Hydrogen Atom with a Gaussian Basis

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Overlap and Hamiltonian matrix elements

We want to calculate the overlap matrix of the non orthogonal sets of s-waves

$$\phi_i(\mathbf{r}) = e^{-\alpha_i r^2} \tag{1}$$

and p-waves

$$\phi_i^\xi(\mathbf{r}) = \xi e^{-\alpha_i^\xi r^2} \qquad \xi = x, y, z \tag{2}$$

An s-wave is clearly orthogonal to a p-wave, moreover p-waves with different ξ are orthogonal. The overlap matrix elements of s-waves are easily calculated

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \left(\frac{\pi}{\alpha_i + \alpha_j} \right)^{3/2} \tag{3}$$

While the overlap between different p-waves is

$$S_{ij}^\xi = \langle \phi_i^\xi | \phi_j^\xi \rangle = \frac{1}{2} \left(\frac{\pi}{\alpha_i^\xi + \alpha_j^\xi} \right)^{3/2} \frac{1}{\alpha_i^\xi + \alpha_j^\xi} \tag{4}$$

Obviously independent of ξ.

Consider now the Hydrogen atom Hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \tag{5}$$

To calculate its matrix elements we first compute the action of the Laplacian operator

$$\nabla^2 \phi_i(\mathbf{r}) = 2\alpha_i (2\alpha_i r^2 - 3) \phi_i(\mathbf{r})$$
$$\nabla^2 \phi_i^\xi(\mathbf{r}) = 2\alpha_i^\xi (2\alpha_i^\xi r^2 - 5) \phi_i^\xi(\mathbf{r}). \tag{6}$$

Then the Hamiltonian matrix elements of the s-wave set are

$$\begin{aligned} H_{ij} = \langle \phi_i | H | \phi_j \rangle &= \int e^{-\alpha_i r^2} \left(-\frac{\hbar^2}{m} \alpha_j (2\alpha_j r^2 - 3) - \frac{e^2}{4\pi\epsilon_0 r} \right) e^{-\alpha_j r^2} \, d^3 r \\ &= \frac{\hbar^2}{m} \frac{3\pi\sqrt{\pi}\alpha_i \alpha_j}{(\alpha_i + \alpha_j)^{5/2}} - \frac{e^2}{4\pi\epsilon_0} \frac{2\pi}{\alpha_i + \alpha_j} \end{aligned} \tag{7}$$

While for the p-waves we obtain

$$H_{ij}^\xi = \langle \phi_i^\xi | H | \phi_j^\xi \rangle = \frac{\hbar^2}{m} \frac{5\pi\sqrt{\pi}\alpha_i^\xi \alpha_j^\xi}{2(\alpha_i^\xi + \alpha_j^\xi)^{7/2}} - \frac{e^2}{4\pi\epsilon_0} \frac{2\pi}{3(\alpha_i^\xi + \alpha_j^\xi)^2} \tag{8}$$

Notice that hermiticity is fulfilled $H_{ij} = H_{ji}$ and $H_{ij}^\xi = H_{ji}^\xi$.
To better address the problem in a computational way we will use atomic units. This means to set $\hbar = 1$, $e = 1$, $m = 1$ and $4\pi\epsilon_0 = 1$. Lengths will then be expressed in Bohr radii $a_0 = 4\pi\epsilon_0 \hbar^2 / me^2$ and energies in Hartrees $E_\mathrm{h} = \hbar^2 / ma_0^2$. Notice that one Hartree is exactly two Rydbergs.

Generalized eigenvalue problem and s-wave expansion

We want to estimate the ground state energy of the Hamiltonian (5), in atomic units. By mean of the variational principle we look for the best expansion of the ground state on a finite number n of s-waves (1). Since we are aiming at the energy of the ground state, the best expansion is the one that minimizes the functional

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \qquad \text{where} \qquad |\Psi\rangle = \sum_{i=1}^{n} c_i |\phi_i\rangle \tag{9}$$

along with the normalization condition $\langle \Psi | \Psi \rangle = 1$. Such minimization leads to the following generalized eigenvalue problem

$$H\mathbf{c} = \varepsilon S \mathbf{c} \tag{10}$$

where H and S are the Hamiltonian and overlap matrix whose elements were calculated in the first section and $\mathbf{c}$ is the vector formed by the coefficients c_i. To solve (10) we first diagonalize S, this is always possible provided $\phi_i \neq \phi_j \ \forall i \neq j$ since Gaussians with different width α are clearly linearly independent. Since S is a real symmetric matrix it can be diagonalized by a orthogonal transformation

$$\begin{bmatrix} s_1 & & 0 \\ & \ddots & \\ 0 & & s_n \end{bmatrix} = U^t S U \qquad U^t U = U U^t = \mathbb{1} \tag{11}$$

