Chem231B: Quiz #4

March 1, 2020

1. What is the spin multiplicity of the ground state of H_2 and of H_2^+?

   H_2 spin multiplicity is 1; H_2^+ is 2.

2. Give the electronic Hamiltonian for H_2.

   $H_{\mathrm{el}} = \hat{h}(1) + \hat{h}(2) + V_{ee}$ where $\hat{h}(i)$ is the one electron Hamiltonian for i-th electron and V_{ee} is the coulombic interaction:

   $\hat{h}(i) = -\frac{\nabla_i^2}{2} - \frac{1}{|r_i - R\hat{z}|} - \frac{1}{|r_i|}$ and $V_{ee} = \frac{1}{|r_1 - r_2|}$

   r is the position of the electron and R is the position of the nucleus. The H_2 is placed along the z-axis where a proton is at the origin.

3. Which one of the following changes significantly when going from H_2 to D_2: R_e, D_e, ω?

   ω.

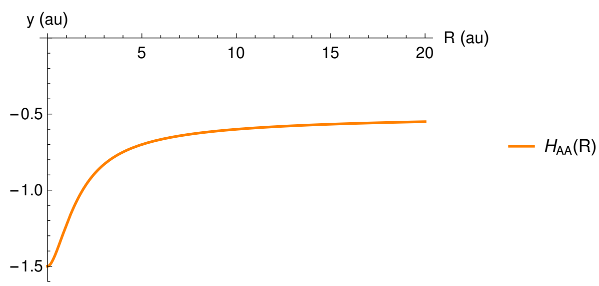
4. Within the harmonic approximation, say how your answer to the previous question will change?

   Still ω.

5. Give an expression for the matrix element H_{AA} in H_2^+ for 1s orbitals ($\gamma = 1$).

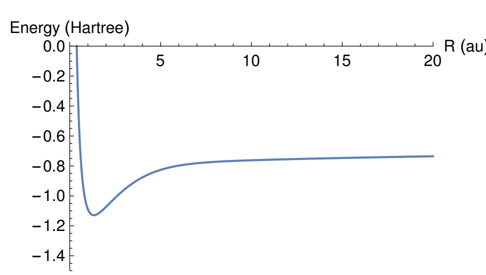
   $h_{AA} = \gamma^2/2 - \gamma f(x) = 1/2 - f(x)$, where $f(x) = 1 - \frac{(1+x)e^{-2x} - 1}{x}$.

6. Sketch how the matrix element H_{AA} should depend on R, giving its value as $R \to \infty$.



   H_{AA} should go to -0.5 Hartree as $R \to \infty$.

7. Sketch a molecular energy curve for H_2 as a function of R, giving its value as $R \to \infty$.



-11/16 or -0.6875 Hartree as $R \to \infty$

8. Sketch the curve within the Hartree-Fock approximation. What qualitative error does it make?

   Sketch which curve within HF?

9. For a molecule with $y_e = 0$, deduce a formula for the number of states it will bind in terms of D_e, ω, and x_e.

   $E_{\text{vib}}(\nu) = \nu_e[(\nu + 1/2) - x_e(\nu + 1/2)^2]$

   Dissociation is when $E_{\text{vib}} = D_e$ and hence, solve for ν which will yield the max number of bounded states $\nu_{\text{max}} \approx \frac{1}{2x_e} - \frac{1}{2} + \frac{\sqrt{(1-x_e)^2 - 4x_e D_e/\nu_e}}{2x_e}$

10. Deduce an expression for x_e in terms of D_e and ω for the Morse potential, for which $\epsilon_n = -V_0 \left(1 - \frac{\alpha(n+\frac{1}{2})}{\sqrt{2\,\mu\,V_0}}\right)^2$

    $x_e = \frac{\alpha}{\sqrt{8\mu D_e}}$