The exact solution of the Schrödinger equation for the hydrogen atom (summary)

The Schrödinger equation (SE) for the hydrogen atom

$$\hat{H}\Psi(x,y,z) = E\Psi(x,y,z) \tag{1}$$

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r} \tag{2}$$

can be solved exactly. Switching to the spherical coordinate system and using the separation of variables technique, we get:

$$\Psi(x,y,z) = \psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{3}$$

where $R(r)$ (the *radial function*) is the solution of *radial equation*:

$$-\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) + \left[\frac{l(l+1)}{2r^2} - \frac{1}{r} - E\right] = 0 \tag{4}$$

and $Y(\theta,\phi)$ (*angular function*) is the solution of the *angular equation*:

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{\partial^2 Y(\theta,\phi)}{\partial\theta^2} + Y(\theta,\phi)l(l+1)\sin^2\theta = 0 \tag{5}$$

The radial function $R_{nl}(r)$ is a function of two quantum numbers, n and l :

$$n = 1, 2, 3, ... \qquad 0 \le l \le n\text{-}1 \tag{6}$$

The general form of $R_{nl}(r)$ is given by

$$R_{nl}(r) = N_{nl}\left(\frac{2}{n}\right)^{l+3/2} r^l e^{-r/n} L_{n-l-1}^{2l+1}\left(\frac{2r}{n}\right) \tag{7}$$

where N_{nl} is the normalization coefficient

$$N_{nl} = \left(\frac{(n-l-1)!}{2n[(n+l)!]^3}\right)^{1/2} \tag{8}$$

and the functions $L_{n-l-1}^{2l+1}(x)$ are called the *associated Laguerre polynomials*:

$$L_{n-l-1}^{2l+1}(x) = L_{i_{max}}^{2l+1}(x) = \sum_{i=0}^{i_{max}} \frac{(-1)^i\left[(n+l)!\right]^2 x^i}{i!(i_{max}-i)!(2l+1+i)!} \tag{9}$$

The angular function $Y(\theta,\phi) = Y_{l,m_l}(\theta,\phi)$ is a function of two quantum numbers, l and m_l :

$$0 \le l \le n\text{-}1 \qquad -l \le m_l \le +l \tag{10}$$

and is represented by *spherical harmonics* $Y_l^m(\theta,\phi)$

$$Y_{l,m_l}(\theta,\phi) = Y_l^m(\theta,\phi) \tag{11}$$

Note that from now on we assume that $m = m_l$ which simplifies the notation. The general form of $Y_l^m(\theta,\phi)$ is given by

$$Y_l^m(\theta,\phi) = \left[\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^m(\cos\theta)e^{im\phi} \tag{12}$$

where functions $P_l^m(x)$ are called the *associated Legendre polynomials*.

For convenience, several of the first few wavefunctions are listed in Table 1 along with their respective n, l, and m_l quantum numbers [1].

Table 1. Complete wavefunctions for hydrogen-like atoms [1].
Z is the nuclear charge.

n	ℓ	m_ℓ	Ψ_{n,ℓ,m_ℓ}
1	0	0	$\left(\dfrac{Z^3}{\pi a^3}\right)^{1/2} e^{-Zr/a}$
2	0	0	$\dfrac{1}{8}\left(\dfrac{2Z^3}{\pi a^3}\right)^{1/2}\left(2 - \dfrac{Zr}{a}\right)e^{-Zr/2a}$
2	1	−1	$\dfrac{1}{8}\left(\dfrac{2Z^3}{\pi a^3}\right)^{1/2}\dfrac{Zr}{a}e^{-Zr/2a}\sin\theta \cdot e^{-i\phi}$
2	1	0	$\dfrac{1}{8}\left(\dfrac{2Z^3}{\pi a^3}\right)^{1/2}\dfrac{Zr}{a}e^{-Zr/2a}\cos\theta$
2	1	+1	$\dfrac{1}{8}\left(\dfrac{2Z^3}{\pi a^3}\right)^{1/2}\dfrac{Zr}{a}e^{-Zr/2a}\sin\theta \cdot e^{i\phi}$
3	0	0	$\dfrac{1}{243}\left(\dfrac{3Z^3}{\pi a^3}\right)^{1/2}\left(27 - \dfrac{18Zr}{a} + \dfrac{2Zr^2}{a^2}\right)e^{-Zr/3a}$
3	1	−1	$\dfrac{1}{81}\left(\dfrac{Z^3}{\pi a^3}\right)^{1/2}\dfrac{Zr}{a}\left(6 - \dfrac{Zr}{a}\right)e^{-Zr/3a}\sin\theta \cdot e^{-i\phi}$
3	1	0	$\dfrac{1}{81}\left(\dfrac{2Z^3}{\pi a^3}\right)^{1/2}\dfrac{Zr}{a}\left(6 - \dfrac{Zr}{a}\right)e^{-Zr/3a}\cos\theta$
3	1	1	$\dfrac{1}{81}\left(\dfrac{Z^3}{\pi a^3}\right)^{1/2}\dfrac{Zr}{a}\left(6 - \dfrac{Zr}{a}\right)e^{-Zr/3a}\sin\theta \cdot e^{i\phi}$
3	2	−2	$\dfrac{1}{162}\left(\dfrac{Z^3}{\pi a^3}\right)^{1/2}\dfrac{Z^2r^2}{a^2}e^{-Zr/3a}\sin^2\theta \cdot e^{-2i\phi}$
3	2	−1	$\dfrac{1}{81}\left(\dfrac{Z^3}{\pi a^3}\right)^{1/2}\dfrac{Z^2r^2}{a^2}e^{-Zr/3a}\sin\theta\cos\theta \cdot e^{-i\phi}$
3	2	0	$\dfrac{1}{486}\left(\dfrac{6Z^3}{\pi a^3}\right)^{1/2}\dfrac{Z^2r^2}{a^2}e^{-Zr/3a}(3\cos^2\theta - 1)$
3	2	+1	$\dfrac{1}{81}\left(\dfrac{Z^3}{\pi a^3}\right)^{1/2}\dfrac{Z^2r^2}{a^2}e^{-Zr/3a}\sin\theta\cos\theta \cdot e^{i\phi}$
3	2	+2	$\dfrac{1}{162}\left(\dfrac{Z^3}{\pi a^3}\right)^{1/2}\dfrac{Z^2r^2}{a^2}e^{-Zr/3a}\sin^2\theta \cdot e^{2i\phi}$

[a]$a = \dfrac{4\pi\epsilon_0\hbar^2}{\mu e^2}$

The variational method [2].

Consider the ground state of some arbitrary system. The ground-state wavefunction ψ_0 and energy E_0 satisfy the Schrödinger equation

$$\hat{H}\psi_0 = E\psi_0 \tag{13}$$

Multiply equation (13) from the left by ψ_0 and integrate over all space to obtain

$$E_0 = \frac{\int \psi_0^* \hat{H}\psi_0 d\tau}{\int \psi_0^* \psi_0 d\tau} \tag{14}$$

where $d\tau$ is represents the appropriate volume element. Note that the denominator in equation (14) is not equal to 1 because we allow for the possibility that ψ_0 is not normalized beforehand. A beautiful theorem says that if we substitute any other function φ for ψ_0 in equation (14) and calculate the corresponding energy according to

$$E_\varphi = \frac{\int \varphi^* \hat{H}\varphi d\tau}{\int \varphi^* \varphi d\tau} \tag{15}$$

then E_φ will be greater than the ground-state energy E_0. In an equation, we have the *variational principle*

$$E_\phi \geq E_0 \tag{16}$$

where equality holds only if $\varphi = \psi_0$, the exact wavefunction.

