,n'_ia,n_{ib}s_b} = \int \frac{n'_ia's_a(i) n_{ib}s_b(i)}{r_{ic}} dr_i.
\]

(9.2)

The integrals of Eqs. (9.1,9.2) differ on the location of the charge distribution of the electrons and the third center. Those centers which are involved in the charge distribution are the focii of the elliptic coordinate system and the third atom is external to the elliptical coordinates. This distinction has consequences for the calculation. We have a Neumann expansion where instead of \( \frac{1}{r_{ij}} \) we have \( \frac{1}{r_{ij}} \), that is the distance of the electron (the three-center nuclear attraction are one-electron integrals) to the external center \( \mu \). The evaluation is based on writing the coordinates \( \xi, \eta \) of that external center with respect to the elliptical system. Symmetrical and asymmetrical conformations of integrals Eq. (9.1) can be calculated using:

\[
K_{a,n'_ia,n_{ic}s_c} = \left( \frac{R_{ab}}{2} \right)^{n'_ia+n_{ic}} \pi \sum_{l=0}^{\infty} (2l+1)
\]

\[
P_l(\eta_a) \sum_{k=0}^{\infty} \sum_{h=0}^{\infty} \left( \frac{n'_ib}{k} \right) \left( \frac{n_{ic}}{h} \right) (-1)^{n_{ic}-h} F_{k+h}^{l}(\alpha) G_{l}^{n'_ib+n_{ic}-k-h}(\beta)
\]

(9.3)

where the auxiliary integrals \( G_{k}^{m} \) are defined in Eq. (8.15) and \( F_{n}^{k} \) is the generalization to a higher order of Eq. (8.18):

\[
F_{n}^{k}(\alpha) = \int_{1}^{\infty} Q_k(\xi) \xi^{n} e^{-\alpha \xi} d\xi.
\]

(9.4)

\[
G_{k}^{n}(\beta) = \int_{-1}^{1} P_k(\eta) \eta^{n} e^{-\beta \eta} d\eta.
\]

(9.5)

The evaluation of all conformations of integral Eq. (9.2), and triangular cases of Eq. (9.1) the following formulation be used:

\[
K_{c,n'_ia,n_{ib}s_b} = \left( \frac{R_{ab}}{2} \right)^{n'_ia+n_{ib}} \pi \sum_{l=0}^{\infty} (2l+1)
\]

\[
Q_l(\xi_c) P_l(\eta_c) \sum_{k=0}^{\infty} \sum_{h=0}^{\infty} \left( \frac{n'_ib}{k} \right) \left( \frac{n_{ib}}{h} \right) (-1)^{n_{ib}-h} D_{k+h}^{l}(\xi_c, \alpha) G_{l}^{n'_ib+n_{ib}-k-h}(\beta)
\]

\[
+ P_l(\xi_c) P_l(\eta_c) \sum_{k=0}^{\infty} \sum_{h=0}^{\infty} \left( \frac{n'_ia}{k} \right) \left( \frac{n_{ib}}{h} \right) (-1)^{n_{ib}-h} C_{k+h}^{l}(\xi_c, \alpha) G_{l}^{n'_ia+n_{ib}-k-h}(\beta)
\]

(9.6)

with \( \alpha = \frac{R_{ab}}{2}(p'_{ia} + p_{ib}) \) and \( \beta = \frac{R_{ab}}{2}(p'_{ia} - p_{ib}) \), \( \xi_c = \frac{R_{ac}+R_{bc} \alpha}{R_{ab}} \) and \( \eta_c = \frac{R_{ac}+R_{bc}}{R_{ab}} \). One can see that although the conformations of the centers are free, one can still express the elliptical coordinates of one of the centers focused in the others. Let us call the coordinate \( \xi = x \) in general, where \( x \) is a variable
from $[1, \infty)$ which can be calculated for a given case, using the definition of an elliptic coordinate which depends on the atomic distances:

$$x = \xi_a = \frac{R_{ab} + R_{ac}}{R_{bc}}, \quad x = \xi_b = \frac{R_{ab} + R_{bc}}{R_{ac}}, \quad x = \xi_c = \frac{R_{ac} + R_{bc}}{R_{ab}}. \quad (9.7)$$

Then the auxiliary integrals $D_n^k(\xi_c, \alpha)$ and $C_n^k(\xi_c, \alpha)$ from Eq. (9.6) are redefined as:

$$D_n^k(x, \alpha) = \int_1^x P_k(\xi)\xi^n e^{-\alpha \xi} d\xi \quad (9.8)$$

$$C_n^k(x, \alpha) = \int_x^\infty Q_k(\xi)\xi^n e^{-\alpha \xi} d\xi \quad (9.9)$$

