Ab initio methods –I (Hartree-Fock Methods)

Key words: Ab initio methods, quantum chemistry, Schrodinger equation, atomic orbitals, well behaved functions, product wavefunctions, determinantal wavefunctions, Hartree method, Hartree Fock Method, Roothan equations.

9.1 Introduction

In the first module, you have been introduced to several elementary numerical (computational) methods to solve simple and isolated problems. Now, we begin applying these methods to problems of chemical interest. We begin with ab initio and semi-empirical methods to solve problems of chemical structures. We will restrict mostly to non-relativistic cases. The theoretical basis of quantum chemistry has been introduced to you in Engineering Chemistry I, and the Web and Video courses in quantum chemistry. In this chapter, we will consider the computational aspects associated with the problem.

9.2 The Schrödinger Equation

The non relativistic Schrödinger equation for hydrogen atom is,

$$-\left(\frac{h^2}{8\pi^2 m}\right)\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi-\frac{e^2}{r}\Psi=E\Psi \qquad (10.1)$$

We can not solve this equation in Cartesian coordinates because we can not separate the potential energy term (1 / r) in terms of independent functions of x, y and z. A more natural option is to separate the Laplacian operator, $\nabla^2=\partial^2/\partial x^2+\partial^2/\partial y^2+\partial^2/\partial z^2$ in spherical coordinates r, θ and φ.

$$\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \qquad (10.2)$$

The potential energy term can now be combined with the r part of the Laplacian operator to give the radial equation and the angular parts can be separately combined to give three separate equations for the functions R(r), Θ(θ) and Φ(φ) and the solution can be written as:

$$\Psi(r,\theta,\varphi)=R_n(r)Y_l^m(\theta,\varphi)=R_{nl}(r)P_l^m(\theta)e^{\pm m\varphi}\ . \qquad (10.3)$$

Table 1.1: Radial and angular parts of hydrogen-atom wave-functions. The quantum numbers *n, l,* and m_l are also indicated in the table.

Radial Part $R_{nl}(r)$; a_0 = Bohr radius	Angular Part $Y_{lm}(\theta,\varphi) = P_l^m(\theta)\Phi(\varphi)$
$R_{1s} = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$; $n = 1,\ l = 0$	$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$; $l = 0,\ ,m_l = 0$
$R_{2s} = \frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(1 - \frac{Zr}{2a_0}\right)e^{-Zr/2a_0}$; $n=2, l=0$	$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$; $l = 1,\ m_l = 0$
$R_{2p} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{5/2} r\, e^{-Zr/2a_0}$; $n = 2,\ l = 1$	$Y_1^1 = \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{i\varphi}$; $l = 1\ m_l = 1$
$R_{3s} = \frac{2}{3\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(1 - \frac{2Zr}{3a_0} + \frac{2Z^2r^2}{27a_0^2}\right)e^{-Zr/3a_0}$ $n = 3,\ l = 0$	$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{-i\varphi}$; $l = 1, m_l = -1$
$R_{3p} = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0} - \frac{Z^2r^2}{6a_0^2}\right)e^{-Zr/3a_0}$ $n = 3,\ l = 1$	$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$; $l = 2, m_l = 0$
$R_{3d} = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{7/2} r^2\, e^{-Zr/3a_0}$; $n = 3,\ l = 2$	$Y_2^1 = \left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta\, e^{i\varphi}$; $l = 2,\ m_l = 1$
	$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{2i\varphi}$; $l = 2\ ,m_l = 2$

9.3 Multielectron atoms: Wavefunctions and Orbitals

In multielectron atoms such as He, Li, etc. the Schrödinger equation may be written as HΨ = EΨ where H is the operator representing the kinetic and potential energies of all the particles and Ψ and E are the wavefunction and energy respectively. For a helium atom, keeping the nucleus fixed (this is not a bad approximation since the nucleus is much heavier than the electrons) the electronic part of H can be written as

$$H = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \qquad (10.4)$$

The first two terms are the kinetic energies of electrons 1 and 2, the third and fourth are the interaction energies of the two electrons with the He nucleus and the last term is the electron electron repulsion. Here $\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$. Similarly for all other ∇_i^2 s.

