

Practice Session 2

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Problem 4. Parts a, b, c.

The present system consists of the dihydrogen atom, H_2^+ , with the H-H bond aligned in the z axis. To approximate the solutions, a LCAO-type variational function will be used with two STO centered on each nucleus, $1s_a$ and $1s_b$, see Equation 1. With two functions in our basis set, we will get an approximation for the ground and first excited state.

$$1s_a = k^{3/2} \pi^{-1/2} e^{-kr_a} \quad 1s_b = k^{3/2} \pi^{-1/2} e^{-kr_b} \quad (1)$$

Solving the secular equation for the electronic Hamiltonian, we obtain two variational energies, W_1 and W_2 , for the ground and excited state, respectively. Which can be expressed with the terms of the Hamiltonian and overlap matrices:

$$W_1 = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} \quad W_2 = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \quad (2)$$

$$H_{ab} = -\frac{1}{2}k^2 S_{ab} + k(k-2)(1+kR)e^{-kR} \quad H_{aa} = \frac{1}{2}k^2 - k - \frac{1}{R} + e^{-2kR} \left(k + \frac{1}{R} \right) \quad (3)$$

$$S_{aa} = S_{bb} = 1 \quad S_{ab} = e^{-kR} \left[1 + kR + \frac{1}{3}k^2 R^2 \right] \quad (4)$$

Then, for calculating the total energy for the system for each state, we just must account the nuclear repulsion, which in this case is just $1/R$. The potential energy surface (PES) of each will be:

$$E_1 = W_1 + \frac{1}{R} \quad E_2 = W_2 + \frac{1}{R} \quad (5)$$

Since we are using STO and the variational method, we must find the optimal (k and R) parameters that minimize the total energy E_1 , for that reason, a set of k and R values is chosen and all possible combinations are computed, while searching for the one that presents the lower E_1 . Doing, that, a sort of surface of E_1 is obtained as a function of k and R , see Figure 1a, from which the minimum will correspond to the optimized combination of k and R .

Once the optimized parameter k is obtained, we can use it compute and visualize the PES of both states as a function of the internuclear distance, R , see Figure 1b. The optimized values for the parameters and energies are found in Table 1. The PES of the two states show how the first one is a bonding state, with the energy minimum, while the excited state is dissociative, and leads to the rupture of the H-H bond.

k_e	R_e (a.u.)	E_1	W_1	V_{NN}
1.2379	2.0035	-0.58651	-1.08563	0.49912

Table 1. Optimized parameter k , and internuclear distance, R , and minimum energies found (total, E_1 , electronic, W_1 , and nuclear repulsion, V_{NN}). All values in their correspondent atomic units.

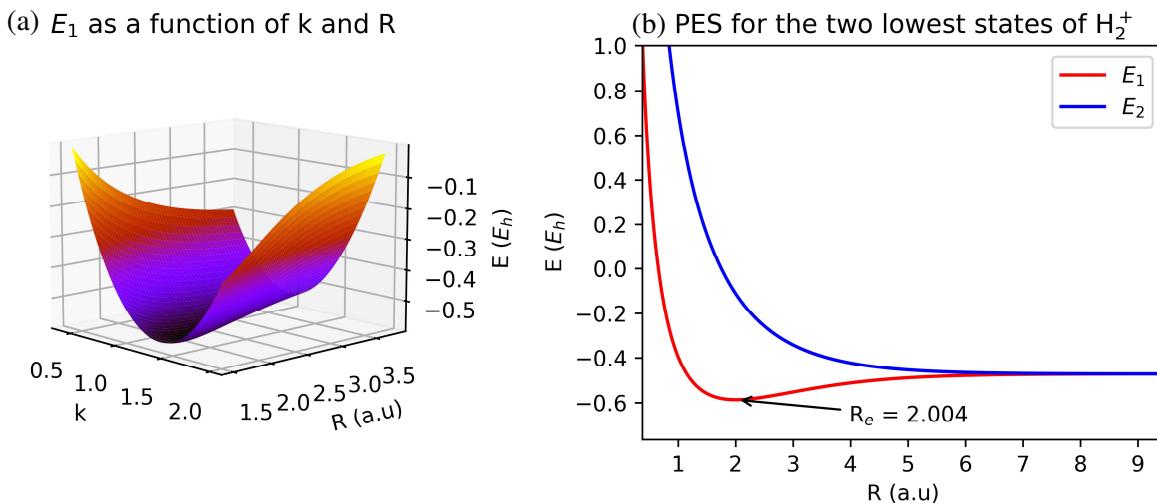


Figure 1. (a) E_1 surface for each k and R value. (b) PES for the ground and excited state of H_2^+ .