Moreover, S is clearly a positive definite matrix and its eigenvalue are all positive $s_i > 0 \ \forall i$. We can then define another matrix

$$V = U \begin{bmatrix} \frac{1}{\sqrt{s_1}} & & 0 \\ & \ddots & \\ 0 & & \frac{1}{\sqrt{s_n}} \end{bmatrix} \qquad VV^t \neq V^t V = \begin{bmatrix} \frac{1}{s_1} & & 0 \\ & \ddots & \\ 0 & & \frac{1}{s_n} \end{bmatrix} \tag{12}$$

which transforms S in the identity matrix: $V^t S V = \mathbb{1}$. Now we mutiply our initial equation (10) on the left by V^t and we insert an identity

$$V^t H V V^{-1} \mathbf{c} = \varepsilon V^t S V V^{-1} \mathbf{c} = \varepsilon V^{-1} \mathbf{c} \tag{13}$$

Defining $H' = V^t H V$ and $\mathbf{c}' = V^{-1} \mathbf{c}$, we remain with a standard eigenvalue problem

$$H' \mathbf{c}' = \varepsilon \mathbf{c}' \tag{14}$$

If we take only one s-wave all the matrices are scalar and therefore already diagonal. Indeed there is no freedom in the choice of the coefficient c_1 which is completely determined by the normalization condition.

$$|\Psi\rangle = \left(\frac{2\alpha_1}{\pi}\right)^{\frac{3}{4}} |\phi_1\rangle \qquad \Longrightarrow \qquad E = \frac{3}{2}\alpha_1 - 2\sqrt{\frac{2\alpha_1}{\pi}} \tag{15}$$

We can also analytically find the best value of α_1 minimizing the energy

$$\frac{dE}{d\alpha_1} = 0 \qquad \Longrightarrow \qquad \alpha_1 = \frac{8}{9\pi} \tag{16}$$

Which corresponds to the following estimate of the ground state energy

$$E\left(\alpha_1 = \frac{8}{9\pi}\right) = -\frac{4}{3\pi} \simeq -0.424 \tag{17}$$

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Remember that, in atomic units, energy is expressed in Hartree (E_{h}) and the exact value of the ground state energy of our Hamiltonian (5) is $-0.5\,E_{\mathrm{h}}$.

If we take more than one s-wave the calculations become rapidly lengthy and the final expression of the minimized energy becomes a rather ugly and complicated function of the Gaussians width α_i. A numerical approach is then preferable. All the diagonalizations and other matrix operations can be done very quickly with suitable routines, like GSL ones.
Our code to solve the generalized eigenvalue problem can be divided in the following steps

1. Given a set of $\{\alpha_1, ..., \alpha_n\}$ construct the matrices S and H using the expressions (3) and (7) for the matrix elements (in atomic units);

2. diagonalize S obtaining its eigenvalues $\{s_1, ..., s_n\}$ and eigenvectors contained in the matrix U (using the routine `gsl_eigen_symmv` for the diagonalization);

3. compute first the matrix V and then $H' = V^t H V$ (using the routine `gsl_blas_dgemm` for the matrix multiplication);

4. diagonalize H' obtaining its eigenvalues $\{\varepsilon_1, ..., \varepsilon_n\}$ and eigenvectors $\{\mathbf{c}'_1, ..., \mathbf{c}'_n\}$. Then compute the eivenvectors of H through the multiplication $\mathbf{c} = V\mathbf{c}'$.

With this procedure we have achieved practically the same results of those obtained using directly the routine `gsl_eigen_gensymmv` in place of points 2 to 4 except. The only difference is that the GSL routine normalizes the eigenvectors $\mathbf{c}$ while the ones we obtain are not normalized, as neither are the s-waves.
Notice that this is not a symbolic computation and the explicit values of the parameters α_i are needed. As a result the whole algorithm can be seen as a function $f(\alpha_1, ..., \alpha_n) = \varepsilon_0$ whose analytic expression is unknown (f should give all the eigenvalues and eigenvectors but here we focus just on the lowest eigenvalue ε_0). It is then impossible to analytically minimize f to find the best values of α_i like we did in the case of only one s-wave. Nevertheless, there are many algorithms to perform the minimization numerically. We chose to use the Nelder-Mead method since it doesn't require the knowledge of the derivative of the function to minimize and it is already implemented in the routine `gsl_multimin_fminimizer_nmsimplex`.
In Table 1 we summarize the results obtained calculating the best expansion on 1, 2 and 3 s-waves.