The variational principle says that we can calculate an upper bound to E_0 by using any trial function φ we wish. The closer φ is to ψ_0 in some sense, the closer E_φ will be to E_0. We can choose a trial function φ such that it depends upon some arbitrary parameters, α, β, γ, ..., called *variational parameters*. The energy will also depend upon these variational parameters, so we get:

$$E_\varphi(\alpha, \beta, \gamma, \ldots) \geq E_0 \tag{17}$$

Now we can minimize E_φ with respect to each of the variational parameters and thereby determine the best possible ground-state energy that can be obtained from the chosen trial wavefunction.

Solution of the Schrödinger equation for the hydrogen atom using a trial wavefunction represented by single Gaussian-type function.

Suppose, we do not know the exact solution of the Schrödinger equation for the hydrogen atom, and would like to solve it using the variational method. In this part of the exercise, we choose a single spherically-symmetric Gaussian-type function (GTF), $g(r)$, as our trial wavefunction:

$$\varphi(r) = g(r) = e^{-\alpha r^2} \tag{18}$$

where α is the variational parameter. At the end of this exercise we will of course compare our approximate solution to the exact solution. Because $l=0$ in the ground state (electronic configuration of the hydrogen atom in the ground state is $1s^1$), the Hamiltonian operator (equation 2) in atomic units reduces to:

$$\hat{H} = -\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{1}{r} \tag{19}$$

The first thing we need to do is check the normalization of GTF, so we do not have to worry about the denominator in equation (15) anymore. The normalization integral S is given by

$$S = \int \varphi^* \varphi d\tau \tag{20}$$

where $d\tau$ is represents integration over all space. Note that because we are working with a real function, integrand $\varphi^*\varphi$ can be replaced with φ^2. For a spherically-symmetric function (i.e. one that does not depend on angles θ and ϕ), the three-dimensional integral (20) reduces to a simple one-dimensional integral

$$S = 4\pi \int_0^\infty \varphi^2(r)r^2 dr \tag{21}$$

The normalization coefficient of GTF, let's call it N_α, is then given by

$$N_\alpha = S^{-1/2} \tag{22}$$

In Mathematica, a GTF given by (18) can be defined as

$$\text{gtf} = \text{Exp}[-\alpha * r^2]; \tag{23}$$

Now we need to evaluate integral (21). By default Mathematica assumes that all variables are complex, so we need to tell Mathematica that the orbital exponent α is not only Real but also is a positive number. This can be done using the `Assuming` option:

$$\text{Sint} = \text{Assuming}[\alpha > 0, \text{Integrate}[\text{gtf}^2 * 4 * \pi * r^2, \{r, 0, \infty\}]]; \tag{24}$$

Mathematica should evaluate this integral to

$$\text{Sint} = \frac{\pi^{3/2}}{2\sqrt{2}\alpha^{3/2}} \tag{25}$$

The normalization coefficient N_α (equation 22) is then

$$\text{Na} = \text{FullSimplify}[\sqrt{1/\text{Sint}}]; \tag{26}$$

which evaluates to

$$\text{Na} = \left(\frac{2}{\pi}\right)^{3/4}\sqrt{\alpha^{3/2}} \tag{27}$$

Now we can combine GTF (18) with the normalization coefficient (27) to get a normalized GTF:

$$\text{ngtf} = \text{Na} * \text{Exp}[-\alpha * r^2]; \tag{28}$$

where "ngtf" stands for a "normalized" GTF. The full form of our normalized function is then:

$$\text{ngtf} = e^{-r^2\alpha}\left(\frac{2}{\pi}\right)^{3/4}\sqrt{\alpha^{3/2}} \tag{29}$$

Note that integration of function (29) as shown in (21) gives 1 no matter what the value of the orbital exponent α is (provided, of course, $\alpha>0$). Because of that, the expression for energy (15) reduces to

$$E_\varphi = \int \varphi \hat{H} \varphi d\tau \tag{30}$$

It needs to be emphasized that because we are dealing with a real function φ, we can replace the complex conjugate φ^* with the function itself. Also, remembering that we are working with a spherically-symmetric trial function, the three-dimensional integral (30) reduces to a one-dimensional integral

$$E_\varphi = 4\pi \int_0^\infty r^2 \varphi(r) \hat{H} \varphi(r) dr \;, \tag{31}$$

the same way we simplified integral S (equations 20 and 21). In order to evaluate this integral, we need to construct the Hamiltonian operator (19), and apply it to our trial wavefunction (29). To make things clear, I define the kinetic $\hat{T}$ and potential $\hat{V}$ energy operators separately, i.e.

$$\hat{H} = \hat{T} + \hat{V} \tag{32}$$

$$\hat{T} = -\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) \tag{33}$$

$$\hat{V} = -\frac{1}{r} \tag{34}$$

$$\hat{H}\varphi = \hat{T}\varphi + \hat{V}\varphi \tag{35}$$

$$\hat{T}\varphi = -\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\varphi\right) \tag{36}$$

$$\hat{V}\varphi = -\frac{\varphi}{r} \tag{37}$$

Equations (35), (36), and (37) can be programmed in Mathematica as follows:

$$\text{T}\varphi = \text{FullSimplify}[-\frac{1}{2*r^2}\text{D}[r^2 * \text{D}[ngtf, r], r]]; \tag{38}$$

$$\text{V}\varphi = -ngtf/r\,; \tag{39}$$

$$\text{H}\varphi = \text{T}\varphi + \text{V}\varphi; \tag{40}$$

Now we can integrate (31) in Mathematica as shown below:

$$\text{Energy} = \text{Assuming}[\alpha > 0, \text{Integrate}[ngtf * \text{H}\varphi * 4 * \pi * r^2, \{r, 0, \infty\}]]; \tag{41}$$

Because r integrates out, the resulting energy is a function of the variational parameter α only:

$$\text{Energy} = -2\sqrt{\frac{2}{\pi}}\sqrt{\alpha} + \frac{3\alpha}{2} \tag{42}$$

If you prefer numerical values,

$$\text{Energy} = \text{N}[\text{Energy}] \tag{43}$$

which gives

$$\text{Energy} = -1.5957691216057308\sqrt{\alpha} + 1.5\alpha \tag{44}$$

The only step left is to find the minimum of energy w.r.t. α. This can be done using several different ways in Mathematica. I will discuss only two. The easiest way by far is to use the `Minimize` option:

$$\text{Emin} = \text{Minimize}[\{\text{Energy}, \alpha > 0\}, \{\alpha\}]; \tag{45}$$

which gives:

$$\text{Emin} = -0.42441 \text{ a. u. with } \alpha = 0.28294 \text{ a. u.} \tag{46}$$

Alternatively, you can calculate the first derivate of energy (equation 42) w.r.t. α, set the derivative to zero, and solve for α:

$$\text{dE} = \text{D}[\text{Energy}, \alpha]; \tag{47}$$

$$\text{alpha} = \text{Solve}[\text{dE} == 0, \alpha] \tag{48}$$

Of course, the two results are identical:

$$\alpha \text{ that minimizes } E = 0.28294 \text{ a. u.} \tag{49}$$

Note that the exact value for the energy is -0.5 a.u., so even a single GTF does a more or less decent job reproducing the total energy (within 15% of the exact value). However, we need to take a closer look at our approximate solution by comparing it with the exact one in terms of the wavefunction itself, as well as kinetic and potential energies.