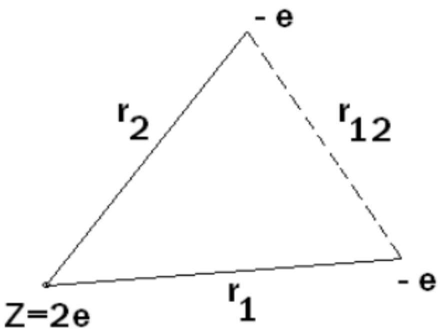

Figure 9.1 Coordinates in He.

The solution of this equation is the wavefunction $\Psi = \Psi(1, 2)$ or $\Psi(r_1, r_2) = \Psi(x_1, y_1, z_1, x_2, y_2, z_2)$. This is a function of six variables and is difficult to handle. A rather simple way to approximate this is to write it as

$$\Psi(r_1, r_2) \cong \phi_1(r_1)\ \phi_2(r_2) \tag{10.5}$$

which is a product of orbitals, $\phi_1(r_1)$ depending on the coordinate of the first electron and $\phi_2(r_2)$, which depends on the coordinate of the second electron. Wavefunctions refer to the solutions of the Schrödinger equation while orbitals refer to the functions of the coordinates of individual electrons and are the solutions to an approximate or an effective equation which is described below.

9.4 Hartree-Fock Equations

In the equation for an orbital, we want to reduce the number of variables from many (in a multielectronic case) to one (actually one r corresponds to three variables x,y,z). This is done by assuming that each electron moves in an average field created by all the other electrons. For example, one of the electrons in He, say electron 1 may be thought of moving in a field of the nucleus plus the average field created by the second electron.

$$\left[\ \frac{-\hbar^2}{8\pi^2 m}\nabla_1^2 - \frac{2e^2}{r_1} + V_{eff}(r_1)\ \right]\varphi_1(r_1) = E_1\,\varphi_1(r_1) \tag{10.6}$$

The three terms refer to the kinetic energy, nuclear attraction energy and the effective field and E_1 is the orbital energy. The effective field at r_1 is obtained by averaging the potential energy between electron 1 at r_1 and electron 2 at r_2 by allowing the second electron at r_2 to cover the whole space

$$V_{eff}(r_1) = \int_{all\ volume} \varphi_2^*(r_2)\varphi_2(r_2)\frac{e^2}{r_{12}}dx_2dy_2dz_2 \tag{10.7}$$

By the same analogy, electron 2 moves in an average field created by electron 1. These equations for electron 1 and electron 2 are solved iteratively starting with optimized basis functions $\phi_1(r_1)$ and $\phi_2(r_2)$ and the iterations (repeated solutions) are stopped when the average field created by electron 1 on electron 2 is consistent with the average field created by electron 2 on electron 1. These orbitals are called self consistent orbitals. This method is the self consistent method and forms a very important method for studying atomic and molecular structure. The above equation is the Hartree's equation for an atomic orbital. The Hartree equation as well as the Hartree Fock equation can be derived from a variational principle, namely,

$$\delta\langle\psi \mid H \mid \psi\rangle = 0 \tag{10.8}$$

This essentially follows from the variation theorem which states that, for the ground state of a system, the expectation value obtained from any (well-behaved) trial function f (satisfying appropriate boundary conditions) is always greater than the true ground state energy E of the system

$$\langle f | H | f \rangle = \int f^* H\, f\, d\tau \geq E \tag{10.9}$$

For molecules containing N electrons and M nuclei, the hamiltonian may be written

$$H = \frac{-\hbar^2}{2m_e}\sum_i^N \nabla_i^2 - e^2 \sum_{i,J}^{N,M} \frac{Z_J}{r_{iJ}} + \frac{1}{2}\sum_{i\neq j}^N \frac{e^2}{r_{ij}} + \frac{1}{2}\sum_{K\neq L}^M \frac{Z_K Z_L}{R_{KL}} \tag{10.10}$$

The first term above is the operator for the electron kinetic energies, the second term is for the electron nucleus attraction, the third term is for the electron electron repulsion and the last term corresponds to the nuclear repulsion energies. There are N electrons and M nuclei their charges represented by Z_J.

