

# Chem231B: Hw 4

March 1, 2020

## BO Approx

a) Making the BO approximation, write the purely electronic Hamiltonian and, by completing the square, write its energy levels  $E_{\text{el},n}(X)$ .

The full Hamiltonian ( $\hat{H}$ ), the full wavefunction ( $\Psi(x, X)$ ), and the Schrödinger equation are defined,

$$\hat{H}\Psi(x, X) = E_{\text{tot}}\Psi(x, X) \quad (1)$$

$$\Psi(x, X) = \phi_{\text{el}}(x)\phi_{\text{nuc}}(X) \quad (2)$$

$$\hat{H} = \hat{T}_{\text{nuc}} + \hat{T}_{\text{el}} + V(X, x). \quad (3)$$

Given:  $V(X, x) = \frac{1}{2}(X^2 + x^2) + \frac{1}{2}(x - X)^2$

Rearrange  $V(X, x)$  and completing the square,

$$\begin{aligned} V(X, x) &= \frac{1}{2}(X^2 + x^2) + \frac{1}{2}(x - X)^2 \\ &= \frac{1}{2}X^2 + \frac{1}{2}x^2 + \frac{1}{2}(x^2 - 2xX + X^2) \\ &= X^2 + x^2 - xX \end{aligned} \quad (4)$$

Perform coordinate transformation by substituting in  $y = x - X/2$ . Hence, the purely electronic Hamiltonian is,

$$\begin{aligned} V(X, y) &= y^2 + xX - xX - \frac{X^2}{4} + X^2 \\ &= y^2 + \frac{3X^2}{4} \end{aligned} \quad (5)$$

$$\begin{aligned} \hat{H}_{\text{el}} &= \hat{T}_{\text{el}} + V(X, y) \\ &= \frac{p_y^2}{2} + y^2 + \frac{3X^2}{4}, \end{aligned} \quad (6)$$

where  $p_y$  is electronic momentum operator. The Schrödinger equation for the electronic part,

$$\hat{H}_{\text{el}}\phi_{\text{el}}(x) = E_{\text{el},n}\phi_{\text{el}}(x) \quad (7)$$

$$\left(\frac{p_y^2}{2} + y^2 - \frac{3X^2}{4}\right)\phi_{\text{el}}(x) = E_{\text{el},n}(X)\phi_{\text{el}}(x). \quad (8)$$

$$E_{\text{el},n}(X) = \left(n + \frac{1}{2}\right)\omega_{\text{el}} + \frac{3X^2}{4} \quad (9)$$

$\omega_{\text{el}}$  is determined to be  $\sqrt{2}$ .

b) Write the nuclear equation for the proton in the field of the electronic energy plus any other parts of the potential, to get an expression for the total energy of the system,  $E_{\nu,n}$ , where  $\nu$  is the quantum number for

proton vibrations.

Since the electronic part of the wavefunction is solved in part a), the nuclear part is left,

$$(\hat{T}_{\text{nuc}} + E_{\text{el},n}(X))\phi_{\text{nuc}}(X) = E_{\text{tot}}\phi_{\text{nuc}}(X) \quad (10)$$

$$\left(\frac{p_{\text{nuc}}^2}{2m_p} + \left(n + \frac{1}{2}\right)\omega_{\text{el}} + \frac{3X^2}{4}\right)\phi_{\text{nuc}}(X) = E_{\text{tot}}\phi_{\text{nuc}}(X) \quad (11)$$

Since the solutions are the harmonic oscillator, the total energy ( $E_{\nu,n}$ ) is,

$$\begin{aligned} E_{\nu,n} &= \left(\nu + \frac{1}{2}\right)\omega_{\text{nuc}} + \left(n + \frac{1}{2}\right)\sqrt{2} \\ &= \left(\nu + \frac{1}{2}\right)\sqrt{\frac{3}{2m_p}} + \left(n + \frac{1}{2}\right)\sqrt{2} \end{aligned} \quad (12)$$

where substituting  $\omega_{\text{nuc}} = \sqrt{\frac{3}{2m_p}}$ .

c) Assume  $m = 25$ , plot the lowest 12 levels, labeling them with their electronic and nuclear quantum numbers.