First, let's plot our approximate wavefunction and the exact wavefunction on the same graph. The exact wavefunction is (Table 1):

$$\psi(r) = \frac{1}{\sqrt{\pi}} e^{-r} \tag{50}$$

This is just a single exponential function, also called a Slater-type function or a Slater-type orbital (STO) in quantum mechanics. We can define (50) in Mathematica as:

$$\psi = \left(\frac{1}{\sqrt{\pi}}\right) * \text{Exp}[-r]; \tag{51}$$

The two functions (φ and ψ) can be plotted together using the following command:

$$\text{Plot}[\{\psi, \text{ngtf}\}, \{r, 0,5\}, \text{PlotLegends} \rightarrow \{\text{"exact"}, \text{"STO} - 3\text{G"}\}, \text{AxesLabel} \rightarrow$$
$$\{\text{"r (a. u.)"}, \text{"}\psi(r) \text{ or } \varphi(r)\text{"}\}] \tag{52}$$

Note that it is assumed that the variable α has already been assigned the optimized value from either (45) or (48). This can be achieved using any of the following two options:

$$\alpha = \alpha/. \text{Emin}[[2]]; \tag{53}$$
$$\alpha = \alpha/. \text{alpha}[[1]]; \tag{54}$$

Whatever the case, the resulting plot should look like this:
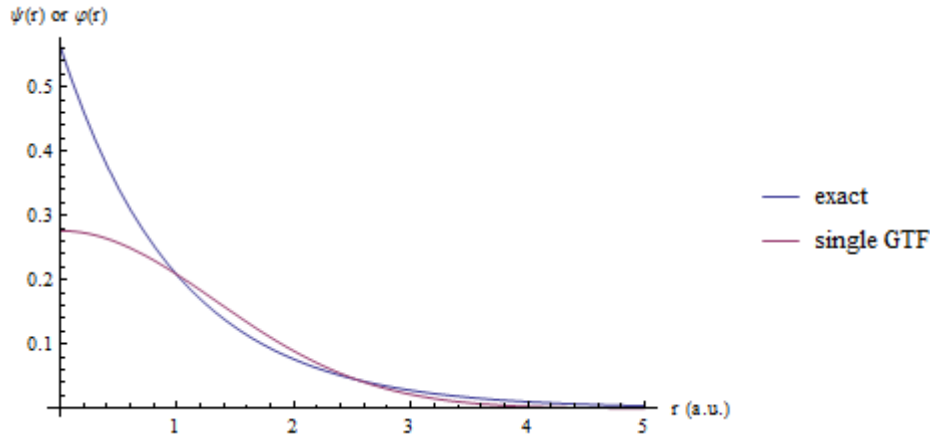
As you can see, a single GTF does not do a good job describing the exact wavefunction at small r. What about kinetic and potential energies? Recall that the kinetic and potential energies are defined as

$$T = \int \varphi \hat{T} \varphi d\tau \tag{55}$$

$$V = \int \varphi \hat{V} \varphi d\tau \tag{56}$$

For a spherically-symmetric wavefunction these three-dimensional integrals reduce to one-dimensional integrals over r

$$T = 4\pi \int_0^\infty r^2 \varphi(r) \hat{T} \varphi(r) dr \tag{57}$$

$$V = 4\pi \int_0^\infty r^2 \varphi(r) \hat{V} \varphi(r) dr \tag{58}$$

Integrating these in Mathematica is essentially the same as (41), except this time you do not need any assumptions for α - we have already found (and assigned) the optimal value. So, equations (57) and (58) in Mathematica are:

$$T = \text{Integrate}[\text{ngtf} * T\varphi * 4 * \pi * r^2, \{r, 0, \infty\}]; \tag{59}$$
$$V = \text{Integrate}[\text{ngtf} * V\varphi * 4 * \pi * r^2, \{r, 0, \infty\}]; \tag{60}$$

The resulting energies are:

$$\text{Kinetic energy, } T = 0.42441 \text{ a. u.} \tag{61}$$
$$\text{Potential energy, } V = -0.84883 \text{ a. u.} \tag{62}$$

The *virial ratio*, the ratio of potential and kinetic energies (usually taken with a negative sign to get a positive number) is then

$$VT = -V/T; \tag{63}$$
$$-V/T = 2.0000000000 \tag{64}$$

The question is how good the kinetic and potential energies based on our trial wavefunction are. We can compare *T* and *V* with those from the exact wavefunction (50). We can very quickly calculate those using the same commands as were used for the trial wavefunction:

$$T\psi = \text{FullSimplify}[-\frac{1}{2*r^2}D[r^2 * D[\psi, r], r]]; \tag{65}$$
$$V\psi = -\psi/r; \tag{66}$$
$$T = \text{Integrate}[\psi * T\psi * 4 * \pi * r^2, \{r, 0, \infty\}]; \tag{67}$$
$$V = \text{Integrate}[\psi * V\psi * 4 * \pi * r^2, \{r, 0, \infty\}]; \tag{68}$$
$$VT = -V/T; \tag{69}$$

The resulting energies are:

$$\text{Kinetic energy, } T = 0.5 \text{ a. u.} \tag{70}$$
$$\text{Potential energy, } V = -1 \text{ a. u.} \tag{71}$$
$$-V/T = 2 \tag{72}$$

Of course, the total energy, *E*, is the sum of *T* and *V*, and is equal to -0.5 a.u., as expected. Note that the energy differences between our approximate wavefunction and the exact one are on the order of 0.1-0.2 a.u. (Hartree) which is huge! Certainly, we can do better. How? What if instead of a single Gaussian function, we use several, i.e. two, three, four, ... After all, several Gaussians should be able to describe the exact wavefunction (exponential) much better, so the energies will also be closer. Indeed, this is the objective of the second part of this exercise.

Solution of the Schrödinger equation for the hydrogen atom using a trial wavefunction represented by a linear combination of several Gaussian-type functions.

A trial wavefunction represented by a linear combination of *n* GTFs is given by

$$\varphi(r) = c_1 g_1(r) + c_2 g_2(r) + \ldots + c_N g_N(r) = \sum_{i=1}^{n} c_i g_i(r) \tag{73}$$

where linear coefficients c_i are called the *expansion coefficients*, and each *i*-th GTF is defined as

$$g_i(r) = N_{\alpha_i} e^{-\alpha_i r^2} \tag{74}$$

where α_i is the orbital exponent and N_{α_i} is the normalization coefficient of the *i*-th GTF. Note that expansion (73) can be based on any other function type, not just GTF. Whatever the case, individual functions in expansion (73) are called *basis functions*. The variational parameters in expansion (73) are [linear] expansion coefficients c_i and [non-linear] orbital exponents α_i. I think you know that it is much more difficult to perform a non-linear optimization, so we are going to focus on optimizing only the expansion coefficients using exponents of GTFs available in the

literature.   A specific set of basis functions for a given atom with already [pre-]optimized exponents is called a *basis set*. An extended library of atomic basis sets is available at
https://www.basissetexchange.org/