It is common practice to use the Born-Oppenheimer approximation which considers the nuclei as fixed, and therefore, the nuclear kinetic energy terms are absent in Eq. (10.10). The correct final energy is obtained for the electronic motion by adding the internuclear repulsion energy. There are several approximation methods available for solving the problem. A common method is the self consistent field molecular orbital (SCF-MO) method where one starts with a trial determinantal wave function (the Hartree-Fock method) with basis functions or orbitals ϕ_i, i =1 to N

$$\psi = |\phi_1(1)\phi_2(2)\phi_3(3)...........\phi_N(N)| \tag{10.11}$$

This contains N! terms whose "diagonal term" is $\phi_1(1)\phi_2(2)\phi_3(3)...........\phi_N(N)$. Terms with odd permutations of 1,2,3,…N such as $\phi_1(2)\phi_2(1)\phi_3(3)...........\phi_N(N)$ appear in the expansion of the determinant with a negative sign. In reality, the electron spin functions also need to be taken into account. The concept of a spatial orbital is extended to that of a spin orbital. Spin orbitals are written as $\phi_i(r_1)\alpha(1)$, $\phi_j(r_2)\beta(2)$, where the spin functions α and β do not depend on the spatial coordinate but are intrinsic properties of electrons 1, 2, etc. For the spin functions, there is no classical analogue.

The determinantal form of the wavefunction is antisymmetric in the exchange of rows/columns. It ensures that the Pauli Exclusion Principle is naturally incorporated, i.e. no two electrons have identical spatial and spin parts. The expression for energy in this Hartree-Fock method is given for a closed shell configuration containing an even number (N) of electrons by

$$E_{HF} = <\psi|H\ |\psi> = 2\sum_{i=1}^{N/2} H_{ii} + \sum_{i=1}^{N/2}\sum_{j=1}^{N/2}(2J_{ij} - K_{ij}) + V_{Nuclear\,\mathrm{Re}\,pulsion} \qquad (10.12)$$

$$H_{ii} = \left\langle \phi_i(1) \right| \frac{\hbar^2}{2m}\nabla_1^2 - \sum_{J=1}^{M}\frac{Z_J}{r_{1J}} \left| \phi_i(1) \right\rangle \qquad (10.13)$$

$$J_{ij} = \left\langle \phi_i(1)\phi_j(2) \right| \frac{e^2}{r_{12}} \left| \phi_i(1)\phi_j(2) \right\rangle \qquad (10.14)$$

$$K_{ij} = \left\langle \phi_i(1)\phi_j(2) \right| \frac{e^2}{r_{12}} \left| \phi_i(2)\phi_j(1) \right\rangle \qquad (10.15)$$

Eqs. (9.14) and (9.15) represent the Coulomb the exchange integrals. The exchange integral has no classical counterpart. $V_{Nucl\ \mathrm{Rep}}$ is the total nuclear repulsion energy at the configuration of the nuclei at which the electronic calculations are carried out (see Eq. 9.10). In terms of operator equations for individual orbitals, these equations can be written as

$$\hat{F}(1)\phi_i(1) = \varepsilon_i\phi_i(1) \qquad (10.16)$$

$$\hat{F}(1) = \hat{H}_1^{Core} = \sum_{j=1}^{N/2} 2J_i(1) - K_i(1) \qquad (10.17)$$

$$\hat{H}_1^{Core} = \frac{\hbar^2}{2m}\nabla_1^2 - \sum_{j=1}^{M}\frac{Z_J}{r_{1J}} \qquad (10.18)$$

$$\hat{J}_j(1)\,f(1) = f(1)\int \phi^*(2)\phi(2)\frac{1}{r_{12}}\,d\vec{r}_2 \qquad (10.19a)$$

$$\hat{K}_j(1)\,f(1) = \phi_j(1)\int \phi_j^*(2)\,f(2)\frac{1}{r_{12}}\,d\vec{r}_2 \qquad (10.19b)$$

Here, $\hat{F}(1)$ is the Fock operator defined in terms of the core electron operator $\hat{H}_{(1)}^{core}$, the Coulomb operator $\hat{J}_j(1)$ and the exchange operator $\hat{K}_j(1)$ which are defined through Eq. (9.16) to (9.19b). It is a common practice to take the functions φ_i**'s** as linear combinations of appropriate basis sets and then obtain the best sets of the coefficients. This method was developed by Roothaan.