Table 1: BO total energy in Hartree ( $E_{\nu,n}$ ) for  $m = 25$ , nuclear, and electronic quantum numbers ( $\nu, n$ ).

$\nu \backslash n$	0	1	2
0	0.830	2.244	3.658
1	1.075	2.489	3.903
2	1.319	2.734	4.148
3	1.564	2.979	4.393
4	1.809	3.224	4.638
5	2.054	3.469	4.883
6	2.299	3.713	5.128
7	2.544	3.958	5.373
8	2.789	4.203	5.618
9	3.034	4.448	5.863
10	3.279	4.693	6.107

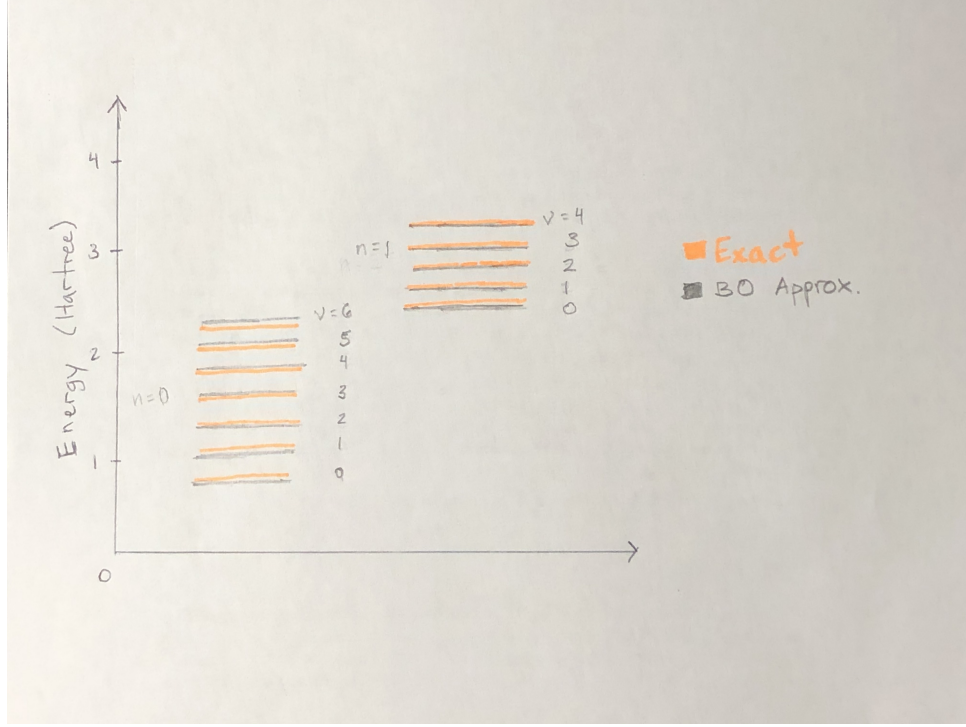


Figure 1: Energy spectrum of the exact and BO approximation energies for the electronic states ( $n$ ) and vibrational states ( $\nu$ ). The mass of proton is  $m = 25$ .

d) The exact solution to this problem is given by the sum of two harmonic oscillators, with frequencies

$$\omega_{\pm}^2 = 1 + \frac{1}{m} \pm \sqrt{1 - \frac{1}{m} + \frac{1}{m^2}} \quad (13)$$

Show that, if  $m \gg 1$ , this agree with your BO solutions above.

Rewrite Eqn (13)

$$1 + \frac{1}{m} \pm \left(1 - \frac{1}{2m}\right) \sqrt{1 + \frac{3}{4(m - 1/2)^2}} \quad (14)$$

Exact solution is  $E_{n',n} = \omega_+ \left(n + \frac{1}{2}\right) + \omega_- \left(n' + \frac{1}{2}\right)$  and since  $m \gg 1$ ,  $\omega_+$  is determined to be

$$\omega_+ \approx \sqrt{2}.$$

For  $\omega_-$ ,

$$\omega_- \approx \sqrt{\frac{3}{2m}}$$

e) Plot the exact energy levels and compare with the BO solution. Plot the errors of the BO energies as a function of energy. How accurate is BO for the lowest energy state? Does the accuracy depend on where you are in the spectrum?