The integrals $D_n^k(\xi_c, \alpha)$ and $C_n^k(\xi_c, \alpha)$ coincide for $m = 0$ with the integrals $K_{l,k}^m$ and $L_{l,k}^m$ of Ref. [59]. The first integral $D_0^k(x, \alpha)$ is solvable by using the recurrence relations:

$$D_0^0(x, \alpha) = \frac{1}{\alpha} (e^{-\alpha} - e^{-\alpha x}) \quad (9.10)$$

$$D_n^0(x, \alpha) = \frac{1}{\alpha} \left( nD_{n-1}^0(x, \alpha) + e^{-\alpha} - x^n e^{-\alpha x} \right) \quad (9.11)$$

$$D_n^k(x, \alpha) = \frac{1}{k} \left( (2k-1)D_{n+1}^{k-1}(x, \alpha) - (k-1)D_n^{k-2}(x, \alpha) \right) \quad (9.12)$$

To obtain Eq. (9.12) the recurrence relation of the Legendre polynomials $P_k$ has been used. The recursion relations necessary to calculate $C_n^k(x, \alpha)$ are:

$$C_0^0(x, \alpha) = \frac{1}{(2\alpha)} \left[ e^{-\alpha x} \ln \left( \frac{x + 1}{x - 1} \right) - e^{\alpha} \text{Ei}(-\alpha(x + 1)) + e^{-\alpha} \text{Ei}(-\alpha(x - 1)) \right] \quad (9.13)$$

$$C_1^0(x, \alpha) = \frac{1}{\alpha} C_0^0(x, \alpha) + \frac{1}{(2\alpha)} \left[ e^{-\alpha x} \ln \left( \frac{x + 1}{x - 1} \right) + e^{\alpha} \text{Ei}(-\alpha(x + 1)) + e^{-\alpha} \text{Ei}(-\alpha(x - 1)) \right] \quad (9.14)$$

$$C_n^0(x, \alpha) = \frac{n}{\alpha} C_{n-1}^0(x, \alpha) + \frac{1}{2\alpha} x^n e^{-\alpha x} \ln \frac{x + 1}{x - 1} - \frac{(-1)^n}{2\alpha} e^{\alpha} \text{Ei}(-\alpha(x + 1)) + \frac{1}{2\alpha} e^{-\alpha} \text{Ei}(-\alpha(x - 1))$$

$$+ \frac{e^{-\alpha x} x^{n-1}}{2} \sum_{i=0}^{n-1} \sum_{j=0}^{i} \frac{(-1)^i (-1)^j (i-j)!}{(i+1)! (i-j)!} \frac{n!}{\alpha^j+2} \quad (9.15)$$

$$C_n^k(x, \alpha) = \frac{1}{k} \left( (2k-1)C_{n+1}^{k-1}(x, \alpha) - (k-1)C_n^{k-2}(x, \alpha) \right) \quad (9.16)$$

and the definition:

$$A_n(x, \alpha) = \frac{e^{-\alpha x}}{\alpha} \sum_{l=0}^{n} \frac{n!}{(n-l)!} \frac{x^{n-l}}{\alpha^l} \quad (9.17)$$

A proof of Eq. (9.15) is given in Ref. [74].

We have compared our results with the ones of Fernández Rico et al [70] by the ellipsoidal coordinate method, reproducing the integral value (Table III) of Ref. [70] with full accuracy (our value has to be multiplied by their normalization constants). In this example, with $R_{ab} = R_{ac} = 3.0$ a.u. and $p_{1,a} = p_{1,b} = 1.6$ our method leads to $0.74157 \ 94666 \ 22132 \ 33784 \times 10^{-1}$ Our integral converge to more than 20 decimal digits because in the case of equal exponents the Neumann expansion breaks
down after some terms. We have also checked our computer program comparing our results with the integral values obtained by Fernández Rico et al [68]. We obtain for the linear asymmetrical conformation $p'_{1a} = p_{1b} = 2.0$, $R_{ab} = 6$ and $R_{ac} = 7$ a.u. (taking into account normalization constants) the value $0.45337\ 75001\ 11513\ 8130 \times 10^{-3}$ which agrees in 11 decimal figures with their value of Table I. The triangular integral of Ref. [70] has been also reproduced. For different exponents $p_{1a} = 3.6$, $p_{1b} = 1.6$, $R_{ab} = 3$, $R_{ac} = \sqrt{18}$ a.u., and $\theta = 45^\circ$, the integral value of $0.27027\ 29019\ 02 \times 10^{-1}$ has been obtained by this method, showing a good agreement with the value of Table IV of Ref. [70].

It is interesting to visualize the three-center nuclear attraction integrals when one of the atoms is very far of the others, the integral looks like a two-center nuclear attraction one. If the atomic center is not involved in the charge distribution, the integral always converges and it is very stable. If the center is involved in the charge distribution, this one is very asymmetrical and the integral does not converge well.

