# 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 $H_2$.

   $H_{\text{el}} = \hat{h}(1) + \hat{h}(2) + V_{ee}$ 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 $D_2$: $R_e$, $D_e$, $\omega$?

   $\omega$.

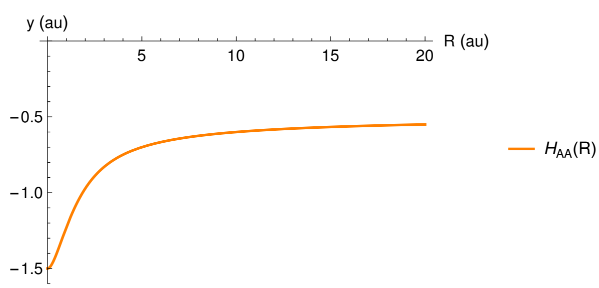
4. Within the harmonic approximation, say how your answer to the previous question will change?

   Still $\omega$.

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

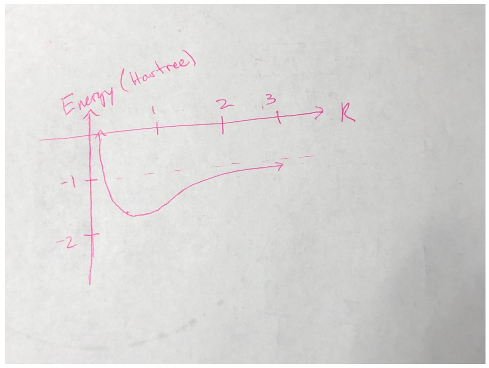
   $h_{AA} = \gamma^2/2 - \gamma f(x) = 1/2 - f(x)$, where $f(x) = 1 - \frac{(1+x)e^{-2x} - 1}{x}$.

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 $R \to \infty$.

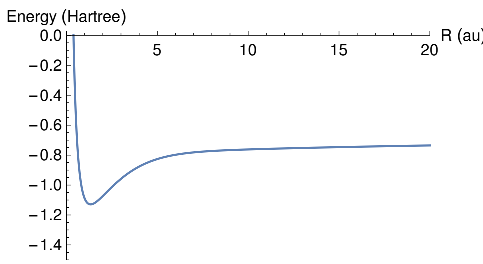
7. Sketch a molecular energy curve for $H_2$ as a function of $R$, giving its value as $R \to \infty$.




-1 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? $H_2$?*




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

9. For a molecule with $y_e = 0$, deduce a formula for the number of states it will bind in terms of $D_e$, $\omega$, 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 $\nu$ 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 $\omega$ for the Morse potential, for which $\epsilon_n = -V_0 \left(1 - \frac{\alpha(n+\frac{1}{2})}{\sqrt{2\,\mu\,V_0}}\right)^2$

    $x_e = \frac{\omega}{8D_e}$