

## Lecture HW 3

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### LCAO Basis functions and how they work:

\*\* means double points

All formulas are in atomic units.

1. Consider a simple Gaussian basis function,  $\chi(\mathbf{r}) = Ce^{-r^2/2}$ . Normalize it, i.e., choose  $C$  so that  $\int d^3r |\chi(\mathbf{r})|^2 = 1$ .

**Hint:** KB:  $\alpha = 1/2$  in the notation of the lecture, so use the formula there to deduce  $C$ . LOW:

$$\int d^3r |\chi(\mathbf{r})|^2 = 4\pi \int_0^\infty dr r^2 |\chi(r)|^2,$$

since  $\chi$  depends on the radial coordinate  $r$  and not the vector  $\mathbf{r}$ .

2. Use  $\chi$  as a trial wavefunction for the hydrogen atom to estimate its energy. What is the percentage error? Plot  $\chi$  and the exact wavefunction. Calculate the overlap between your approximate wavefunction and the exact one.

**Hint:** KB: In atomic units, the exact wavefunction is  $\psi(\mathbf{r}) = e^{-r}/\sqrt{\pi}$ . LOW: The overlap is then  $\langle \chi | \psi \rangle = \int d^3r \chi(\mathbf{r})\psi(\mathbf{r})$ . Use the same hint as earlier to reduce this to an integration over  $dr$  and not  $d^3r$ .

3. Repeat #1 for Gaussian A with  $e^{-r^2/4}$  and Gaussian B for  $e^{-2r^2}$ , i.e., Calculate  $C_A$  and  $C_B$  by requiring normalization. Find the value of the overlap integral.

**Hint:** LOW: Use Eq. (5). KB: Again, the normalization constants can be found from the lecture, noticing  $\alpha = 1/4$  for A and 2 for B. All the matrix elements for this problem can be found with the formulas at the end of this pdf. Here  $a = 1/4$ ,  $b = 2$ , so  $c = (9/8)^2$ , so  $s_{ab} = (32/81)^{3/4}$ .

4. \*\* Find the matrix elements of the Hamiltonian for the hydrogen atom in your basis set of two Gaussians.

**Hint:** KB: Again, use formulas at the end of this pdf, rather than calculating the integrals yourselves. LOW: the Hamiltonian matrix is:

$$H = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}. \quad (1)$$

where for example  $H_{ab} = \langle \phi_a | \hat{H} | \phi_b \rangle = T_{ab} + V_{ab}$ . For  $H_{AA}$ , plug in  $a = b = 1/4$  into the formulas at the end of the pdf; for  $H_{AB}$ , use  $a = 1/4$  and  $b = 2$ ; finally for  $H_{BB}$ , use  $a = b = 2$ .

5. \*\* Solve the 2x2 eigenvalue problem to get the ground-state wavefunction and energy in this basis. Plot with the exact wavefunction and your previous estimate. What is the new percentage error and overlap with the exact wavefunction?

**Hint:** KB: This means find both the eigenvalues and eigenvectors. This is a generalized eigenvalue problem

$$Hc = SEc, \quad (2)$$

where  $H$  is the Hamiltonian matrix and  $S$  is the overlap matrix. You must solve  $\det(H - SE) = 0$ ; the roots are the eigenvalues and the vectors  $c$  that satisfy  $(H - SE) \cdot c = 0$  are the eigenfunctions. LOW: Recall that the overlap matrix is

$$S = \begin{pmatrix} s_{AA} & s_{AB} \\ s_{BA} & s_{BB} \end{pmatrix} = \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix}, \quad (3)$$

where  $s_{ab} = \langle \phi_a | \phi_b \rangle$  is the overlap integral between  $\phi_a$  and  $\phi_b$ . Since each basis function is normalized for us,  $s_{AA} = s_{BB} = 1$ , and  $s_{AB} = s_{BA} = s$  is the overlap integral you calculated in problem 3.

**Hint:** You can solve the determinant by hand. Or, to solve a generalized eigenvalue problem in Mathematica, you can use `Eigensystem[ { H, S } ]`, where  $H$  is the matrix whose elements you calculated in problem 4, and where  $S$  is the matrix in Eq. (3). The result of the Mathematica evaluation will be `{ { E1, E2 }, { c1, c2 } }`, where  $E1$  and  $E2$  are the energies, and  $c1$  and  $c2$  are the eigenvectors corresponding to  $E1$  and  $E2$ . Each of  $c1$  and  $c2$  will have two components, i.e.  $c1 = \{ c1_A, c1_B \}$ . Choose the lower energy eigenvalue (should be close to -0.5, but above it), and the corresponding eigenvector.

**Hint:** To obtain your best trial wavefunction, composed of the gaussians A and B, you need to normalize the lowest energy eigenvector  $c$  that you obtain, so that our trial wavefunction will be normalized. Do this by setting

$$c := c/\sqrt{c^T S c}, \quad (4)$$

or by `c /= Sqrt[ c.S.c ]` in Mathematica. Then our trial wavefunction is

$$\phi_T(\mathbf{r}) = c_A \phi_A(\mathbf{r}) + c_B \phi_B(\mathbf{r}),$$

where  $c_A$  is the first component of  $c$  and  $c_B$  is the second.