Let's take a look at a couple of basis sets for the hydrogen atom. Go to the basis set website, select the hydrogen atom, and in the menu on the left scroll down and find the following basis sets: STO-2G, STO-3G, STO-4G, STO-5G, and STO-6G.   These are the simplest basis sets that were optimized to reproduce data obtained with a single exponential (Slater) function. The name "STO-nG" means that n Gaussian-type functions (where n = 2, 3, 4, 5, 6, …) are used to represent a single Slater-type function. You may ask as to where one can find the STO-1G basis set. Actually, you created your very own STO-1G basis set for the hydrogen atom in the first part of this exercise :) Now, let's take a closer look at those basis sets. For example, find the STO-2G basis set for hydrogen, under "Format" select "Gaussian", and click on "Get Basis Set". A new browser window should appear with the following data:

```
!  STO-2G  EMSL  Basis Set Exchange Library   3/25/16 8:36 PM
! Elements                           References
! --------                          ----------
!  H - He: W.J. Hehre, R.F. Stewart and J.A. Pople, J. Chem. Phys. 2657 (1969).
! Li - Ne:
! Na - Ar: W.J. Hehre, R. Ditchfield, R.F. Stewart, J.A. Pople, J. Chem. Phys.
!  K - Kr: 52, 2769 (1970).
!


****
H     0
S   2   1.00
     1.309756377              0.430128498
     0.233135974              0.678913531
****
```

Ignore blank lines, lines that contain "****", and lines that start with "!" (these are comments), and copy and paste the remaining data (shown above in bold font) into a text file. Now save the file to your hard drive with the "H_STO-2G.txt" name. It should contain the following data:

```
S   2   1.00
     1.309756377              0.430128498
     0.233135974              0.678913531
```

Out of these data, only those that I highlighted with colors are relevant to us. Let me explain what these numbers mean. The first symbol (here, "S") indicates the orbital angular momentum quantum number l of each basis function that follows. Recall that, orbitals with l=0 are called "s", l=1 - "p", l=2 - "d" etc. The second number (here, "2") tells us that there are 3 basis functions of type "S" (i.e. with l=0). Ignore the next number (1.00) - we shall not use it.   Notice there are two lines that follow the first line, one line for each basis function. The first number in each line is the value of the orbital exponent of the corresponding basis function. In this particular example, α_1=1.309756377 and α_2= 0.233135974. We shall ignore the second number in each basis function line. Thus, in this particular example, our trial wavefunction has the following form:

$$\varphi(r) = c_1 N_{\alpha_1} e^{-\alpha_1 r^2} + c_2 N_{\alpha_2} e^{-\alpha_2 r^2} \tag{75}$$

where the values of α_1 and α_2, are listed above. Thus, only the expansion coefficients c_i are unknown, and it is our job to find the set of coefficients that minimizes the energy. While it is tempting to follow the same strategy as in the single GTF minimization, this may or may not work. After all, minimization in several dimensions is not trivial. Are you sure that Mathematica will be able to find a local minimum in six dimensions when you will use the STO-20G basis set (you can

find the STO-20G basis set file "H_STO-20G.txt" in the D2L Project 5 section)? We need to use some sort of a minimization technique that works reliably in many dimensions.

Secular equations and secular determinant

Let's rewrite equation (75) in a more concise form, similar to that of (73):

$$\varphi(r) = c_1 g_1(r) + c_2 g_2(r) \tag{76}$$

We substitute this expansion into the expression for energy (5) modified to take into account the fact that we are dealing with real basis functions.

$$E_\varphi = \frac{\int \varphi \hat{H} \varphi d\tau}{\int \varphi^2 d\tau} = \frac{\int (c_1 g_1 + c_2 g_2) \hat{H} (c_1 g_1 + c_2 g_2) d\tau}{\int (c_1 g_1 + c_2 g_{23})^2 d\tau} \tag{77}$$

Let's look at the denominator first (because it is easier). Expanding the denominator gives:

$$\int (c_1 g_1 + c_2 g_2)^2 d\tau =$$

$$\int \left(c_1 g_1 c_1 g_1 + c_1 g_1 c_2 g_2 + c_2 g_2 c_1 g_1 + c_2 g_2 c_2 g_2 + \right) d\tau = \tag{78}$$

$$\int c_1 g_1 c_1 g_1 d\tau + \int c_1 g_1 c_2 g_2 d\tau + \int c_2 g_2 c_1 g_1 d\tau + \int c_2 g_2 c_2 g_2 d\tau$$

While equation (78) looks pretty intimidating, it is actually not that bad, and can be simplified further because

$$\int c_i g_i c_j g_j d\tau = \int c_j g_j c_i g_i d\tau \tag{79}$$

$$c_i c_j \int g_i g_j d\tau = c_j c_i \int g_j g_i d\tau \tag{80}$$

Note that coefficients c are constants, and thus can be pulled out of the integral. Taking this into account, equation (78) simplifies to:

$$c_1 c_1 \int g_1 g_1 d\tau + c_1 c_2 \int g_1 g_2 d\tau + c_1 c_2 \int g_1 g_2 d\tau + c_2 c_2 \int g_2 g_2 d\tau \tag{81}$$

Integrals

$$S_{ij} = \int g_i g_j d\tau \tag{82}$$

are called the *overlap integrals* and are abbreviated as S_{ij}. Also looking at equation (81) one can notice that overlap integrals S_{ij} form a 2×2 *overlap matrix* **S** :

$$\mathbf{S} = \begin{vmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{vmatrix} \tag{83}$$

Of course, the overlap matrix is symmetric because of relations (79) and (80). Now let's take a look at the numerator of (77). First, we apply the Hamiltonian operator $\hat{H}$ to each function in φ to the right of it:

$$\int (c_1 g_1 + c_2 g_2) \hat{H} (c_1 g_1 + c_2 g_2) d\tau =$$

$$\int (c_1 g_1 + c_2 g_2)(c_1 \hat{H} g_1 + c_2 \hat{H} g_2) d\tau \tag{84}$$

Then we multiply φ on the left of $\hat{H}$ (a linear combination of GTFs) by the sum on the right:

$$\int \left(c_1 c_1 g_1 \hat{H} g_1 + c_1 c_2 g_1 \hat{H} g_2 + c_2 c_1 g_2 \hat{H} g_1 + c_2 c_2 g_2 \hat{H} g_2 \right) d\tau \tag{85}$$

An integral of a sum is a sum of integrals, so

$$\int c_1 c_1 g_1 \hat{H} g_1 d\tau + \int c_1 c_2 g_1 \hat{H} g_2 d\tau + \int c_2 c_1 g_2 \hat{H} g_1 d\tau + \int c_2 c_2 g_2 \hat{H} g_2 d\tau \tag{86}$$

Finally, we note that coefficients c are constants, and thus can be pulled out of the integrals:

$$c_1 c_1 \int g_1 \hat{H} g_1 d\tau + c_1 c_2 \int g_1 \hat{H} g_2 d\tau + c_2 c_1 \int g_2 \hat{H} g_1 d\tau + c_2 c_2 \int g_2 \hat{H} g_2 d\tau \qquad (87)$$

For these integrals, we can introduce the same notation as was used for the overlap integrals

$$H_{ij} = \int g_i \hat{H} g_j d\tau \qquad (88)$$

Using this notation, equation (87) reduces to :

$$c_1 c_1 H_{11} + c_1 c_2 H_{12} + c_2 c_1 H_{21} + c_2 c_2 H_{22} \qquad (89)$$

A natural question is whether relation (80) also holds for integrals H_{ij}, i.e.:

$$c_i c_j \int g_i \hat{H} g_j d\tau \quad (= ?) \quad c_j c_i \int g_j \hat{H} g_i d\tau \qquad (90)$$

Let's see if we can figure it out. We know that the Hamiltonian operator $\hat{H}$ is Hermitian, so

$$\int g_i^* \hat{H} g_j d\tau = \int g_j^* \hat{H} g_i d\tau \qquad (91)$$

However, because our functions g are real,

$$g_i^* = g_i \quad \text{and} \quad g_j^* = g_j \qquad (92)$$

it follows that

$$\int g_i \hat{H} g_j d\tau = \int g_j \hat{H} g_i d\tau \qquad (93)$$

Thus,

$$H_{ij} = H_{ji} \qquad (94)$$

So, integrals H_{ij} also form a 2×2 symmetric matrix $\mathbf{H}$:

$$\mathbf{H} = \begin{vmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{vmatrix} \qquad (95)$$

For the reason that we shall discuss later, this matrix is called a *Fock matrix*.

