Physikalische Chemie III für Lehramt

Übungsblatt 9

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1 Hydrogen molecule

In Problem Set 7 you observed that the Bohr radius

$$a_0 = \frac{4\pi\epsilon_0}{e^2}\frac{\hbar^2}{m} \tag{1}$$

emerged as a natural distance scale from the Schrödinger equation of the hydrogen atom. You also observed that the energy of the ground state was proportional to the square of the reciprocal of the Bohr radius:

$$E_{1s} = -\frac{\hbar}{2m}\frac{1}{a_0^2} = -\mathrm{Ry}. \tag{2}$$

The positive value of this energy is called the Rydberg unit of energy. Like the Bohr radius, it is a natural unit for measuring electronic energies in the hydrogen atom.

In the current problem, you will work with distances in units of a_0, and energies in units of Ry. I will denote such dimensionless energies with a tilde. For example, the ground-state energy in units of Ry is

$$\tilde{E}_{1s} = \frac{E_{1s}}{\mathrm{Ry}} = -1. \tag{3}$$

a. Linear combination of atomic orbitals and variational principle

In the lecture, when discussing the quantum mechanics of the molecule H_2, you encountered the idea of forming candidate molecular orbitals as a **L**inear **C**ombination of **A**tomic **O**rbitals (LCAO). In particular, a candidate wave function for the electronic ground state of H_2 was written as a linear combination of two $1s$ atomic orbitals, each centered at one of the protons (denoted by A and B):

$$\Psi \approx c_A\psi_{1s}^A + c_B\psi_{1s}^B. \tag{4}$$

The coefficients c_A and c_B were complex numbers and were to be determined from the *Variational Principle*, which is a method of finding approximations to the state with lowest energy (i.e., the ground state). In this question, you will visually examine some of the results of this procedure.

The $1s$ wave function of the hydrogen atom depends only on the distance from the proton, r. Since we agreed to measure distances in units of the Bohr radius a_0, we have

$$\psi_{1s}(x) = \frac{1}{\sqrt{\pi}} \mathrm{e}^{-x} \tag{5}$$

where $x = r/a_0$.

Moving on to the hydrogen molecule, let us place proton A at the origin and proton B along the x axis at a distance R from the origin. In other words, R is the distance between of the two protons in H_2. Again, we will work with $X = R/a_0$. Then, the $1s$ atomic orbitals that are centered at A and B will be

$$\psi_{1s}^{A}(x) = \frac{1}{\sqrt{\pi}} \mathrm{e}^{-x} \qquad \text{and} \qquad \psi_{1s}^{B}(x) = \frac{1}{\sqrt{\pi}} \mathrm{e}^{-(x-X)}. \tag{6}$$

The molecular wave function in eq. (4) is a linear combination of these two functions.

- Plot the two functions in eq. (6) against x in the interval $x \in [-10, 10]$ for $X = 2$ and $X = 4$.

From the variational principle one finds two solutions for the constants c_A and c_B in eq. (4), namely either $c_A = c_B$ or $c_A = -c_B$. These two solutions correspond to two molecular wave functions:

$$\Psi_{+} = \frac{1}{\sqrt{2 + 2S_{AB}}} (\psi_{1s}^{A} + \psi_{1s}^{B}) \qquad \text{and} \qquad \Psi_{-} = \frac{1}{\sqrt{2 - 2S_{AB}}} (\psi_{1s}^{A} - \psi_{1s}^{B}). \tag{7}$$

The molecular wave functions Ψ_+ and Ψ_- are referred to as bonding and antibonding orbitals, respectively. The energies that correspond to these wave functions were given in class as

$$E_{+} = \frac{\alpha + \beta}{1 + S_{AB}} \qquad \text{and} \qquad E_{-} = \frac{\alpha - \beta}{1 - S_{AB}}, \tag{8}$$

where α, β and S_{AB} were some complicated integrals.

The integral S_{AB}, which is referred to as the overlap integral, is dimensionless (i.e., unitless). The integrals α and β, on the other hand, have units of energy. Since we agreed to measure all energies in units of Ry, below you will work with $\tilde{\alpha} = \alpha/\mathrm{Ry}$ and $\tilde{\beta} = \beta/\mathrm{Ry}$.

For the $1s$ atomic orbitals given above the integrals S_{AB}, α and β can actually be calculated in closed form:

$$\begin{aligned} S_{AB} &= \left[1 + X + \frac{1}{3}X^2\right] \mathrm{e}^{-X} \\ \tilde{\alpha} &= -1 - 2\left[\frac{1}{X} - (1 + \frac{1}{X})\mathrm{e}^{-2X}\right] + \frac{2}{X} \\ \tilde{\beta} &= -(1 - \frac{2}{X}) \left[1 + X + \frac{1}{3}X^2\right] \mathrm{e}^{-X} - 2(1 + X)\mathrm{e}^{-X}. \end{aligned} \tag{9}$$

The three integrals are functions of the inter-atomic distance X because the wave function ψ_{1s}^{B} in eq. (6) contains X as a variable.

- Plot the overlap integral S_{AB} as a function of X in the interval $X \in [0, 10]$. Observe that it varies between zero (when the two atoms are far apart) and one (when they are on top of each other).

- Plot $\tilde{\alpha}$ and $\tilde{\beta}$ as functions of X. Because these functions contain $1/X$, it does not make sense to have $X = 0$. So plot them in the interval $X \in [0.7, 10]$.
  Which one of $\tilde{\alpha}$ and $\tilde{\beta}$ is non-monotonic in X?
- Now calculate the (dimensionless) energies $\tilde{E}_+$ and $\tilde{E}_-$ using eq. (8) and plot these against X.
  Which one of the two energies is non-monotonic in X?
- From your plot, visually determine the value of X for which $\tilde{E}_+$ reaches its minimum.
  Similarly, determine the minimum value of the (dimensionless) energy $\tilde{E}_+$.

b. Visualizing the bonding and antibonding wave functions

The optimal bond distance (in units of a_0) appears to be at $X_{\mathrm{min}} = 2.5$. For this value of X

- plot the wave functions Ψ_+ and Ψ_- in eq. (7);
- plot the probabilities that correspond to these two wave functions.
  Where are the two electrons of H_2 mostly located?

c. Relation of the bonding energy to Morse potential

The Morse potential is

$$V_{\mathrm{Morse}}(X) = D_e \left(1 - \mathrm{e}^{-a(X - X_{\mathrm{min}})}\right)^2, \tag{10}$$

where D_e and a are some constants. Note that this potential is written such that it becomes equal to D_e for large distances between the two protons, i.e., when $X \to \infty$. On the other hand, the energies $\tilde{E}_+$ and $\tilde{E}_-$ both become equal to -1 at large separations of the two protons, as you can verify from your plots in part **a**. This only means that the zero energy is defined differently in the two cases. To account for the different choices of zero energy, we will subtract D_e from the Morse potential and will add 1 to E_+. In this way, both of them will become zero for $X \to \infty$.

- Plot $V_{\mathrm{Morse}}(X) - D_e$ for some arbitrary values of the parameters D_e and a. On the same plot, show the energy $\tilde{E}_+ + 1$ from part **a**.
  Now manually adjust D_e and a until you achieve a satisfactory agreement between the two curves. Report the values that you find.