**Hint:** Find the percentage error by comparing the lower  $E$  value obtained with the exact result, -0.5. Find the overlap by taking  $\langle \phi_T | \psi \rangle$  and performing the two resulting integrals.

6. What does the other eigenstate and energy correspond to? Plot the wavefunction and comment on the accuracy of its energy.

**Hint:** KB: Compare with another exact wavefunction of the H-atom. LOW: The diagonalization that we did will come up with two orthogonal eigenfunctions, i.e.  $c_1^T S c_2 = 0$ . The lower energy  $c$  is the ground state; so the higher energy one is an excited state. As such, it will have a “node” in it (a place where the wavefunction is zero). The first excited state of the real Hydrogen atom is the 2s ( $n = 2$ ,  $l = 0$ ), which you can find [online here](#) (recall that  $a_0$  is the Bohr radius = 1 in atomic units). Surprisingly enough, it also has a node. Recall that the Hydrogen energy spectrum is  $-1/(2n^2)$ , so the exact energy is negative. Your excited state energy from diagonalization will be very far off.

7. \*\* Let's calculate the binding energy curve for  $H_2^+$ . In the minimal basis set of a single 1s orbital for each H atom,  $\phi_A$  is a 1s orbital on atom A and  $\phi_B$  is a 1s orbital on atom B. The matrix elements of the Hamiltonian and overlap are, in atomic units:

$$s = (1 + R + R^2/3)e^{-R},$$

$$H_{AA} = H_{BB} = -\frac{1}{2} - \frac{1}{R} + \left(1 + \frac{1}{R}\right)e^{-2R},$$

and

$$H_{AB} = -s/2 - (1 + R)e^{-R},$$

where  $R$  is the bond length. As in Eq. (3),  $s = \langle \phi_A | \phi_B \rangle$ . Plot each of these as a function of  $R$  and explain their behavior as  $R$  gets very small and very large.

**Hint:** First consider the overlap integral. As  $R \rightarrow \infty$ , the two 1s functions on each atom will have smaller and smaller overlap, because the atoms are moving away from each other. As  $R \rightarrow 0$ , the two 1s functions will lie directly on top of each other. Therefore you should be able to explain what values the overlap goes to.

**Hint:** For  $H_2^+$ , as the bond length goes to infinity, the energy should go to that of a single Hydrogen atom. As the two atoms come close together, i.e.  $R \rightarrow 0$ , note that  $H_{AA}$  will be the energy of a Hydrogen ( $Z = 1$ ) 1s function on top of a Helium ( $Z = 2$ ) nucleus (since both Hydrogen atoms are on top of each other). This will not produce the correct energy for the  $He^+$  atom, since the correct  $He^+$  wavefunction is not a Hydrogen 1s function.

**Hint:** LOW: Since  $R$  is the bond length of  $H_2^+$ , it will never be negative. Therefore you can start the plots at  $R = 0$ .

8. For the previous question, diagonalize the Hamiltonian and plot the eigenvalues as function of  $R$ . Also plot the binding energy curve as a function of  $R$ , giving the well-depth bond length, and compare with reference data. How could you improve the calculation?

**Hint:** KB: Repeat the procedure you used for the two Gaussians. Its exactly the same math. LOW: Follow through the hints on problem 5, but you do not have to worry about renormalizing the trial wavefunction at the end. Now the energy eigenvalue will be a function of  $R$ , so you'll want to put everything into Mathematica symbolically (i.e., depending on  $R$ ). Again, you will have two eigenvalues, and the lower one will correspond to the “bonding” orbital and the higher energy will be the “anti-bonding” orbital.

**Hint:** Remember to only plot from  $R = 0$  on. Negative values of  $R$  do not make sense. To find the binding energy curve, we need to know that our hamiltonian above, with matrix elements  $H_{AA}$ , etc., did not include the nucleus-nucleus repulsion. So to our energy, add in  $1/R$  to include this repulsion. Compare the bond length (located at the minimum energy with nuclear-repulsion added in), with experiment.

**Hint:** Do not find the vibrational energy this time. We'll do it next time...

9. From reading 3.2-3.9, give a definition for each of the following terms: self-consistency (86), Fock operator(91), Roothaan-Hall equations (94), ROHF (99), SCF convergence (101), direct minimization (103), spin contamination(106), direct SCF(108), divide and conquer(111).

Helpful formulas for a single atom: For two Gaussians of decay constants  $a$  and  $b$ , e.g.  $\phi(\mathbf{r}) = \left(\frac{2a}{\pi}\right)^{3/4} e^{-a r^2}$ , the overlap between them is:

$$s_{ab} = \langle \phi_a | \phi_b \rangle = \left(\frac{ab}{c}\right)^{3/4}, \quad (5)$$

where  $c = ((a + b)/2)^2$ .

$$V_{ab} = \langle \phi_a | v | \phi_b \rangle = -4 \frac{(ab)^{3/4}}{\sqrt{\pi}(a + b)},$$

where  $v(\mathbf{r}) = -1/r$ , and

$$T_{ab} = \frac{3}{4} \frac{(ab)^{7/4}}{c^{5/4}}$$