Table 2: Exact total energy of the sum of two harmonic oscillators in Hartree ( $E_{\nu,n}$ ) for  $m = 25$  and states  $(\nu, n)$ .

$\nu \backslash n$	0	1	2
0	0.833	2.254	3.676
1	1.076	2.498	3.919
2	1.320	2.741	4.163
3	1.564	2.985	4.407
4	1.807	3.229	4.650
5	2.051	3.473	4.894
6	2.295	3.716	5.138
7	2.538	3.960	5.381
8	2.782	4.204	5.625
9	3.026	4.447	5.869
10	3.270	4.691	6.113

See Fig. 1 for the exact total energy compared to the BO. The BO energies are fairly accurate for the lowest energy state (0,0), see Table 3. The errors do not go higher than 0.5% and the accuracy depends on the nuclear vibrational state  $\nu$ .

Table 3: Relative error (%) between the exact and BO for given state  $(\nu, n)$  and  $m = 25$ .

$\nu \backslash n$	0	1	2
0	-0.361	-0.456	-0.477
1	-0.163	-0.361	-0.416
2	-0.038	-0.283	-0.361
3	0.048	-0.218	-0.313
4	0.111	-0.163	-0.270
5	0.159	-0.116	-0.231
6	0.196	-0.074	-0.195
7	0.227	-0.038	-0.163
8	0.252	-0.006	-0.134
9	0.273	0.022	-0.107
10	0.291	0.048	-0.082

Relative error approaches 0 with increasing  $\nu$  and rises as degeneracy is approached in the next  $n$  state.  
f) Repeat your calculation for  $m = 27$ , and comment on the errors in the BO states near the first electronic excitation. In particular, comment on (near)-degeneracies.

Table 4: BO total energy of coupled proton and electron in Hartree ( $E_{\nu,n}$ ) for  $m = 27$ , nuclear, and electronic quantum numbers  $(\nu, n)$ .

$\nu \backslash n$	0	1	2
0	0.825	2.239	3.653
1	1.061	2.475	3.889
2	1.296	2.711	4.125
3	1.532	2.946	4.360
4	1.768	3.182	4.596
5	2.003	3.418	4.832
6	2.239	3.653	5.068
7	2.475	3.889	5.303
8	2.711	4.125	5.539
9	2.946	4.360	5.775
10	3.182	4.596	6.010

Table 5: Exact energy of the sum of two harmonic oscillator in Hartree ( $E_{\nu,n}$ ) for  $m = 27$  and states  $(\nu, n)$ .

$\nu \backslash n$	0	1	2
0	0.828	2.249	3.670
1	1.062	2.483	3.904
2	1.297	2.718	4.139
3	1.532	2.952	4.373
4	1.766	3.187	4.608
5	2.001	3.422	4.843
6	2.235	3.656	5.077
7	2.470	3.891	5.312
8	2.704	4.125	5.546
9	2.939	4.360	5.781
10	3.174	4.595	6.016

Table 6: Percent error (%) between the exact and BO for given state  $(\nu, n)$  and  $m = 27$ .

$\nu \backslash n$	0	1	2
0	-0.338	-0.423	-0.442
1	-0.159	-0.328	-0.387
2	-0.044	-0.268	-0.338
3	0.035	-0.209	-0.295
4	0.094	-0.159	-0.256
5	0.138	-0.115	-0.220
6	0.173	-0.077	-0.188
7	0.202	-0.044	-0.159
8	0.226	-0.015	-0.132
9	0.246	0.012	-0.107
10	0.263	0.035	-0.085

The errors of BO energies at near degeneracy e.g. states (6,0) and (0,1) are larger in n=1 than n=0 state.

