Chemistry 691 Homework #4

Chapter 3,

#1 $S(\rho) = 1 - \frac{\rho^2}{6} + \dots$ $\quad V_{aba} = -\zeta(1+\rho)e^{-2\rho} = -\zeta\left(1 - \frac{\rho^2}{2}\right)$

$V_{aaa} = -\zeta\left(1 - \frac{2\rho^2}{3}\right)$ $\quad T_{ab}(\rho) \approx \zeta^2\left[\frac{1}{2} - \frac{5\rho^2}{12}\right]$

so $E_{el} = \frac{1}{1+S}\left[\underbrace{-\zeta}_{V_{aaa}} \underbrace{-\zeta\left(1-\frac{2\rho^2}{3}\right)}_{V_{aaa}} \underbrace{-2\zeta\left(1-\frac{\rho^2}{2}\right)}_{2V_{aba}} + \underbrace{\zeta^2\left(1-\frac{5\rho^2}{12}\right)}_{T_{aa}+T_{ab}}\right]$

$= \frac{1}{1+S}\left[-4\zeta + \zeta^2 + \rho^2\left(\frac{5\zeta}{3} - \frac{\zeta^2}{12}\right) + \dots\right]$

$\frac{1}{1+S} \approx \frac{1}{2-\rho^2/6} = \frac{1}{2(1-\rho^2/12)} \approx \frac{1}{2}\left(1 + \frac{\rho^2}{12} + \dots\right)$

so $E_{el} \approx \frac{1}{2}\left(1 + \frac{\rho^2}{12} + \dots\right)\left(-4\zeta + \zeta^2 + \rho^2\left(\frac{5\zeta}{3} - \frac{\zeta^2}{12}\right) + \dots\right)$

$= \zeta\left(-2 + \frac{2\rho^2}{3}\right) + \frac{\zeta^2}{2}\left(1 - \frac{\rho^2}{6}\right)$

$\frac{\partial E_{el}}{\partial R} = \frac{\partial E_{el}}{\partial \rho}\frac{d\rho}{dR}$ $\quad \frac{dE}{d\rho} = \left(\frac{4\rho\zeta}{3} - \frac{\rho\zeta^2}{3}\right) + \Theta(\rho^3)$ $\quad \frac{d\rho}{dR} = \zeta$

so $\frac{dE_{el}}{dR} = \frac{4\rho\zeta^2}{3} - \frac{\rho\zeta^3}{3}$ $\quad$ at $\rho = 0$ $\quad \frac{\partial E}{dR} = 0$

1st derivative = 0 $\quad E_{el}(R)$ is flat, no cusp

problem 3 minimum value is $R = 1.4$ $E = -2.9775$

fit to quadratic for $R = 1.2, 1.4, 1.6$ $\quad E = -2.413926 - 0.855142R + 0.221275R^2$

differentiate and set to zero $\quad \frac{dE}{dR} = 0 = 0.442455R - 0.855142$

$R_e = 1.4807$ $\quad E(R_e) = -2.979950$

asymptotic limit $\quad E = E(H_2) = -2.90357$ (page 52, chap 2)

so $D_e = 0.07539$ hartree $= 2.051$ eV

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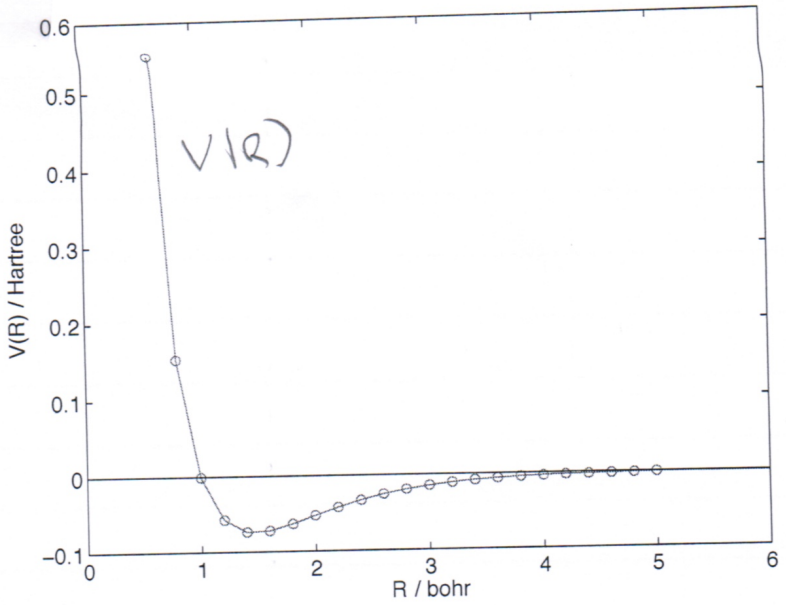

The nuclear repulsion is $Z_1 Z_2 / R$

So subtract this off to get the electronic energy