- Python Script available at: [GitHub](#) or attached to the task as `p4abc.py`.

Problem 4. Part d.

As mentioned early, the variational function used is a linear combination using the $1s_a$ and $1s_b$ STO, of the form of Equation 1. This gives the following wavefunctions for the molecular orbitals of the ground (φ_1) and excited (φ_2) state:

$$\varphi_1 = \frac{1s_a + 1s_b}{\sqrt{2(1 + S_{ab})}} \quad \varphi_2 = \frac{1s_a - 1s_b}{\sqrt{2(1 - S_{ab})}} \quad (6)$$

Using the optimized parameters for k and R , the wavefunctions can be represented depending on the distances of the nucleus to the electron, r_a and r_b , respectively. If we consider that the electron is fixed in the z -axis, where the H atoms are present, and that the atom H_A is in the origin. r_a and r_b will be $abs(z)$ and $abs(z - R)$, respectively (taking only the absolute value, since r cannot be negative). We can use that to visualize the wave functions and the probabilities of the electron along the z -axis of the ground and excited state, see Figure 2.

In the ground state, the electron density is mostly located between the atoms, creating a bond, while in the excited state, there is a node in the wave function just in between the H, leading to an antibonding state, where there is no probability of finding the electron in the middle between the atoms, and the density is localized in each H. If we considered only two independent STO orbitals, no interaction between them would be achieved and there would not be a node between them, leading to an incorrect description of the system.

- Python Script available at: [GitHub](#) or attached to the task as `p4d.py`.