## $\text{H}_2^+$

The matrix elements in the calculation of the energy levels of  $\text{H}_2^+$  are  $S = e^{-x}(1+x+\frac{x^2}{3})$ ,  $h_{AA} = \gamma^2/2 - \gamma f(x)$ , where  $f = 1 - \frac{(1+x)e^{-2x}-1}{x}$ , and  $h_{AB} = -\gamma^2 s/2 - \gamma(2-\gamma)e^{-x}(1+x)$ , where  $x = \gamma R$ . Here  $\gamma$  is the scale factor for the 1s orbitals on each proton, separated by  $R$ .

a) Write formulas for the energy levels of the bonding and anti-bonding orbitals,  $\epsilon_{\pm}$

Bonding orbital energy is defined

$$\epsilon_+ = \frac{H_{AA} + H_{AB}}{1 + S_{AB}}. \quad (15)$$

Antibonding orbital energy is defined

$$\epsilon_- = \frac{H_{AA} - H_{AB}}{1 - S_{AB}}. \quad (16)$$

b) For  $\gamma = 1$ , plot  $s$ ,  $h_{AA}$ , and  $h_{AB}$  as a function of  $R$ . Explain their behavior as  $R \rightarrow \infty$ , as  $R \rightarrow 0$ , and their shapes.

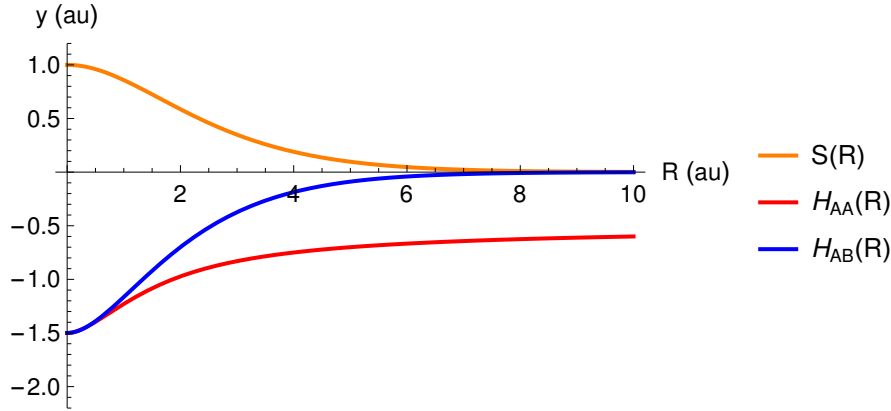


Figure 2: For  $\gamma = 1$ , the overlap ( $S(R)$ ), the diagonal element of the Hamiltonian ( $H_{AA}$ ), and the off-diagonal element of the Hamiltonian ( $H_{AB}$ ) is shown as a function of  $R$ .

At  $R \rightarrow \infty$ , the overlap ( $S(R)$ ) and the off-diagonal element of the Hamiltonian ( $H_{AB}(R)$ ) both approach 0 indicating that the two H nuclei are completely separated and non-interaction. Meanwhile, the diagonal element of the Hamiltonian ( $H_{AA}(R)$ ) approach  $-1/2$  Hartree as  $R \rightarrow \infty$ . At  $R \rightarrow 0$ , the H atoms are at maximal overlap and the electronic bonding energy becomes more negative and finite.

c) Repeat previous question for  $\epsilon_{\pm}(R)$ , using your insight from those answers. Then add the nuclear repulsion and plot both energy levels. Deduce the bond length and well-depth  $D_e$  for this approximate calculation.

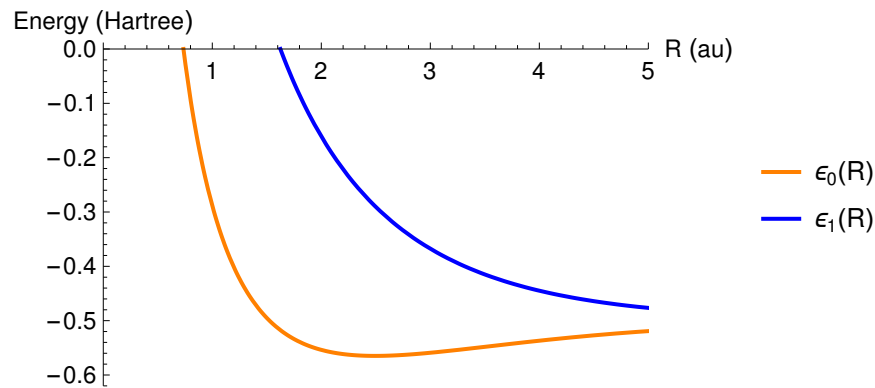


Figure 3: The ground state curve ( $\epsilon_0$ ) and first excited state curve ( $\epsilon_1$ ) are shown as a function of the distance between two H nuclei ( $R$ ).