n	α_i	c_i	$\varepsilon_0\,[E_{\mathrm{h}}]$
1	$\alpha_1 = 0.282\,942$	$c_1 = 0.276\,492$	$-0.424\,413$
2	$\alpha_1 = 0.201\,530$	$c_1 = 0.176\,049$	$-0.485\,813$
	$\alpha_2 = 1.332\,54$	$c_2 = 0.242\,550$	
3	$\alpha_1 = 0.151\,376$	$c_1 = 0.112\,024$	$-0.496\,979$
	$\alpha_2 = 0.681\,289$	$c_2 = 0.217\,995$	
	$\alpha_3 = 4.500\,36$	$c_3 = 0.155\,197$	

Table 1: Coefficients and widths of the best expansion of the ground state onto 1, 2 and 3 s-waves.

We now compare our results with the STO-3G basis set of standard quantum chemistry calculations. Such standard expands the ground state on three Gaussians of width

$$\alpha_1 = 0.109\,818 \qquad \alpha_2 = 0.405\,771 \qquad \alpha_3 = 2.227\,76 \qquad (18)$$

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With our code we find that the best coefficients for such Gaussians are

$$c_1 = 0.061\,498\,4 \qquad\qquad c_2 = 0.193\,011 \qquad\qquad c_3 = 0.191\,364 \qquad (19)$$

and correspond to a ground state energy estimate $\varepsilon_0 = -0.495\,011\,E_{\mathrm{h}}$. One may see that, even if the used widths differ for more than 100%, the ground state energy differs for only 0.4%. To further investigate the differences between the two results we plot (Figure 1a) the radial square modulus of the true ground state together with our and STO-3G expansions. Remember that the ground state of our Hamiltonian (5) is $\Psi_{exact}(\mathbf{r}) = e^{-r}/\sqrt{\pi}$. We also compute (Figure 1b) the radial square modulus of the difference between our and STO-3G expansions with the exact ground state.
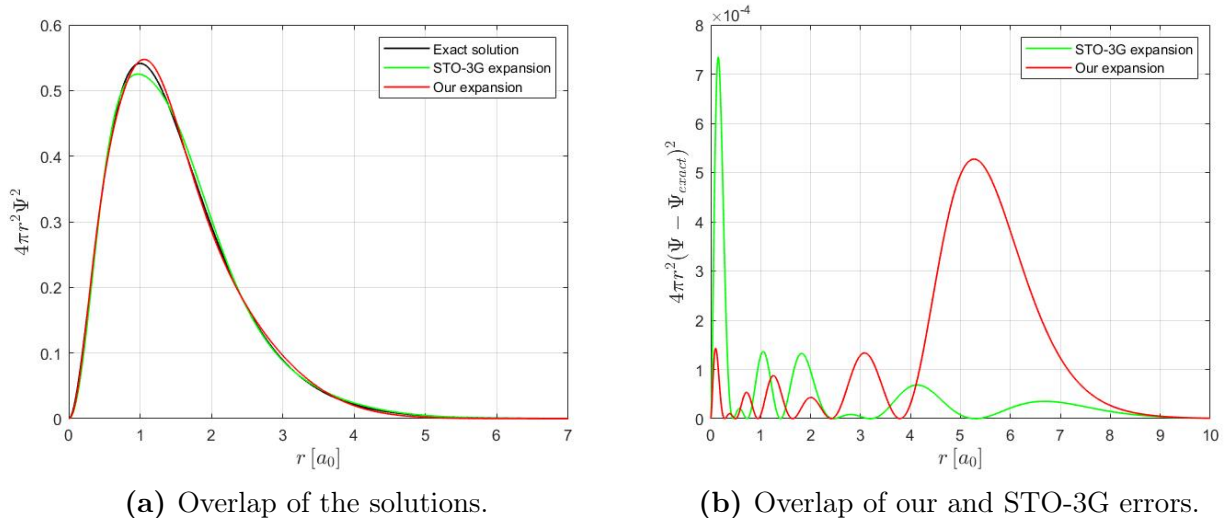

(a) Overlap of the solutions.   **(b)** Overlap of our and STO-3G errors.

Figure 1: Comparison between the true ground state, our and STO-3G expansions.

To put it more quantitatively we compute the root mean square value of the error made by our and STO-3G expansions. Namley, we calculate the norm of the difference of the wave functions

$$\sigma = \sqrt{\int \left(\Psi_{expansion} - \Psi_{exact}\right)^2 d^3 r} \qquad (20)$$

obtaining

$$\sigma_{our} = 0.035\,314\,9 \qquad\qquad \sigma_{STO-3G} = 0.020\,239\,7 \qquad (21)$$

Using p-waves to solve the generalized problem

As we did with the set of s-waves, we try to calculate the ground state energy solving the same generalized problem with a set of p-waves.