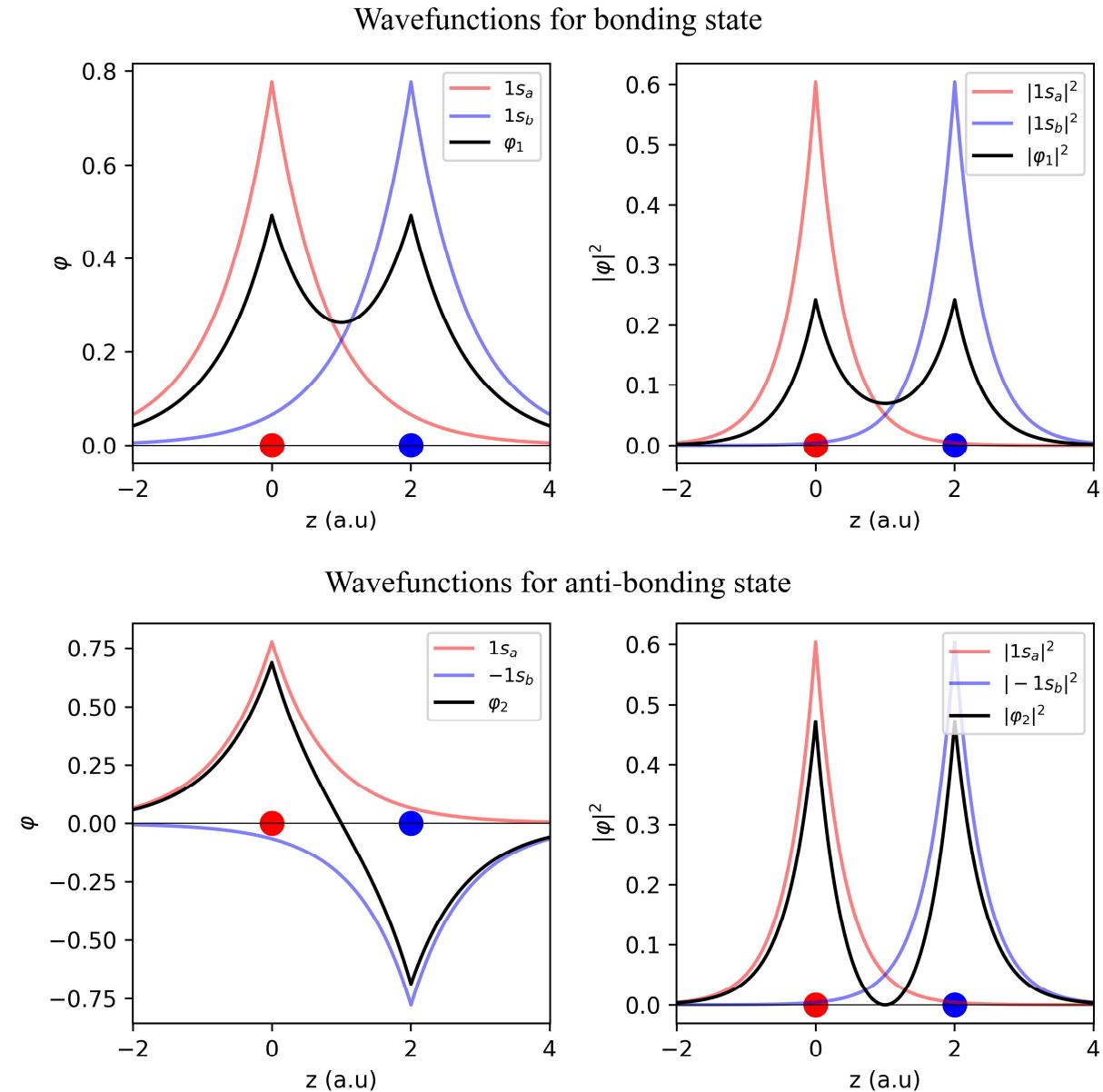


Figure 2. Wavefunctions (left) and probabilities (right) of the ground (top) and excited (bottom) states. Black lines indicate the state wavefunction, or probability density, and the red and blue lines correspond to the A and B individual STO, respectively. The red and blue circles represent the A and B H atoms at the origin and distance R_e , respectively.

Problem 5

We can calculate again the energies for the ground and excited states but now using a LCAO of 1s STO-NG functions, one centered on each nucleus. Now we can follow the same procedure of calculating the variational energy integral and PES, but now, we must take into account all the GTO primitives of each STO-NG, so the overlap and Hamiltonian integrals will be:

$$S_{ab} = \sum_{p=1}^N \sum_{q=1}^N d_{pa} d_{qb} S_{pq} \quad H_{ab} = \sum_{p=1}^N \sum_{q=1}^N d_{pa} d_{qb} H_{pq} \quad (7)$$

where S_{pq} and H_{pq} are the overlap and Hamiltonian integrals between individual primitive GTO.

The individual overlap integrals, are calculated with:

$$S_{pq} = \langle A|B \rangle = \left(\frac{\pi}{\alpha + \beta} \right)^{\frac{3}{2}} \exp \left(-\frac{\alpha\beta}{\alpha + \beta} |R_A - R_B|^2 \right) \quad (8)$$

The individual kinetic integrals with:

$$T_{pq} = \left\langle A \left| -\frac{1}{2} \nabla^2 \right| B \right\rangle = \frac{\alpha\beta}{\alpha + \beta} \left(3 - 2 \frac{\alpha\beta}{\alpha + \beta} |R_A - R_B|^2 \right) \langle A|B \rangle \quad (9)$$

And the individual electron-nucleus attraction with:

$$\left\langle A \left| -\frac{Z_C}{r_{1C}} \right| B \right\rangle = \frac{-2\pi}{\alpha + \beta} Z_C \exp \left(\frac{-\alpha\beta}{\alpha + \beta} |R_A - R_B|^2 \right) F_o((\alpha + \beta)|R_p - R_C|^2) \quad (10)$$

where Z_C and R_C are the nuclear charge and position of the C atom, respectively, R_p the intermediate point between two gaussians, calculated with $R_p = (\alpha R_A + \beta R_B)/(\alpha + \beta)$, and F_o an auxiliary function related to the error function, $F_o(t) = 1/2\sqrt{\pi/t} \operatorname{erf}(\sqrt{t})$. For small values of t ($t < 10^{-6}$), the approximation $F_o(t) \approx 1 - t/3$ is used to avoid division by zero.