$$\phi_i = \sum_{s=1}^{B} c_{si}\chi_s \qquad (10.20)$$

The coefficient of the s th basis function in the i th MO is c_{si}. The set of equations to be solved are called the Hartree-Fock-Roothaan equations and are given as follows. Here, B is the number of basis functions used in the calculation.

$$\sum_{s=1}^{B} c_{si}(F_{rs} - \varepsilon_i S_{rs}) = 0; \qquad r = 1,....B \qquad (10.21)$$

The Fock matrix element is denoted by F_{rs}, the overlap integral between orbitals r and s is S_{rs} and ε_i is the energy of the i th orbital. The atomic orbitals were initially taken as Slater-type orbitals which are given by

$$\chi_s(\varsigma, r, \theta, \phi) = \frac{(2\varsigma / a_0)^{n+1/2}}{(2n!)^{1/2}} r^{n-1} e^{-\varsigma r/a_0} Y_l^m(\theta, \varphi) \qquad (10.22)$$

Slater gave rules to assign the values of ς for different atoms and quantum numbers n, l, and m. You may have noted that the computational problem involves solving integro-differential equations. It also involves finding the roots of the secular equation to obtain the energy levels of the system after diagonalising the Fock matrix (Eq. 9.21). The attempts of solving the problem using Slater orbitals could not be executed satisfactorily as it is not yet possible to calculate all the integrals analytically and an alternative had to be found.

9.5 Gaussian Functions

A convenient way was found by writing the Slater orbitals in terms of suitably chosen linear combination of Gaussian functions. For example, the 1s orbital can be written as a linear combination of several Gaussian functions as follows.

$$\chi_{1s}(\varsigma, r) = \sum_{i=1}^{N} c_i g_i(\alpha_i) \qquad (10.23)$$

Where, $g_i(\alpha_i)$ are Gaussian functions with exponent α_i. For example, when N = 3, the coefficients and the exponents (c_i, α_i) of the three Gaussian functions in the STO-3G case are given by (0.444635, 0.109818), (0.535328, 0.405771) and (0.154329, 2.22766) respectively. It is instructive to plot both functions and see the extent to which they agree and disagree with each other in different regions of space, especially at the origin. The normalized Gaussian function centered at r $= \mathbf{R_A}$ is given by

$$g_{1s}(\alpha_i, \vec{r} - \vec{R}_A) = (2\alpha_i / \pi)^{3/4} e^{-\alpha_i |\vec{r} - \vec{R}_A|^2} \qquad (10.24)$$

The main advantage is that the product of two Gaussians at two different centers is a single Gaussian centered on the line joining the two Gaussians. Thus, all multi center integrals can be reduced to two center integrals and these can be evaluated analytically. We list some elementary examples of these integrals.

$$e^{-\alpha(x-x_A)^2} e^{-\beta(x-x_B)^2} = e^{-\frac{\alpha\beta}{\alpha+\beta}(x_A - x_B)^2} e^{-(\alpha+\beta)(x - \frac{\alpha x_A + \beta x_B}{\alpha+\beta})^2} \qquad (10.25)$$

To see this, start with

$$\alpha(x-x_A)^2 + \beta(x-x_B)^2 = \alpha x^2 - 2\alpha x x_A + \alpha x_A^2 + \beta x^2 - 2\beta x x_B + \beta x_B^2$$

$$= (\alpha+\beta)x^2 - 2\alpha x x_A - 2\beta x x_B + \alpha x_A^2 + \beta x_B^2$$

$$(\alpha+\beta)x^2 - 2x(\alpha x_A + \beta x_B) + \frac{\alpha+\beta}{\alpha+\beta}(\alpha x_A^2 + \beta x_B^2)$$

$$= (\alpha+\beta)x^2 - 2x(\alpha x_A + \beta x_B) + \frac{\alpha^2 x_A^2 + \alpha\beta x_A^2 + \alpha\beta x_B^2 + \beta^2 x_B^2 + (2-2)\alpha\beta x_A x_B}{\alpha+\beta}$$