10. TRANSFORMATION OF REAL SLATER ORBITALS INTO ELLIPTICAL ONES

In molecular calculations it is also common to use the so-called "real Slater orbitals" or "real spherical harmonics". Another way to evaluate molecular integrals between Slater molecular orbitals (MO) is to transform the angular charge distributions of real STOs into elliptical ones. We have obtained a transformation based on geometrical considerations without any rotation of the orbitals [75]. As an example we show here the transformation using the orthogonal unnormalized $p_r$, defined as:

\[
\begin{align*}
n_i p_{\nu i}(q_{i\nu}) &= n_i s_{\nu i}(q_{i\nu}) \sin \theta_{i\nu} \sin \varphi_{i\nu}, \\
n_i p_{z\nu i}(q_{i\nu}) &= n_i s_{\nu i}(q_{i\nu}) \cos \theta_{i\nu}, \\
n_i p_{x\nu i}(q_{i\nu}) &= n_i s_{\nu i}(q_{i\nu}) \sin \theta_{i\nu} \cos \varphi_{i\nu}.
\end{align*}
\] (10.1)

With the s-orbitals defined as:

\[
n_i s_{\nu i}(q_{i\nu}) = r_{i\nu}^{n_{i\nu}-1} e^{-q_{i\nu} r_{i\nu}}
\] (10.2)

where $\nu$ denotes the atom $a$ or $b$ and $i$ the electron. $R$ is the distance between the centers. In Fig. 3 the Cartesian and polar coordinates of a two center system are defined. The elliptical coordinates are defined as $\xi$, $\eta$, $\phi$, to distinguish from the polar $\varphi$. The formed parallelepiped keeps some equalities.
It can be seen in Figure 4 that (note that $\varphi_{1b} = 360^\circ - \varphi_{1a}$):

\begin{align*}
x &= r_{1a} \sin(\theta_{1a}) \cos(\varphi_{1a}) = r_{1b} \sin(\theta_{1b}) \cos(\varphi_{1b}) & (10.3) \\
y &= r_{1a} \sin(\theta_{1a}) \sin(\varphi_{1a}) = R - r_{1b} \sin(\theta_{1b}) \sin(\varphi_{1b}) & (10.4) \\
z &= r_{1a} \cos(\theta_{1a}) = r_{1b} \cos(\theta_{1b}) & (10.5) \\
d^2 &= x^2 + z^2 & (10.6) \\
\sin(\phi) &= \frac{x}{d} & (10.7) \\
\sin(\tau_{1a}) &= \frac{d}{r_{1a}} & (10.8) \\
x^2 &= d^2 \sin^2(\phi) = r_{1a}^2 \sin^2(\tau_{1a}) \sin^2(\phi) & (10.9) \\
y &= r_{1a} \cos(\tau_{1a}) & (10.10) \\
\sin^2(\tau_{1a}) &= \frac{\xi \eta + 1}{\xi + \eta} & (10.11) \\
\cos(\tau_{1a}) &= \frac{\xi + \eta}{\xi + \eta} & (10.12) \\
r_{1a} &= \frac{R}{2}(\xi + \eta) & (10.13) \\
r_{1b} &= \frac{R}{2}(\xi - \eta) & (10.14)
\end{align*}

The MOs $\pi_1 = (p_{x1a} + p_{x1b})$, $\sigma_1 = (p_{y1a} - p_{y1b})$, and $\pi_2 = (p_{z1a} + p_{z1b})$ lead to charge distributions which can be expressed into elliptical coordinates:

\begin{align*}
p_{x1a}p_{x1b} &\sim \sin(\theta_{1a}) \sin(\varphi_{1a}) \sin(\theta_{1b}) \sin(\varphi_{1b}) = \frac{r_{1a}}{r_{1b}} \sin^2(\theta_{1a}) \cos^2(\varphi_{1a}) \\
 &\quad = \frac{r_{1a}}{r_{1b}} \frac{x^2}{r_{1a}^2} = \frac{r_{1a}^2}{r_{1b}^2} \frac{\sin^2(\tau_{1a}) \sin^2(\phi)}{r_{1a} r_{1b}} \\
 &\quad = \frac{(\xi + \eta)(\xi^2 - 1)(1 - \eta^2)}{(\xi - \eta)(\xi + \eta)^2} \sin^2(\phi) \\
 &\quad = \frac{(\xi^2 - 1)(1 - \eta^2)}{(\xi - \eta)(\xi + \eta)} \sin^2(\phi) & (10.15) \\
p_{y1a}p_{y1b} &\sim \sin(\theta_{1a}) \sin(\varphi_{1a}) \sin(\theta_{1b}) \sin(\varphi_{1b}) = \frac{R}{r_{1b}} \sin(\theta_{1a}) \sin(\varphi_{1a}) - \frac{r_{1a}}{r_{1b}} \sin^2(\theta_{1a}) \sin^2(\varphi_{1a}) \\
 &\quad = \frac{R y}{r_{1a} r_{1b}} - \frac{y^2}{r_{1a}^2 r_{1b}^2} = \frac{R \cos(\tau_{1a})}{r_{1b}} - \frac{r_{1a} \cos(\tau_{1a})}{r_{1b}} \\
 &\quad = \frac{2(\xi + 1)}{(\xi - \eta)(\xi + \eta)} - \frac{(\xi + 1)^2}{(\xi - \eta)(\xi + \eta)} \\
 &\quad = \frac{1 - \xi^2 \eta^2}{\xi^2 - \eta^2} & (10.16) \\
p_{z1a}p_{z1b} &\sim \cos(\theta_{1a}) \cos(\theta_{1b}) = \frac{r_{1a}^2}{r_{1b}} \cos^2(\theta_{1a}) - \frac{r_{1a}^2}{r_{1b}} \cos^2(\theta_{1a}) \\
 &\quad = \frac{r_{1a}^2 \cos^2(\phi) \sin^2(\tau_{1a})}{r_{1a}^2 r_{1b}} \\
 &\quad = \frac{(\xi^2 - 1)(1 - \eta^2)}{(\xi - \eta)(\xi + \eta)} \cos^2(\phi) & (10.17)
\end{align*}
We have used these transformations to calculate first some overlap integrals. We have obtained using quadruple precision i.e. for \( \langle 2p|2p \rangle \) for \( R = 1.4 \) a.u. and \( p_a = p_b = 2 \) the value 0.10074 03821 47441 08953 03462 16521 04379 compared with 0.10074 03821 47441 08953 of Ref. [76], and \( \langle 2p|2p \rangle \) for different exponents \( p_a = 0.6, p_b = 2.3 \) and \( R = 2.5 \) the value 0.01765 76741 87582 05865 68980 01790 09261 compared with 0.01765 76741 875 of Ref. [77].