If we consider coefficients c arranged in a column vector $\mathbf{c}$,

$$\mathbf{c} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \qquad (96)$$

then its transpose $\mathbf{c}^\mathrm{T}$ is a row vector

$$\mathbf{c}^T = \begin{pmatrix} c_1 & c_2 \end{pmatrix} \qquad (97)$$

Using this (matrix) notations, the expression for energy becomes very simple:

$$E = \frac{\mathbf{c}^T \mathbf{H} \mathbf{c}}{\mathbf{c}^T \mathbf{S} \mathbf{c}} \qquad (98)$$

or

$$E \mathbf{c}^T \mathbf{S} \mathbf{c} = \mathbf{c}^T \mathbf{H} \mathbf{c} \qquad (99)$$

The lowest possible E for a given trial wavefunction expansion is achieved when

$$\frac{\partial E}{\partial c_i} = 0 \qquad (100)$$

Differentiating E w.r.t. coefficients c_i gives

$$(H_{11} - E S_{11}) c_1 + (H_{12} - E S_{12}) c_2 = 0$$
$$(H_{21} - E S_{21}) c_1 + (H_{22} - E S_{22}) c_2 = 0 \qquad (101)$$

or in matrix notation:

$$(\mathbf{H} - E\mathbf{S}) \mathbf{c} = \mathbf{H}\mathbf{c} - E\mathbf{S}\mathbf{c} = 0 \qquad (102)$$

These are called the *secular equations*. Non-trivial solution is obtained when the determinant of the coefficients vanishes:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \tag{103}$$

or in the matrix notation

$$|\mathbf{H} - E\mathbf{S}| = 0 \tag{104}$$

The determinant in equation (103) is called the *secular determinant*. In general, a 2×2 determinant expands as follows:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc \tag{105}$$

Applying (105) to (103) gives:

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{12} - ES_{12})(H_{21} - ES_{21}) = 0 \tag{106}$$

which results in a quadratic equation in E. According to the variational principle, out of the two roots of this equation, the lowest energy root gives the best energy achievable with a given basis set.

Of course, in this simple example we used only two functions in the trial wavefunction expansion. More advanced expansions can include 20(!) and more functions, which brings a trial wavefunction very close to an exact wavefunction.

Solving secular equations

So, if we solve equation (106), we get energy E and a set of coefficients $\mathbf{c}$. That is all nice, but how do we actually do that? First, let's take a step back to equation (102). It is important, so I retype it here:

$$(\mathbf{H} - E\mathbf{S})\mathbf{c} = \mathbf{Hc} - E\mathbf{Sc} = 0 \tag{107}$$

Rearranging it gives

$$\mathbf{Hc} = E\mathbf{Sc} \tag{108}$$

Because we are dealing with 2×2 matrices, and essentially have to solve a quadratic equation in E, we are going to end up with 2 sets of solutions, i.e. we will end up with 2 possible wavefunctions φ_i ($i=1...2$) with different energies but each being a solution of the Schrödinger equation. These wavefunctions are also called *orbitals*, and their energies are called *orbital energies*. It follows that solutions for E will be in a form of a diagonal matrix of orbital energies ε_i, let's call it $\boldsymbol{\varepsilon}$:

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix} \tag{109}$$

and solutions for coefficients c will be in a form of a 2×2 matrix, let's call it $\mathbf{C}$:

$$\mathbf{C} = \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} \tag{110}$$

where (c_{11} c_{21}) are coefficients corresponding to ε_1, and (c_{12} c_{22}) are coefficients corresponding to ε_2. Note that in each column of $\mathbf{C}$ the c's belong to the same orbital.

It is a general feature of the trial wavefunction expansion method that using n basis functions will result in n possible orbitals. This is clearly because n basis functions will produce an n-order equation in E, which will have n roots. Of course, for now we are interested only in the one with the lowest energy.

Anyway, based on everything discussed above, equation (108) is transformed to

$$\mathbf{HC} = \mathbf{SC}\boldsymbol{\varepsilon} \tag{111}$$

However, what we really want to do is to reduce (111) to the *standard eigenvalue form* [3]:
$$\mathbf{HC} = \mathbf{C\varepsilon} \qquad (112)$$
In order to do that, we need to transform the original set of basis functions $\{g\}$ into an orthonormal set $\{g'\}$.

$$\varphi = c_1' g_1' + c_2' g_2' + c_3' g_3' \qquad (113)$$

It is constructed in such a way that with a new set of coefficients c', we have orbitals φ with the same energy levels as before:

$$S_{ij}' = \int g_i' g_j' d\tau = \delta_{ij} \qquad (114)$$

where δ_{ij} is the Kronecker delta

$$\delta_{ij} = \begin{cases} 0 \text{ if } i \neq j \\ 1 \text{ if } i = j \end{cases} \qquad (115)$$

so that the overlap matrix $\mathbf{S}'$ becomes the unit matrix. The result of such a process, called *orthogonalization*, is

$$\mathbf{HC} = \mathbf{SC\varepsilon} \xrightarrow{\text{Orthogonalization}} \mathbf{H'C'} = \mathbf{S'C'\varepsilon} \qquad (116)$$
$$\mathbf{HC} = \mathbf{SC\varepsilon} \xrightarrow{\text{Orthogonalization}} \mathbf{H'C'} = \mathbf{C'\varepsilon} \qquad (117)$$

Note that the energy $\mathbf{\varepsilon}$ does not depend on manipulation of a given basis set functions, so we still have $\mathbf{\varepsilon}$ instead of $\mathbf{\varepsilon'}$.