$$= (\alpha+\beta)[\ \ x^2 - 2x\frac{(\alpha x_A + \beta x_B)}{\alpha+\beta} + \frac{\alpha^2 x_A^2 + \beta^2 x_B^2 + 2\alpha\beta x_A x_B}{(\alpha+\beta)^2} + \frac{\alpha\beta x_A^2 + \alpha\beta x_B^2 - 2\alpha\beta x_A x_B}{(\alpha+\beta)}$$

$$= (\alpha+\beta)[\ \ x^2 - 2x\frac{(\alpha x_A + \beta x_B)}{\alpha+\beta} + \left(\frac{\alpha x_A + \beta x_B}{\alpha+\beta}\right)^2\ \ ] + \left(\frac{\alpha\beta}{\alpha+\beta}\right)(x_A^2 + x_B^2 - 2x_A x_B)$$

$$= (\alpha+\beta)(\ \ x - \frac{(\alpha x_A + \beta x_B)}{\alpha+\beta}\ \ )^2 + \left(\frac{\alpha\beta}{\alpha+\beta}\right)(x_A - x_B)^2$$

In case of functions centered at $\mathbf{R_A}$ and $\mathbf{R_B}$, the above result corresponds to

$$e^{-\alpha(\vec{R}-\vec{R}_A)^2} e^{-\beta(\vec{R}-\vec{R}_B)^2} = e^{-\frac{\alpha\beta}{\alpha+\beta}(\vec{R}_A - \vec{R}_B)^2} e^{-(\alpha+\beta)(\vec{R}-\vec{R}_P)^2} \qquad (10.26)$$

$$\vec{R}_P = \frac{\alpha \vec{R}_A + \beta \vec{R}_B}{\alpha + \beta} \qquad (10.27)$$

9.6 Molecular Integrals Involving Gaussians

In this section we will outline how to calculate some of the integrals using Gaussian functions. The overlap integral is the easiest as it involves an elementary integral involving a single Gaussian.

$$< g_{1s}(R_A) \mid g_{1s}(R_B) > = \int d\vec{r}_1 e^{-\alpha(\vec{r}_1-\vec{R}_A)^2} e^{-\beta(\vec{r}_1-\vec{R}_B)^2} \qquad (10.28)$$

$$= e^{-\frac{\alpha\beta}{\alpha+\beta}(\vec{R}_A-\vec{R}_B)^2} \int d\vec{r}_1 e^{-(\alpha+\beta)(\vec{r}_1-\vec{R}_P)^2} = e^{-\frac{\alpha\beta}{\alpha+\beta}|\vec{R}_A-\vec{R}_B|^2} 4\pi \int_0^\infty dr\, r^2\, e^{-(\alpha+\beta)\,r^2} \qquad (10.29)$$

The standard integrals that will be useful are

$$\int_0^\infty e^{-\alpha x^2} dx = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{1/2} ; \quad \int_0^\infty x^2 e^{-\alpha x^2} dx = \frac{1}{4}\left(\frac{\pi}{\alpha^3}\right)^{1/2} \qquad (10.30)$$

Using the above integrals, Eq. (9.28) reduces to

$$< g_{1s}(R_A) \mid g_{1s}(R_B) > = \left(\frac{\pi}{\alpha+\beta}\right)^{3/2} e^{-\frac{\alpha\beta}{\alpha+\beta}|\vec{R}_A-\vec{R}_B|^2} \qquad (10.31)$$

The kinetic energy integral can be evaluated to give

$$< g_{1s}(R_A) \mid -\frac{\nabla_1^2}{2} \mid g_{1s}(R_B) > = \frac{\alpha\beta}{\alpha+\beta}\left[3 - \frac{2\alpha\beta}{\alpha+\beta}|\vec{R}_A - \vec{R}_B|^2\right]\left(\frac{\pi}{\alpha+\beta}\right)^{3/2} e^{-\frac{\alpha\beta}{\alpha+\beta}|\vec{R}_A-\vec{R}_B|^2} \qquad (10.32)$$