11. THE CLASSICAL METHOD FOR TWO-CENTER CORRELATED INTEGRALS

We call ”classical method” of solving two-center correlated integrals the elliptical method to solve them, the easiest method which is the same used for the usual repulsion integrals and leads to the same kind of auxiliary integrals, and to distinguish from the Budzinski’s method for two-, three and four-electron integrals two-center integrals [30]. Budzinski introduced a set of polynomials and transformed the Neumann expansion, see a Chapter in this Volume. The classical method consist on expressing the interelectronic coordinate \( r_{ij} \) to the first power as \( r_{ij}^2/r_{ij} \) and substitute \( r_{ij}^2 \) by the cosine theorem in elliptical coordinates and \( 1/r_{ij} \) by the usual Neumann expansion:

\[
\frac{r_{12}}{r_{12}} = \left( \frac{R}{2} \right)^2 \left( \xi_1^2 + \xi_2^2 + \eta_1^2 + \eta_2^2 - 2 \xi_1 \xi_2 \eta_1 \eta_2 - 2 \right)
- \left[ (\xi_1^2 - 1)(\xi_2^2 - 1)(1 - \eta_1^2)(1 - \eta_2^2) \right]^{1/2} \left( e^{i(\phi_1 - \phi_2)} + e^{-i(\phi_1 + \phi_2)} \right)
\times \frac{4}{R} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{(-1)^m (l-m)!}{(l+m)!} P^m_1(\xi_1) Q^m_1(\xi_2) P^m_1(\mu_1) P^m_1(\mu_2) e^{im(\phi_1 - \phi_2)} \tag{11.1}
\]

with the Legendre polynomials and \( \xi_s, \eta_s \) defined in Eq. (8.6). The charge distributions:

\[
\Omega_{ab}^{\ast}(\xi, \eta, \phi)(\xi^2 - \eta^2) \left( \frac{R}{2} \right)^3 = \left( \frac{R}{2} \right)^{n_a+n_b+1} e^{-\alpha \xi e^{\beta \eta} K_{ab} \left( (\xi^2 - 1)(1-\eta^2) \right) (m_a+m_b)/2} \omega_{\xi,\eta} e^{-iM \phi_1} \tag{11.2}
\]

\[
\Omega_{ab}^{\ast}(\xi, \eta, \phi)(\xi^2 - \eta^2) \left( \frac{R}{2} \right)^3 = \left( \frac{R}{2} \right)^{n'_a+n'_b+1} e^{-\alpha' \xi e^{\beta' \eta} K'_{ab} \left( (\xi^2 - 1)(1-\eta^2) \right) (m_a+m_b)/2} \omega_{\xi,\eta} e^{-iM' \phi_1} \tag{11.3}
\]

with \( M = m_a + m_b \) and \( M' = m'_a + m'_b \) the integral

\[
I = (-1)^{M} \int \int \Omega_{ab}^{\ast}(1) r_{12} \Omega_{ab}(2) d\tau_1 d\tau_2 \tag{11.4}
\]

substituting Eqs. (11.1-11.3) in Eq. (11.4) and integrating over \( \phi_1 \) and \( \phi_2 \) with the considerations of Eq. (8.7), the sum over \( m \) breaks down into three terms: \( m = M = M' \), \( m = M - 1 = M' - 1 \), and \( m = M + 1 = M' + 1 \). Then one can separate the integral into three integrals:

\[
I = (-1)^{M} \delta(M, M')(2\pi)^2 R K_{ab} K'_{ab} \sum_{l=0}^{\infty} \left( I^M_l - I^{M+1}_l - I^{M-1}_l \right) \tag{11.5}
\]
Let us evaluate the first:

\[
I_I^M = (-1)^M \frac{(l - M)!}{(l + M)!} \sum_{n_j} \sum_{n'_j} C_{n_j} C_{n'_j} \int \int \int \xi_1^{n_1} e^{-\alpha_1 \xi_1} \eta_1^{n_1} e^{\beta_1 \eta_1} \xi_2^{n_2} + e^{-\alpha_2 \xi_2} \eta_2^{n_2} e^{\beta_2 \eta_2} \times (\xi_1^2 + \xi_2^2 + \eta_1^2 + \eta_2^2 - 2\xi_1 \xi_2 \eta_1 \eta_2 - 2) [(\xi_1^2 - 1)(\xi_2^2 - 1)(1 - \eta_1^2)(1 - \eta_2^2)]^{M/2} \times P_I^m(\xi_s) Q_I^m(\xi_s) P_I^m(\mu_1) P_I^m(\mu_2) d\xi_1 d\xi_2 d\eta_1 d\eta_2
\]