It is necessary to make a brief discussion about symmetries of the system we are studying and the basis we are using. The ground state of Hydrogen atom is described by a symmetric wavefunction (relative to the transformation $\vec{r} \to -\vec{r}$), but the p-waves which compose our set are all anti-symmetric. Therefore we cannot expect to obtain an approximate value of energy of the real ground state, we would rather obtain an approximation of the lowest bound state in the set of antisymmetric states of the hydrogen atom. This is supported by the variational theorem, which guarantees that given a set of function onto which expand the generalized eigenvalue problem of the Hamiltonian, the minimum eigenvalue is always greater or equal to the real minimum value of energy which satisfies the same symmetries the set of functions

which compose the basis set do. This means that the expected value which should come out of the minimization procedure should be greater or equal to the energy of Hydrogen atom's first excited state $E_1 = -0.125 E_h$. We will call this the "ground state" in this section (Hydrogen atom's ground state will be called "real ground state").

The basis of p-waves can be split into three subsets each orthogonal to the other, depending on the Cartesian direction the functions point to. Hence we may expand the wave function of the ground state over all three directions or choose a particular direction and expand the wave function over a set of non-orthogonal p-waves distinguishable through different parameters α_i. The best choice is to expand the wave function over only one of the orthogonal sets of p-waves. Once again symmetries of the system we want to describe and of the basis we are going to expand the state onto can be used to understand what will happen.

Since the three sets of p-waves are orthogonal and the Hamiltonian we deal with does not mix them, solving the problem expanding the ground state wave function over three different directions is equal to solve simultaneously three identical one dimensional problems. This problem can be solved analytically, similarly to the previous case of s-waves, by minimizing the energy

$$E = \left\langle \Phi^\xi \middle| H \middle| \Phi^\xi \right\rangle = \frac{5}{2}\alpha_1 - \frac{4\sqrt{2}}{3}\sqrt{\frac{\alpha_1}{\pi}} \qquad \Longrightarrow \qquad \frac{\mathrm{d}E}{\mathrm{d}\alpha_1} = \frac{5}{2} + \frac{2\sqrt{2}}{3\sqrt{\pi\alpha_1}} = 0 \qquad (22)$$

for which $\alpha_1 = \dfrac{32}{225\pi} \approx 0.0453$ and $E_1 = -0.113177 E_h$. Notice that in this case we used a properly normalized function

$$\Phi^\xi(\vec{r}) = \frac{1}{\sqrt{S_{ii}^\xi}}\xi \exp\left(-\alpha_1 r^2\right), \qquad (23)$$

with $\xi = x, y, z$.

In fact this is what we find if we apply the numerical minimization expanding the ground state over a single p-waves or a combination of p-waves (either two or three) pointing in different directions. The algorithm stops performing the minimization once one of the initial parameters α_i reaches the value α_1, returning the energy E_1.

If we let the number of p-waves change, say we use n_x, n_y, n_z p-waves over each direction, the minimization process effectively works only in the direction for which we use more functions.

It is evident that the best choice is to expand the ground state wave function over only one of the orthogonal set of our p-waves basis. The accuracy of the approximation increases as the number of functions that we use increases. In the following table (2) we report the values of parameters and coefficients relative to each p-wave we expand the wave function onto.

n	α_i	c_i	$\varepsilon_0 \, [E_\mathrm{h}]$
1	$\alpha_1 = 0.045\,271$	$c_1 = 1$	$-0.113\,177$
2	$\alpha_1 = 0.032\,392$	$c_1 = 0.931\,801$	$-0.123\,289$
	$\alpha_2 = 0.139\,278$	$c_2 = 0.362\,971$	
3	$\alpha_1 = 0.079\,834$	$c_1 = 0.637\,543$	$-0.124\,728$
	$\alpha_2 = 0.024\,685$	$c_2 = 0.749\,226$	
	$\alpha_3 = 0.337\,073$	$c_3 = 0.179\,441$	

Table 2: Coefficients and widths of the best expansion of the ground state onto 1, 2 and 3 functions belonging to the same set of p-waves directed along the same Cartesian direction.

It is easy to understand now that any mixing of the two sets would not improve the approximation of the real ground state. This is due to the fact the s-waves set is orthogonal to the p-waves sets, and the latter being orthogonal to the Hydrogen atom's ground state means that they wouldn't contribute in any way to the expansion.

The approximation of the ground state would be rather improved if we increase the number of functions which compose the set over we expand the actual wave function. This is true in general, as it is experienced in all previous discussions about the expansion made over the s-waves and the p-waves.