The well-depth  $D_e$  is approximately 0.55 Hartree and the bond length is approximately  $2.49a_0$ .

d) Repeat (b + c) using  $\gamma = 1 + 1/2^R$ , but only for the lower curve. Plot all quantities on the same plots as before, and explain all differences. Calculate bond length and depth. Compare with exact answers (google or NIST).

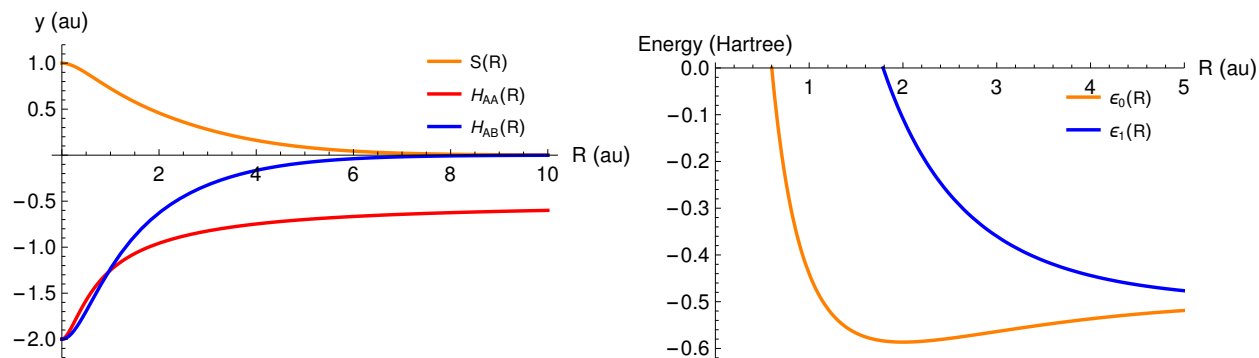


Figure 4: Side by side figures of the effect when  $\gamma = 1 + 1/2^R$  on the  $S(R)$ ,  $H_{AA}(R)$ ,  $H_{AB}(R)$ , and energy curve of  $H_2^+$  (left). The ground state ( $\epsilon_0$ ) and first excited state curves ( $\epsilon_1$ ) are shown (right).

Well-depth is approximately 0.0864 Hartree and exact well-depth is 0.102 Hartree (google). Bond length is approximately  $2.00a_0$  and reported equilibrium bond length of  $H_2^+$  is  $2.00 \pm 0.01$  (DOI: 10.1063/1.1674078).

## H<sub>2</sub>

a) Plot the HF binding energy of H<sub>2</sub>, approximating the Hartree energy as  $U_H = \frac{5\gamma}{8}(1 + e^{-x/4})$ , using the HF energy  $E = 2\epsilon + U_H/2$ , and using the same  $\gamma$  as in H<sub>2</sub><sup>+</sup>.

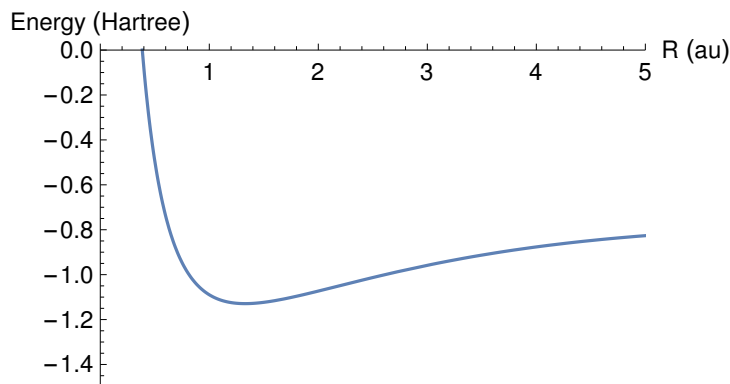


Figure 5: Approximated HF binding energy of H<sub>2</sub> for  $\gamma = 1 + 1/2^R$ .

b) Find the equilibrium bond distance and well-depth from your curve. Compare with the accurate HF values and comment.