Now we define the following auxiliary integrals which are a generalization of the ones of Eqs. (8.13, 8.16):

\[
B_{j+2}^{MI}(\beta) = \int_{-1}^{+1} \eta^{j} e^{\beta \eta}(1 - \eta^2)^{M/2} P_I^M(\eta) d\eta
\]

\[
W^M_l(n, n'; \alpha, \alpha') = \int_{1}^{\infty} d\xi_1 \int_{1}^{\infty} d\xi_2 \xi_1^{n} \xi_2^{n'} e^{-\alpha_1 \xi_1 - \alpha_2 \xi_2} P_I^M(\xi_s) Q_I^M(\xi_s) [(\xi_1^2 - 1)(\xi_2^2 - 1)]^{M/2}
\]

The integrals \(B_{j+2}^{MI}(\beta)\) are easy to evaluate using hypergeometric functions and are given in Ref. [59].

The integrals \(W^M_l(n, n'; \alpha, \alpha')\) are the same that the ones used for the exchange integral [59, 56].

Finally we have

\[
I_I^M = (-1)^M \frac{(l - M)!}{(l + M)!} \sum_{n_j} \sum_{n'_j} C_{n_j} C_{n'_j} \left\{ W^M_l(n, n'; \alpha, \alpha') \times \left[ B_{j+2}^{MI}(\beta) B_{j+1}^{MI}(\beta') + B_{j+1}^{MI}(\beta) B_{j+2}^{MI}(\beta') - 2B_{j+1}^{MI}(\beta) B_{j+1}^{MI}(\beta') \right] - 2W^M_l(n + 1, n' + 1; \alpha, \alpha') B_{j+1}^{MI}(\beta) B_{j+1}^{MI}(\beta') + W^M_l(n + 2, n'; \alpha, \alpha') B_{j+1}^{MI}(\beta) B_{j+1}^{MI}(\beta') \right\}
\]

\[
I_I^{M-1} = (-1)^{M+1} \frac{(l - |M + 1|)!}{(l + |M + 1|)!} \sum_{n_j} \sum_{n'_j} C_{n_j} C_{n'_j} B_{j+1}^{M+1}(\beta) B_{j+1}^{M+1}(\beta') W^M_{l+1}(n, n'; \alpha, \alpha')
\]

\[
I_I^{M-1} = (-1)^{M-1} \frac{(l - |M - 1|)!}{(l + |M - 1|)!} \sum_{n_j} \sum_{n'_j} C_{n_j} C_{n'_j} \left[ B_{j+1}^{M-1}(\beta) B_{j+1}^{M-1}(\beta') \left( B_{j+1}^{M-1}(\beta) - B_{j+1}^{M-1}(\beta') \right) \right] \times \left( W^M_{l-1}(n + 2, n' + 2; \alpha, \alpha') + W^M_{l-1}(n, n'; \alpha, \alpha') - W^M_{l-1}(n + 2, n'; \alpha, \alpha') - W^M_{l-1}(n, n' + 2; \alpha, \alpha') \right)
\]

In Hylleraas-CI calculations the integral \(\langle r^2_{12} \rangle\) is also necessary. To calculate these integrals we use the expression of \(r^2_{12}\) in elliptical coordinates:

\[
r^2_{12} = \left( \frac{R}{2} \right)^2 \left( \xi_1^2 + \xi_2^2 + \eta_1^2 + \eta_2^2 - 2\xi_1 \xi_2 \eta_1 \eta_2 - 2 \right) - \left[ (\xi_1^2 - 1)(\xi_2^2 - 1)(1 - \eta_1^2)(1 - \eta_2^2) \right]^{1/2} \left( e^{i(\phi_1 - \phi_2)} + e^{-i(\phi_1 + \phi_2)} \right)
\]
Using the charge distributions definitions Eqs. (11.2,11.3), the integral is

\[ J = (-1)^M \int \int \Omega_{ab}^*(1)r_{12}^2\Omega_{ab}(2)d\tau_1d\tau_2 \quad (11.13) \]

as in the integral before we integrate first over \( \phi_1 \) and \( \phi_2 \). Here the integral vanish except for the cases:

\[ \int_0^{2\pi} \int_0^\pi d\phi_1 e^{-iM\phi_1} \int_0^{2\pi} \int_0^\pi d\phi_2 e^{-iM'\phi_2} = (2\pi)^2, \quad \text{for } M = M' = 0 \quad (11.14) \]