Orthogonalization by Löwdin [3]

Define matrix $\mathbf{C'}$ such as

$$\mathbf{C'} = \mathbf{S}^{1/2}\mathbf{C} \text{ i.e. } \mathbf{C} = \mathbf{S}^{-1/2}\mathbf{C'} \qquad (118)$$

Substituting back into

$$\mathbf{HC} = \mathbf{SC\varepsilon} \qquad (119)$$

and multiplying on the left by $\mathbf{S}^{-1/2}$ we get:

$$\mathbf{S}^{-1/2}\mathbf{HS}^{-1/2}\mathbf{C'} = \mathbf{S}^{-1/2}\mathbf{SS}^{-1/2}\mathbf{C'\varepsilon} \qquad (120)$$

Let

$$\mathbf{S}^{-1/2}\mathbf{HS}^{-1/2} = \mathbf{H'} \qquad (121)$$

and note that

$$\mathbf{S}^{-1/2}\mathbf{SS}^{-1/2} = \mathbf{S}^{1/2}\mathbf{S}^{-1/2} = \mathbf{1} \qquad (122)$$

then we have

$$\mathbf{H'C'} = \mathbf{1C'\varepsilon} \qquad (123)$$
$$\mathbf{H'C'} = \mathbf{C'\varepsilon} \qquad (124)$$

Thus the orthogonalizing process (or rather one possible orthogonalization process, Löwdin orthogonalization) is the use of an *orthogonalizing matrix* $\mathbf{S}^{-1/2}$ to transform $\mathbf{H}$ by pre- and postmultiplication into $\mathbf{H'}$. $\mathbf{H'}$ satisfies the standard eigenvalue equation, so

$$\mathbf{H'} = \mathbf{C'\varepsilon C'}^{-1} \qquad (125)$$

In other words, using $\mathbf{S}^{-1/2}$ we transform the original Fock matrix $\mathbf{H}$, which is not directly diagonalizable into a related matrix $\mathbf{H'}$ which is diagonalizable to eigenvector and eigenvalue matrices $\mathbf{C'}$ and $\mathbf{\varepsilon}$. The matrix $\mathbf{C'}$ is then transformed to the desired $\mathbf{C}$ by multiplying by $\mathbf{S}^{-1/2}$. So without using the drastic $\mathbf{S} = \mathbf{1}$ approximation we can use matrix diagonalization to get the coefficients and energy levels from the Fock matrix.

The orthogonalizing matrix $\mathbf{S}^{-1/2}$ is calculated from $\mathbf{S}$: the integrals S are calculated and assembled into $\mathbf{S}$, which is then diagonalized:

$$\mathbf{S} = \mathbf{PDP}^{-1} \tag{126}$$

Now it can be shown that any function of a matrix $\mathbf{A}$ can be obtained by taking the same function of its corresponding diagonal *alter ego* and pre- and postmultiplying by the diagonalizing matrix $\mathbf{P}$ and its inverse $\mathbf{P}^{-1}$:

$$f(\mathbf{A}) = \mathbf{P}f(\mathbf{D})\mathbf{P}^{-1} \tag{127}$$

and diagonal matrices have the nice property that f($\mathbf{D}$) is the diagonal matrix whose diagonal element $i, j = f$ (element i, j of $\mathbf{D}$). So the inverse square root of $\mathbf{D}$ is the matrix whose elements are the inverse square roots of the corresponding elements of $\mathbf{D}$. Therefore

$$\mathbf{S}^{-1/2} = \mathbf{PD}^{-1/2}\mathbf{P}^{-1} \tag{128}$$

and to find $\mathbf{D}^{-1/2}$ we (or rather the computer) simply take the inverse square root of the diagonal (i.e. the nonzero) elements of $\mathbf{D}$. To summarize: $\mathbf{S}$ is diagonalized to give $\mathbf{P}$, $\mathbf{P}^{-1}$ and $\mathbf{D}$, $\mathbf{D}$ is used to calculate $\mathbf{D}^{-1/2}$, then the orthogonalizing matrix $\mathbf{S}^{-1/2}$ is calculated from $\mathbf{P}$, $\mathbf{D}^{-1/2}$ and $\mathbf{P}^{-1}$. The orthogonalizing matrix is then used to convert $\mathbf{H}$ to $\mathbf{H}'$ which is then diagonalized to give the eigenvalues and the eigenvectors.

The sequence of steps [3]

(1)   Calculate the overlap integrals over basis functions $S_{ij} = \int g_i g_j d\tau$ and assemble the overlap matrix $\mathbf{S}$.

(2)   Calculate the Fock matrix elements $H_{ij} = \int g_i \hat{H} g_j d\tau$ and assemble the Fock matrix $\mathbf{H}$.

(3)   The overlap matrix $\mathbf{S}$ is diagonalized to give $\mathbf{P}$, $\mathbf{D}$ and $\mathbf{P}^{-1}$, and $\mathbf{D}^{-1/2}$ is calculated by finding the inverse square roots of the diagonal elements of $\mathbf{D}$. The orthogonalizing matrix $\mathbf{S}^{-1/2}$ is calculated from $\mathbf{P}$, $\mathbf{D}^{-1/2}$, and $\mathbf{P}^{-1}$.

(4)   The Fock matrix $\mathbf{H}$ in the nonorthogonal basis $\{g\}$ is transformed into the matrix $\mathbf{H}'$ in the orthogonal basis $\{g'\}$ by pre- and postmultiplying $\mathbf{H}$ by the orthogonalizing matrix $\mathbf{S}^{-1/2}$.

(5) $\mathbf{H}'$ is diagonalized to give $\mathbf{C}'$, $\boldsymbol{\varepsilon}$ and $\mathbf{C}'^{-1}$. We now have the energy levels ε (the diagonal elements of the $\boldsymbol{\varepsilon}$ matrix).

(6) $\mathbf{C}'$ must be transformed to give the coefficients c of the original set of basis functions $\{g\}$ in the orbitals (i.e. to convert the elements c' to c). To get the c's in the

$$\varphi_j = c_{1j}g_1 + c_{2j}g_2 + \dots \tag{129}$$

we transform $\mathbf{C}'$ to $\mathbf{C}$ by premultiplying by $\mathbf{S}^{-1/2}$.

How to diagonalize a matrix in Mathematica

Based on our discussion above, diagonalizing $\mathbf{S}$ gives $\mathbf{D}$ as:
$$\mathbf{S} = \mathbf{P}\,\mathbf{D}\,\mathbf{P}^{-1} \tag{130}$$
However, this is equivalent to:
$$\mathbf{S} = \mathbf{P}\,\mathbf{D}\,\mathbf{P}^{-1} \tag{131}$$
$$\mathbf{P}^{-1}\,\mathbf{S} = \mathbf{P}^{-1}\,\mathbf{P}\,\mathbf{D}\,\mathbf{P}^{-1} \tag{132}$$
$$\mathbf{P}^{-1}\,\mathbf{S} = \mathbf{D}\,\mathbf{P}^{-1} \tag{133}$$
$$\mathbf{P}^{-1}\,\mathbf{S}\,\mathbf{P} = \mathbf{D}\,\mathbf{P}^{-1}\,\mathbf{P} \tag{134}$$
$$\mathbf{P}^{-1}\,\mathbf{S}\,\mathbf{P} = \mathbf{D} \tag{135}$$
$$\mathbf{D} = \mathbf{P}^{-1}\,\mathbf{S}\,\mathbf{P} \tag{136}$$

In Mathematica, such operation is obtained using the following procedure [4] :
$$\mathbf{vecs}=\text{Eigenvectors}[\mathbf{S}] \tag{137}$$
$$\text{Inverse[Transpose[vecs]]}.\text{S}.\text{Transpose[vecs]}//\text{Chop} \tag{138}$$