In the case of diatomic molecules, the nuclear-electron retraction term is obtained by summing all contributions for each atom:

$$V_{pq} = \langle A|V|B \rangle = \left\langle A \left| -\frac{Z_A}{r_{1A}} \right| B \right\rangle + \left\langle A \left| -\frac{Z_B}{r_{1B}} \right| B \right\rangle \quad (11)$$

The above equations depend are integrals between two gaussian functions, and depend on their exponents, α and β , and the position they are centered on, R_A and R_B . In this case, A is chosen to be centered at 0 and B at a distance R, but different centres could be selected, and the results should be the same.

The only thing to add to the integrals is the normalization constant, since those are for non-normalized gaussian functions. In each case the normalization constant will be the product of the normalization constant of each gaussian: $N(\alpha, \beta) = [(2\alpha/\pi)(2\beta/\pi)]^{3/4}$. Notice that in Equation 10, if S_{pq} is normalized and is used for the computation of T_{pq} , there is no need to normalize T_{pq} since S_{pq} carries the normalization.

With that, the overlap, \mathbf{S} , and Hamiltonian, \mathbf{H} , matrices can be easily computed, which can be used to compute the ground and excited state energies by solving the following characteristic polynomial:

$$\det(\mathbf{H} - W\mathbf{S}) = 0 \quad (12)$$

In the code developed, the SymPy module is used to solve this polynomial, although Equation 2 is also a valid solution. The code computes the ground state and first excited state energies for a given R and number of gaussians (NG). It also computes the PES of both states, as in the previous problem, see Figure 3. The shapes of the PES are very similar to the ones in Figure 1a. The values for the energies at the optimized distance found in the previous problem ($R_e = 2.0035 \text{ a.u.}$) are found in Table 2. Notice how increasing the number of primitive gaussians lowers the total energy and brings it closer to the STO minimum found (-0.58651 a.u., Table 1).

	V_{nn}	W_1	E_1	W_2	E_2
STO-1G	0.49913	-1.02918	-0.53005	-0.57098	-0.07185
STO-2G	0.49913	-1.07047	-0.57134	-0.59008	-0.09096
STO-3G	0.49913	-1.08182	-0.58270	-0.60541	-0.10628

Table 2. Nuclear repulsion, V_{nn} , electronic, W , and total, E , energies for the ground and first excited states of H_2^+ at the equilibrium geometry $R_e = 2.0035 \text{ a.u.}$ using different STO-NG basis set.

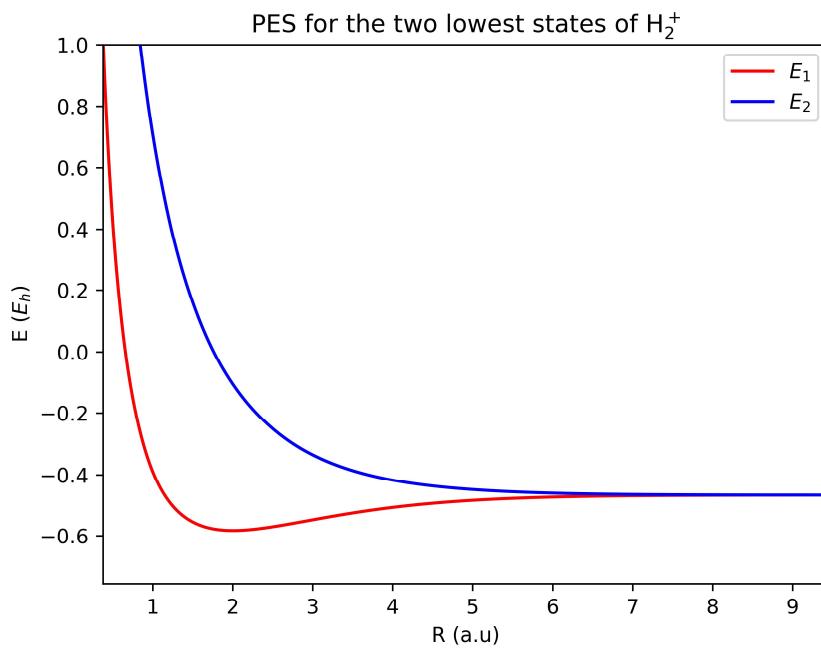


Figure 3. PES for the ground and excited state of H_2^+ using a STO-3G basis set.

- Python Script available at: [GitHub](#) or attached to the task as `p5.py`.