\[ \int_0^{2\pi} \int_0^\pi d\phi_1 e^{-iM\phi_1} e^{i\phi_1} \int_0^{2\pi} \int_0^\pi d\phi_2 e^{-iM'\phi_2} e^{-i\phi_2} = (2\pi)^2, \quad \text{for } M = M' = 1 \quad (11.15) \]

\[ \int_0^{2\pi} \int_0^\pi d\phi_1 e^{-iM\phi_1} e^{-i\phi_1} \int_0^{2\pi} \int_0^\pi d\phi_2 e^{-iM'\phi_2} e^{i\phi_2} = (2\pi)^2, \quad \text{for } M = M' = -1 \quad (11.16) \]

for \( M \leq 2 \) and \( M \geq 2 \) the integral vanishes. Substituting Eqs. (11.14-11.16) in Eq. (11.13) and integrating over \( \phi_1 \) and \( \phi_2 \), we can separate the integral into three integrals:

\[ J = (-1)^M \delta(M, M')(2\pi)^2 R^2 K \sum_{l=0}^{\infty} (J^0_l - J^1_l - J^{-1}_l) \quad (11.17) \]

Let us evaluate the first \( J^0_l \). For this the auxiliary integrals \( A_n(\alpha) \) and \( B_j(\beta) \) of Eqs. (8.12,8.13) are used\(^1\):

\[ J^0_l = \sum_{n_j}^{N-M} \sum_{n'_{j'}}^{N' - M} C_{n_j} C_{n'_{j'}} \int \int \int \int \xi_1^\alpha \xi_2^\alpha \eta_1^\beta \eta_2^\beta e^{2i\eta_1 \eta_2 e^{2i\eta_1 \eta_2}} \times (\xi_1^2 + \xi_2^2 + \eta_1^2 + \eta_2^2 - 2\xi_1 \xi_2 \eta_1 \eta_2 - 2) \quad (11.18) \]

Finally we have

\[ J^0_l = \sum_{n_j}^{N} \sum_{n'_{j'}}^{N'} C_{n_j} C_{n'_{j'}} B_j(\beta) B_{j'}(\beta') [A_{n+2}(\alpha)A_{n'}(\alpha') + A_n(\alpha)A_{n'+2}(\alpha')] + A_n(\alpha)A_{n'}(\alpha') [B_{j+2}(\beta)B_{j'}(\beta') + B_j(\beta)B_{j'+2}(\beta')] - 2A_{n+1}(\alpha)A_{n'+1}(\alpha')B_{j+1}(\beta)B_{j'+1}(\beta') - 2A_n(\alpha)A_{n'}(\alpha')B_j(\beta)B_{j'}(\beta') \quad (11.19) \]

\[ J^1_l = \sum_{n_j}^{N-1} \sum_{n'_{j'}}^{N'-1} C_{n_j} C_{n'_{j'}} (A_{n+2}(\alpha) - A_n(\alpha)) (A_{n'+2}(\alpha) - A_{n'}(\alpha)) \times (B_j(\beta) - B_{j+2}(\beta)) (B_{j'}(\beta') - B_{j'+2}(\beta')) \quad (11.20) \]

\[ J^{-1}_l = \sum_{n_j}^{N+1} \sum_{n'_{j'}}^{N'+1} C_{n_j} C_{n'_{j'}} A_n(\alpha)A_{n'}(\alpha')B_j(\beta)B_{j'}(\beta') \quad (11.21) \]

The extension of this method to evaluate correlated three-electron integrals is very complex because it leads to three-fold integrals corresponding to \( W^M_{li}(n, n', \alpha, \alpha') \). We can observe, that the evaluation

---

\(^1\)Note that in this integral the Legendre Polynomials of first and second kind do not appear, as \( r_{12}^2 \) is a finite expansion.
of uncorrelated and correlated Coulomb and exchange integrals do not differ much. In the usual repulsion integrals one expands $1/r_{12}$ while in the correlated one uses another expansion for $r_{12}$ raised to the power of one. If more than interelectronic distance appears into the integrals, then one has to expand all of them, where many terms fall out due to the angular integration. In the Hylleraas-CI method the appearing three-electron integrals are of the type $\langle r_{12} r_{13} \rangle$, $\langle r_{12}/r_{13} \rangle$ and the so-called ”triangle integral” (in atoms this is the only integral which is an infinite summation) $\langle r_{12} r_{13}/r_{23} \rangle$ and two types of four-electron integrals $\langle r_{12} r_{13}/r_{14} \rangle$ and $\langle r_{12} r_{23}/r_{34} \rangle$. For techniques of integration of many-electron integrals see King’s Chapter in this Volume.

As an alternative to the classical method, it is more favorable to use the Budzinski method to evaluate the three- and four-electron integrals for two atomic centers which are necessary for Hylleraas-CI calculations, see Chapter in this Volume.

