

Assignment 1

This exercise develops intuition about the **chemical bond**. You will examine in detail the hydrogen molecule, and although the model is greatly simplified and may seem artificial, it contains nearly all the ingredients of realistic models. This assignment is due Monday, September 3, in lecture.

1. First consider a **single hydrogen atom**. Use the Born-Oppenheimer approximation, where the proton has a definite position, and we are only interested in the wavefunction of the electron. For simplicity, consider only motion along the x -axis and replace the singular Coulomb potential by an attractive Dirac delta function. With the proton located at the origin, the Hamiltonian for electron motion is:

$$H = \frac{p^2}{2m} - e^2\delta(x)$$

Note that the simplified Coulomb term has the correct dimensions when e is the elementary (cgs) unit of charge. In preparation for the more complicated calculations below, adopt the Bohr radius ($a_B = \hbar^2/me^2$) and Rydberg ($\text{Ry} = e^2/2a_B$) as your implicit units of length and energy. In other words, if your wavefunction has the form $\exp(-x/a_B)$, say, then you should just write $\exp(-x)$.

(a) For this warm-up you should:

- calculate the spectrum (bound and unbound energy levels)
- compare the spectrum to the true hydrogen spectrum
- congratulate yourself, that apart from some missing very weakly bound states, the model is doing a great job!

(b) For just one hydrogen atom compute the expectation $\langle p^2/2m \rangle$ in the ground state. You should be worried if you get a negative result!

(c) Now consider the molecule, H_2 . Place the two protons at $x = \pm b$ (in units of a_B) and find the ground state wavefunction of this two electron system. Neglect any interaction between the two electrons but don't forget that each electron has a singular attraction to both protons and a spin that may be up or down. Make a sketch of the ground state energy $E_0(r)$ (in Ry units) as a function of the proton separation, $r = 2b$. Your function should be monotonic with minimum at $r = 0$. Obtain (analytically) the asymptotic behavior

$$E_0(r) \sim -2\text{Ry} - C \exp(-r) \quad (r \rightarrow \infty)$$

and evaluate the constant C .

(d) Interpret your asymptotic form for $E_0(r)$ above in terms of the 2×2 Hamiltonian matrix

$$\begin{pmatrix} -1 & t \\ t & -1 \end{pmatrix} .$$

What is the value of the effective tunneling matrix element t , and what are the implied basis states?

(e) The attraction in a chemical bond is simply the fact that $E_0(r)$ decreases with decreasing r . **Based on what you learned from the explicit wavefunction for this model of H_2** , explain in words the quantum mechanism for energy minimization responsible for the attraction. Please avoid jargon you may have picked up in chemistry courses.

Also, speculate on what was omitted in the model that, when restored, keeps the bond length larger than $r = 0$. This will be addressed in a future exercise.

(f) The actual bond length of H_2 is $r = 1.4$. Using this value, obtain a numerical value for the energy of the lowest electronic excitation of the molecule, ΔE . This will involve finding another wavefunction, but the work is very similar to your ground state calculation (do not use the 2×2 matrix approximation).