Now the nuclear attraction and the electron electron repulsion integrals can be evaluated by using the method of Fourier transforms. The results are as follows. The nuclear attraction integral is given by

$$< g_{1s}(R_A) \mid -Z_C / r_{1C} \mid g_{1s}(R_B) > = -Z_C \int d\vec{r}_1 e^{-\alpha(\vec{r}_1-\vec{R}_A)^2} e^{-\beta(\vec{r}_1-\vec{R}_B)^2} / |\vec{r}_1 - \vec{R}_C| \qquad (10.33)$$

$$= \frac{-2\pi Z_C}{\alpha+\beta}\left(\frac{\pi}{\alpha+\beta}\right)^{3/2} e^{-\frac{\alpha\beta}{\alpha+\beta}|\vec{R}_A-\vec{R}_B|^2} F_0\left[(\alpha+\beta)\,|\vec{R}_P - \vec{R}_C|^2\right] \qquad (10.34)$$

Where F_0(x) is related to the error function erf (x) and is given by

$$F_0(x) = x^{-1/2} \int_0^{x^{-1/2}} dy\, e^{-y^2} = x^{-1/2}\, erf(x^{-1/2}) \qquad (10.35)$$

There are very efficient algorithms to evaluate the error function and the complementary error function defined by

$$erf(x) = \int_0^x dy\, e^{-y^2} \qquad (10.36)$$

And finally, the electron-electron repulsion integral is given by

$$\begin{aligned} &< g_{1s}(R_A)\, g_{1s}(R_B) \,|\, 1/r_{12} \,|\, g_{1s}(R_C)\, g_{1s}(R_D) > \\ &= e^{-\frac{\alpha\beta}{\alpha+\beta}|\vec{R}_A - \vec{R}_B|^2}\; e^{-\frac{\gamma\delta}{\gamma+\delta}|\vec{R}_C - \vec{R}_D|^2} \iint d\vec{r}_1\, d\vec{r}_2\, e^{-\mu|\vec{r}_1 - \vec{R}_P|^2}(1/r_{12})e^{-\nu|\vec{r}_1 - \vec{R}_P|^2} \end{aligned} \qquad (10.37)$$

Here, α, β, γ and δ are the exponents of Gaussians centered at R_A, R_B, R_C and R_D and $\mu = \alpha + \beta$ and $\nu = \gamma + \delta$. The product of the two Gaussians on the left is centered at R_P and the product of the two Gaussians on the right is located at R_Q. The value of the integral is

$$< g_{1s}(R_A)\, g_{1s}(R_B) \,|\, 1/r_{12} \,|\, g_{1s}(R_C)\, g_{1s}(R_D) > = C_1\, e^{-\frac{\alpha\beta}{\alpha+\beta}|\vec{R}_A - \vec{R}_B|^2}\; e^{-\frac{\gamma\delta}{\gamma+\delta}|\vec{R}_C - \vec{R}_D|^2} F_0(x) \qquad (10.38)$$

$$\begin{aligned} &C_1 = 2\pi^{5/2} / [(\alpha+\beta)(\gamma+\delta)(\alpha+\beta+\gamma+\delta)^{1/2}]; \\ &x = [\{(\alpha+\beta)(\gamma+\delta)/(\alpha+\beta+\gamma+\delta)\} |\, \vec{R}_P - \vec{R}_Q\, |^2] \end{aligned} \qquad (10.30)$$

Using the formulae given in this chapter, it is in principle to proceed to compute the required energies and wavefunctions for molecules at the Hartree-Fock level. This is only a starting point and the improvements and details are the subject of this module. Calculations of these electron repulsion integrals (ERI) is a time consuming process and this has to be done for every molecular configuration until a minimum energy configuration is arrived at. The computational time increases very rapidly with increase in the number of basis sets used. Because of these difficulties, it is still quite difficult to do near exact calculations for systems with a large number of electrons (>50).

9.7 Summary

In this chapter, we have outlined the basic equations relevant to the problem of structural chemistry governed by the Schrödinger equation (at the Hartree-Fock level) and discussed a common approach to solve the problem of a multielectronic system using Gaussian functions. The rest of the module will outline the computations of various molecular properties with the available computational methods with illustrative examples. Several problems will also be given solving which, you should get a good feel for doing calculations of interest to you. Methods of geometry optimization of molecules, determination of molecular properties and computational effort involved in HF calculations etc. will be considered in detail in the next modules

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