12. TEST CALCULATIONS ON THE H2 MOLECULE

The hydrogen molecule has always been an object of test of new methods. As pointed out by McLean et al. [78], (see this Ref. for an historical review of hydrogen molecule wave functions and calculations), a CI on the hydrogen molecule with its two electrons can help us to understand the different types of correlation: 1) the in-out correlation or radial correlation, where the electrons tend to repel each other radially, 2) the angular correlation, where the electrons tend to keep different sides of an axial plane, and finally, 3) the left-right correlation where the electrons tend to stay at opposite places of the molecule.

It has been found from early calculations [78, 79, 80, 81], that the two more important configurations are the basic configuration $\sigma_g(1)\sigma_g(2)$ and $\sigma_u(1)\sigma_u(2)$.

$$\sigma_g(1)\sigma_g(2) = (a_1 + b_1)(a_2 + b_2) \quad (12.1)$$

$$\sigma_u(1)\sigma_u(2) = (a_1 - b_1)(a_2 - b_2) \quad (12.2)$$

where $a, b$ denote the centers and 1, 2 the electrons. The addition of configurations like the first maybe interpreted as taking into account the radial correlation. The second configuration and others like that maybe understood as the left-right correlation. Note that the orbitals located in $a$ and $b$ must be equal by symmetry: $a_1 = b_1$ and $a_2 = b_2$. But $\sigma(1)$ maybe different of $\sigma(2)$, what would be ”open shell”, if $\sigma(1)$ is equal $\sigma(2)$ is ”closed shell”. The closed shell basis functions build configurations for themselves. The account of angular correlation is when one adds configurations $\pi_g(1)\pi_g(2)$, $\pi_u(1)\pi_u(2)$, $\delta_g(1)\delta_g(2)$, $\delta_u(1)\delta_u(2)$. If using open shell the possible symmetry adapted configurations are [80]:

$$\sigma_g(1)\sigma'_g(2) + \sigma'_g(1)\sigma_g(2)$$

$$\sigma_u(1)\sigma'_u(2) + \sigma'_u(1)\sigma_u(2) \quad (12.3)$$

The first calculations on the hydrogen molecule were on the binding energy. We can mention the one-configuration calculation from Coulson [7] leads to a binding energy of 3.488 eV, we have calculated it using his orbital exponents 1.197, 1.197. With these exponents we have got a binding energy of 3.4887949 eV which reproduces the Coulson’s one, with a corresponding energy of -1.12812 12577 05
Table 2: Comparison of one-configuration wave functions. R=1.40 a.u.

<table>
<thead>
<tr>
<th>Type of function</th>
<th>Energy (a.u.)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulson, scaled MO</td>
<td>-1.1282</td>
<td>[7]</td>
</tr>
<tr>
<td>Shull and Ebbing, scaled floating MO</td>
<td>-1.1316</td>
<td>[82]</td>
</tr>
<tr>
<td>Coulson</td>
<td>-1.1332</td>
<td>[83]</td>
</tr>
<tr>
<td>Hagstrom and Shull, NO (ellip)</td>
<td>-1.133444</td>
<td>[80]</td>
</tr>
<tr>
<td>Davidson and Jones, NO (ellip)</td>
<td>-1.133467</td>
<td>[81]</td>
</tr>
<tr>
<td>SCF, $\alpha = 0.95$</td>
<td>-1.13362</td>
<td>[10]</td>
</tr>
<tr>
<td>This work, MO</td>
<td>-1.131710953169 a.u.</td>
<td></td>
</tr>
</tbody>
</table>

a.u. at 1.4011 and a virial factor of 1.99559. Compared with McLean et al. who got at R=1.4055 a.u. a binding energy of 3.4850 eV, we obtain 3.488794964 eV which correspond to an energy of -1.12807 30551 65 a.u. using the same orbital exponents 1.197, 1.197.

Traditionally the calculations on the hydrogen molecule were done at the minimum distance 1.4011 a.u. and also at 1.40 a.u. to compare among the methods. Also traditionally there was some kind of optimization or variation of the orbital exponents. In our MO method we optimize the orbital exponents using a simple parabolic procedure, with step sizes, cycles and macrocycles. For one configuration "closed shell" wave function we have obtain a lower energy results of -1.128182295254 a.u. for the two equal exponents 1.18924 06025 24 with a virial 2.0071. Optimizing the exponents for the "open shell" one configuration we have got -1.13169 93599 78 and the exponents are 0.93028 90902 45, and 1.44527 03041 72 at R=1.4011 and virial 2.01351. As one can see, an improvement.

We compare the energy of different one-configuration wave functions, at R=1.40 a.u. in Table 1. Note that Hagstrom and Shull, and Davidson and Jones used a basis set of elliptical orbitals, and constructed them with natural orbitals. Therefore the energy results in both cases are better than ours, where we have used STOs, one orbital per electron. In Section 2, we have discussed that elliptical wave functions lead to lower energy results as some terms from the kinetic energy operator do not vanish. Our results compare well with those of the MO method. Further results for one-configuration wave functions can be found in Ref. [79].

For our result in Table 2, we used the optimized exponents 0.93081 60790 18 and 1.44533 88986 78, virial 2.01351, using quadruple precision. We see that we have obtained a lower energy result for one-configuration wave function for R=1.40 than for 1.4011. The minimum is not well described. The wave function need more terms.