Thus to get $\mathbf{D}, \mathbf{P}$ and $\mathbf{P}^{-1}$ from $\mathbf{S}$ in Mathematica, we use:
$$\mathbf{P}=\text{Transpose[Eigenvectors[}\mathbf{S}]] \tag{139}$$
$$\mathbf{D}=\text{Inverse}[\mathbf{P}].\mathbf{S}.\mathbf{P}//\text{Chop} \tag{140}$$
Then we calculate $\mathbf{D}^{-1/2}$:
$$\mathbf{Dminushalf}= \text{MatrixPower}[\mathbf{D},-1/2] \tag{141}$$
Now we need $\mathbf{S}^{-1/2}$. We can get it using
$$\mathbf{S}^{-1/2}=\mathbf{P}\mathbf{D}^{-1/2}\mathbf{P}^{-1} \tag{142}$$
$$\mathbf{Sminushalf} = \mathbf{P}.\mathbf{Dminushalf}.\text{Inverse}[\mathbf{P}]//\text{Chop} \tag{143}$$
The matrix $\mathbf{S}^{-1/2}$ is used to convert $\mathbf{H}$ to $\mathbf{H'}$:
$$\mathbf{H'}=\mathbf{S}^{-1/2}\mathbf{H}\,\mathbf{S}^{-1/2} \tag{144}$$
$$\mathbf{Hprime}=\mathbf{Sminushalf}.\mathbf{H}.\mathbf{Sminushalf} \tag{145}$$
The only step left is to diagonalize $\mathbf{H'}$ as
$$\mathbf{H'} = \mathbf{C'}\,\varepsilon\,\mathbf{C'}^{-1} \tag{146}$$
$$\mathbf{C'}^{-1}\,\mathbf{H'}\,\mathbf{C'} = \varepsilon \tag{147}$$
$$\varepsilon = \mathbf{C'}^{-1}\,\mathbf{H'}\,\mathbf{C'} \tag{148}$$
which can be done in Mathematica as
$$\mathbf{Cprime}=\text{Transpose[Eigenvectors[}\mathbf{Hprime}]] \tag{149}$$
$$\mathbf{energy}=\text{Inverse}[\mathbf{Cprime}].\mathbf{Hprime}.\mathbf{Cprime}//\text{Chop} \tag{150}$$
The energy levels are the diagonal elements of matrix **energy.**

$\mathbf{C'}$ must be transformed to give the coefficients $\mathbf{C}$ of the original set of basis functions
$$\mathbf{C} = \mathbf{S}^{-1/2}\,\mathbf{C'} \tag{151}$$
$$\mathbf{C}=\mathbf{Sminushalf}.\mathbf{Cprime} \tag{152}$$
The first column of $\mathbf{C}$ gives coefficients for $\mathbf{energy}_{11}$, the second row of $\mathbf{C}$ gives coefficients for $\mathbf{energy}_{22}$ etc.

The calculation of the **S** and **H** matrix elements

     This part should actually be familiar to you - you have done it for a single GTF, but now you need to do it for products of several GTFs. The overlap integrals are given by

$$S_{ij} = \int g_i g_j d\tau \tag{153}$$

Because the functions g we are using are spherically symmetric, this integral reduces to

$$S_{ij} = 4\pi \int_0^\infty g_i(r) g_j(r) r^2 dr \tag{154}$$

It can be further simplified as we expand each function g

$$S_{ij} = 4\pi \int_0^\infty N_{\alpha_i} e^{-\alpha_i r^2} N_{\alpha_j} e^{-\alpha_j r^2} r^2 dr \tag{155}$$

Because normalization coefficients do not depend on r, they can be pulled out of the integral. Also, the two exponents can be combined into one:

$$S_{ij} = 4\pi N_{\alpha_i} N_{\alpha_j} \int_0^\infty e^{-(\alpha_i + \alpha_j) r^2} r^2 dr \tag{156}$$

This integral can be evaluated analytically, but perhaps it is easier here to let Mathematica evaluate (155):

$$\text{gi} = \left(\frac{2*\alpha i}{\pi}\right)^{3/4} e^{-r^2 \alpha i}; \tag{157}$$

$$\text{gj} = \left(\frac{2*\alpha j}{\pi}\right)^{3/4} e^{-r^2 \alpha j}; \tag{158}$$

$$\text{Sij} = \text{Assuming}[\alpha i > 0 \&\& \alpha j > 0, \text{Integrate}[gi * gj * 4 * \pi * r^2, \{r, 0, \infty\}]]; \tag{159}$$

This integration results in a very simple analytical formula for S_{ij}:

$$\text{Sij} = \frac{2\sqrt{2}(\alpha i \alpha j)^{3/4}}{(\alpha i + \alpha j)^{3/2}} \tag{160}$$

Now we turn our attention to the Fock matrix elements H_{ij}:

$$H_{ij} = \int g_i \hat{H} g_j d\tau \tag{161}$$

Unfortunately, these are not as simple to evaluate as S_{ij}. Perhaps, it is a good idea to use the same approach we employed in the first part of the exercise. That is, the three-dimensional integral H_{ij}

$$H_{ij} = \int g_i \hat{H} g_j d\tau \tag{162}$$

is first reduced to a one-dimensional integral

$$H_{ij} = 4\pi \int_0^\infty r^2 g_i \hat{H} g_j dr \tag{163}$$

The normalization coefficients are pulled out of the integral:

$$H_{ij} = 4\pi N_{\alpha_i} N_{\alpha_j} \int_0^\infty r^2 e^{-\alpha_i r^2} \hat{H} e^{-\alpha_j r^2} dr \tag{164}$$

The Hamiltonian operator is separated into the kinetic and potential energy operators:

$$H_{ij} = 4\pi N_{\alpha_i} N_{\alpha_j} \int_0^\infty r^2 e^{-\alpha_i r^2} (\hat{T} + \hat{V}) e^{-\alpha_j r^2} dr \tag{165}$$

$$H_{ij} = 4\pi N_{\alpha_i} N_{\alpha_j} \left(\int_0^\infty r^2 e^{-\alpha_i r^2} \hat{T} e^{-\alpha_j r^2} dr + \int_0^\infty r^2 e^{-\alpha_i r^2} \hat{V} e^{-\alpha_j r^2} dr \right) \tag{166}$$

$$H_{ij} = 4\pi N_{\alpha_i} N_{\alpha_j} \int_0^\infty r^2 e^{-\alpha_i r^2} \hat{T} e^{-\alpha_j r^2} dr + 4\pi N_{\alpha_i} N_{\alpha_j} \int_0^\infty r^2 e^{-\alpha_i r^2} \hat{V} e^{-\alpha_j r^2} dr \qquad (167)$$

$$H_{ij} = T_{ij} + V_{ij} \qquad (168)$$

$$T_{ij} = 4\pi N_{\alpha_i} N_{\alpha_j} \int_0^\infty r^2 e^{-\alpha_i r^2} \left[-\frac{1}{2r^2} \frac{d}{dr}\left(r^2 \frac{d}{dr} e^{-\alpha_j r^2} \right) \right] dr \qquad (169)$$

$$V_{ij} = 4\pi N_{\alpha_i} N_{\alpha_j} \int_0^\infty r^2 e^{-\alpha_i r^2} \frac{1}{r} e^{-\alpha_j r^2} dr \qquad (170)$$

Each of these can be evaluated analytically in Mathematica [separately]. Using previously defined functions g_i and g_j (equations 157 and 158), we evaluate integrals (169) and (170):

$$\text{Tgj} = \text{FullSimplify}[-\tfrac{1}{2*r^2} D[r^2 * D[gj, r], r]]; \qquad (171)$$

$$\text{Tij} = \text{Assuming}[\alpha i > 0 \&\& \alpha j > 0, \text{Integrate}[gi * Tgj * 4 * \pi * r^2, \{r, 0, \infty\}]]; \qquad (172)$$

$$\text{Vgj} = -gj/r; \qquad (173)$$

$$\text{Vij} = \text{Assuming}[\alpha i > 0 \&\& \alpha j > 0, \text{Integrate}[gi * Vgj * 4 * \pi * r^2, \{r, 0, \infty\}]]; \qquad (174)$$

which gives for T_{ij} and V_{ij}:

$$\text{Tij} = \frac{6\sqrt{2}(\alpha i \alpha j)^{7/4}}{(\alpha i + \alpha j)^{5/2}} \qquad (175)$$

$$\text{Vij} = -\frac{4\sqrt{\frac{2}{\pi}}(\alpha i \alpha j)^{3/4}}{\alpha i + \alpha j} \qquad (176)$$

Of course, if you want, you can evaluate each integral T_{ij} and V_{ij} by direct integration (equations 169 and 170). In this exercise, these are not too time consuming (but obviously, they can be!).