As we have mentioned the second configuration $\sigma_u(1)\sigma'_u(2)$ is very important for the energy. We compare the results of two-configuration wave functions in Table 3, further results can be found in Ref. [79].
Table 3: Comparison of two-configuration wave functions at R=1.40 a.u.

<table>
<thead>
<tr>
<th>Type of function</th>
<th>Energy (a.u.)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Davidson and Jones, NO (ellip)</td>
<td>-1.151939</td>
<td>[81]</td>
</tr>
<tr>
<td>Hagstrom and Shull, NO (ellip)</td>
<td>-1.151948</td>
<td>[80]</td>
</tr>
<tr>
<td>Weinbaum floating</td>
<td>-1.1501</td>
<td>[82]</td>
</tr>
<tr>
<td>This work, MO</td>
<td>-1.150510803543</td>
<td></td>
</tr>
</tbody>
</table>

In our work we have used in addition of the first configuration already given, the exponent 1.176752686077 for the second one, closed shell leading to a virial 2.010437. Our result compares well with the ones of Weinbaum. The results using elliptical orbital basis have a lower energy.

The $\sigma$-limit is given by Hagstrom and Shull to be about -1.1428 a.u. The $\sigma_u$-limit is calculated by them -1.16087 a.u. Now if we compare these calculations from about 45 years with actual ones made within a Hylleraas calculation of Sims and Hagstrom [9], the $\sigma$-limit using a fixed exponent in closed shell 1.32075 for a 1491 configuration expansion with an energy -1.1615 1824 0453 5174 a.u., we realize of the deep insight and understanding about the choice of configurations in the earlier calculations.

It seems then that it is very important the inclusion of $\pi$ and $\delta$ MO orbitals to take into account the angular correlation. Hagstrom and Shull [80] got using them an energy of -1.173128 a.u. and Davidson and Jones [81] -1.173044 a.u., while Kolos and Roothaan got -1.174440 including $r_{12}$. The best correlated calculation nowadays leads to -1.1747 59314 00027 a.u. for $R = 1.40$ a.u. [28]. A good strategy to perform the calculation would be to make a $\sigma$-, $\pi$-, $\delta$-CI to include the main angular correlation and to include then the interelectronic coordinate $r_{ij}$ to pick up the of the correlation energy, what accelerate the convergence of the wave function expansion.

In polyconfiguration closed shell wave functions (CI) we have studied the effect of the optimization of the orbital exponents per configuration. First we give in Table 4 the calculations of a 38 term wave function using Coulson exponents fixed to 1.197 (note that Coulson exponents are very good and already optimized, the results using other exponents would be worse). In Table 5 the wave function expansion is shown for optimized orbital exponents. The optimization of exponents helps to construct shorter wave function expansions, but according to Table 5, the effect in MO calculations affects only the forth decimal digit.

13. DISCUSSION AND PERSPECTIVES

In the year 1960 Kolos and Roothaan [10] described their goals: 1) to increase the accuracy of energy calculations in several significant figures, 2) to perform calculations for different values of R, the Potential Energy curve, 3) to carry out accurate calculations for various operators others than the energy, 4) to compare the energy values with other more accurate wave functions. Today we can say these goals are still valid. A combination of the techniques of calculating molecular integrals over STOs
Table 4: 38-term configuration wave function with fixed exponents $\alpha$ and $\beta$. $R=1.40$ a.u.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Configuration</th>
<th>Energy (a.u.)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>virial</th>
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<tr>
<td>Nr.</td>
<td>Configuration</td>
<td>Energy (a.u.)</td>
<td>$\alpha$</td>
<td>$\beta$</td>
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</tr>
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<td>1.99556</td>
</tr>
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</tr>
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<tr>
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<td>3.12612788</td>
<td>1.99554</td>
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with the techniques of calculation of correlated integrals would be very promising [84, 85]. In the last years there have been progress in calculating multicenter Coulomb and exchange integrals over Slater type orbitals [71, 86, 87]. Elliptical Slater functions can be expressed as finite linear combination of B-functions [88] which multicenter integrals are analytically evaluable. For highly precision calculations in molecules an accuracy of the integrals, like in the atomic case of more than 30 decimal figures would be desirable, as many integrals solution involves infinite expansions. For this, the use of higher precision arithmetic packages like MPFUN [89] and Brent package [90] would be of great help. Also the use of algebraic program packages like Maple [91, 92] and online mathematical libraries like Mathworld [93] will contribute very much to developments.

Other possibilities to improve the results of molecular calculations is to improve the quality of the radial part of the orbitals, as for example using hydrogenlike orbitals [94] and Sturmians [95, 96, 97], optimizing the orbitals [98], and introducing the flexibility of including fractionary powers of \( r \) in the orbitals [99].

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References


Figure 1: Definition of the internal polar coordinates of an electron with respect to a center.
Figure 2: Definition of the elliptical coordinates.
Figure 3: Definition of the internal radial coordinates of an electron with three centers.
Figure 4: Transformation of the angular polar coordinates into elliptical ones.