<u>The calculation of total energies</u>

Once you have found the set of coefficients for the orbital with the lowest energy (let's call this array of coefficients **Cmin**), the kinetic, potential, and total energies can be calculated as follows:

$$\text{Kinetic energy} = T = \left(\sum_{i=1}^n \sum_{j=1}^n Cmin_i Cmin_j T_{ij} \right) / S \qquad (177)$$

$$\text{Potential energy} = V = \left(\sum_{i=1}^n \sum_{j=1}^n Cmin_i Cmin_j V_{ij} \right) / S \qquad (178)$$

$$\text{Total energy} = E = T + V = \left(\sum_{i=1}^n \sum_{j=1}^n Cmin_i Cmin_j H_{ij} \right) / S \qquad (179)$$

where n is the number of basis functions in the trial wavefunction expansion, and S is the normalization integral calculated as

$$S = \sum_{i=1}^n \sum_{j=1}^n Cmin_i Cmin_j S_{ij} \qquad (180)$$

Of course, in our case the normalization integral should be equal to 1 because we have normalized our wavefunction.

The following table summarizes (for debugging purposes) the energies for the exact wavefunction and for the STO-1G and STO-2G basis sets:

| Wavefunction	Kinetic energy (a.u.)	Potential energy (a.u.)	Total energy (a.u.)	-V/T (virial ratio)
STO-1G	0.424413181578388	-0.848826363156775	-0.424413181578388	2.
STO-2G	0.521984597458032	-1.00513599697136	-0.483151399513326	1.92560470532308
Exact	0.5	-1	-0.5	2

As you can see, there is a significant improvement when a linear combination of several Gaussian functions is used.

The plot of the trial and exact wavefunctions

The final step is to plot the optimized trial wavefunction vs the exact wavefunction. The optimized trial wavefunction is given by

$$\varphi(r) = \sum_{i=1}^{N} Cmin_i \, g_i(r) \tag{181}$$

The form of the exact wavefunction is discussed in the first part of this exercise. For the STO-2G basis set discussed here, the agreement with the exact wavefunction is much better than that for a single Gaussian (see image below):
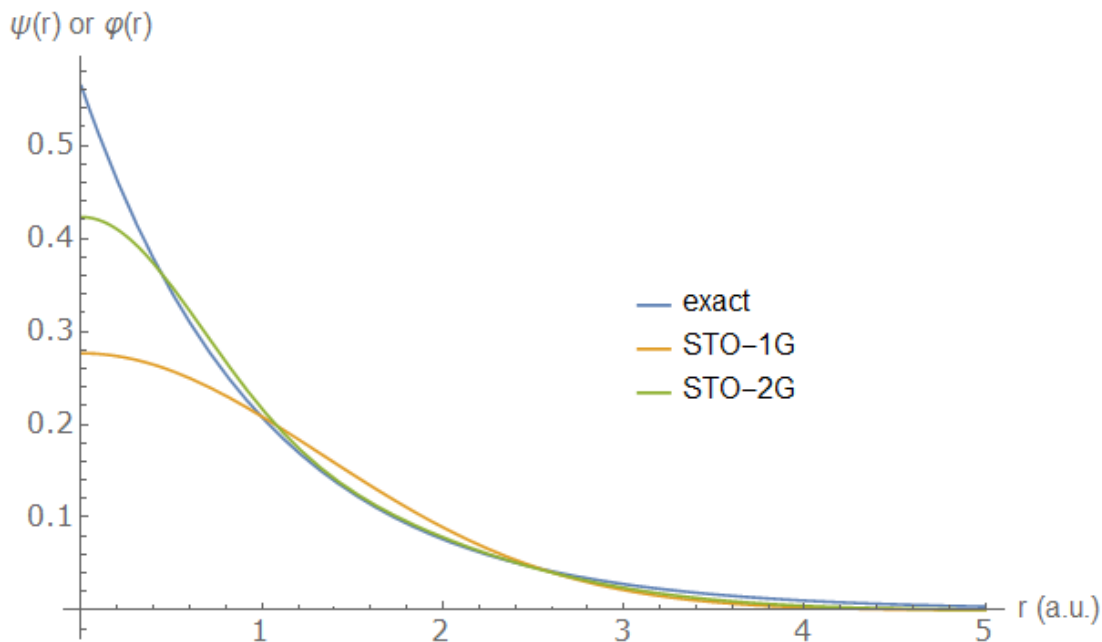
Note that it is expected that the STO-3G, STO-4G, STO-5G, STO-6G and especially STO-20G basis sets will do even better job approximating the exact wavefunction.

Final remarks

Your task is to write a Mathematica code that can perform energy optimization of a linear combination of _any_ number of Gaussian-type functions (from one and above!). The input wavefunction file format is discussed at the beginning of the second part of the exercise. Get the STO-2G, STO-3G, STO-4G, STO-5G, and STO-6G basis sets from https://www.basissetexchange.org/ and the STO-20G basis set from the D2L Project 5 section, and perform calculations with all of them! Also, run a calculation with the exact wavefunction and the STO-1G basis set (single GTF). Then, create a table (in MS Word, Mathematica etc.) which compares energies (kinetic, potential, and total) and the virial ratio for all the wavefunctions (exact, and STO-nG, where n = 1, 2, 3, 4, 5, 6, 20). For example,

Table 1. Energies and the virial ratio from the performed calculations.

	KE (a.u.)	PE (a.u.)	TE (a.u.)	-V/T
STO-1G	0.424413181578388	-0.848826363156775	-0.424413181578388	2.
STO-2G	0.521984597458032	-1.00513599697136	-0.483151399513326	1.92560470532308
STO-3G	0.50747589121518	-1.00321669584466	-0.495740804629481	1.97687557815289
STO-4G	0.502931448649698	-1.00169311302688	-0.498761664377182	1.99170904049904
STO-5G	0.501220971861377	-1.00082008173227	-0.499599109870896	1.99676417771496
STO-6G	0.500522373555967	-1.00038204283975	-0.499859669283779	1.99867597472721
STO-20G	0.499999953047226	-0.999999940383854	-0.499999987336628	2.00000006857881
Exact	0.5	-1.	-0.5	2.

Create a plot with the exact wavefunction and all the Gaussian-based wavefunctions (STO-nG, where n = 1, 2, 3, 4, 5, 6, 20). Finally, upload all the required materials to D2L. Good luck!

References

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[2] McQuarrie, D. A., Simon, J. D. *Physical Chemistry: A Molecular Approach*, University Science Books, 1997.

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[4] http://reference.wolfram.com/legacy/v5_2/Built-inFunctions/AdvancedDocumentation/LinearAlgebra/LinearAlgebraInMathematica/MatrixComputations/EigensystemComputations/AdvancedDocumentationLinearAlgebra3.3.1.html