The well-depth is approximately 0.129 Hartree and the equilibrium bond distance is approximately 1.33 au.

c) Estimate the effective force constant and hence harmonic vibrational frequency and compare with exact value. Comment on what this means about the error in the shape of the curve

Computed effective force constant  $\left. \frac{d^2 E_{\text{binding}}}{dR^2} \right|_{R=R_e} = 0.804 \text{ au}$  which is lower than the exact value 1.018 au.

d) Plot the Morse potential corresponding to H<sub>2</sub> on the same plot. Plot their difference near the equilibrium bond length. This would be the correlation energy if both curves were accurate. The correlation energy at equilibrium is -0.042H. Compare with the He atom. Comment on the variation of  $E_C$  with  $R$  and what this means for HF errors in bond lengths.

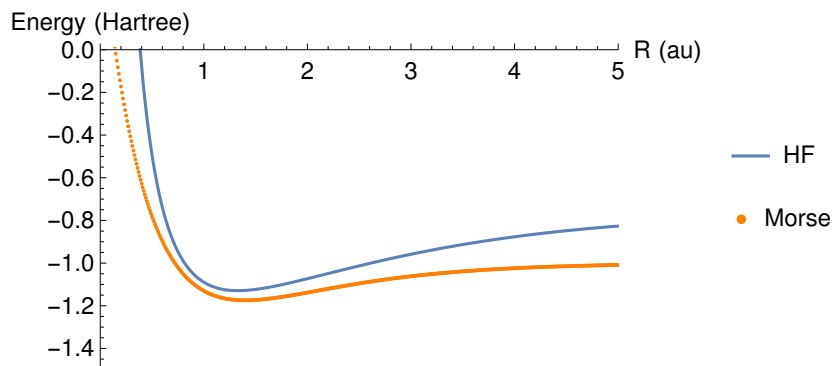


Figure 6: Morse potential corresponding to H<sub>2</sub> and HF binding energy of H<sub>2</sub> are shown.

$E_C$  is smaller near the equilibrium distance ( $R_e$ ). Anything outside  $R_e$  then  $E_C$  grows.



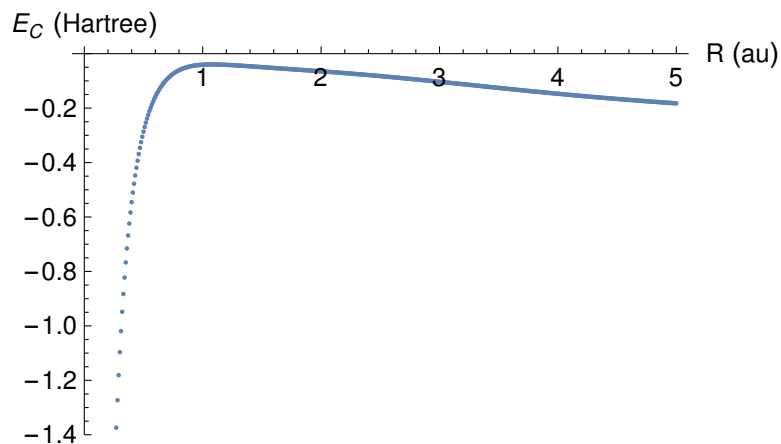


Figure 7: Difference between the Morse potential and HF curve of  $H_2$  shown near the equilibrium bond length.

e) Consider your curve as  $R \rightarrow \infty$ . What value is it approaching? Is this correct? If not, why not? What should differ in your energy expression?

The HF binding energy curve for  $H_2$  approaches  $-11/16$  or  $-0.6875$  Hartrees. This is wrong and it should go to  $-1$  Hartree. Error due to  $E_x = -U/2$  for  $N=2$  but for each separate H atom,  $E_x = -U$ . In HF,  $E_x$  is always  $-U/2$ , so difference for H atom is  $5/16$  (recall He calculations with exponential orbital).

## Analyzing Experimental Numbers on Diatomic Isotopes

This problem uses the first three rows of Table 7.2 of BRR. Ignore the last two columns ( $B$  and  $\alpha_e$ ) which refer to rotations. You will want to type the rest into some software, such as excel. Do all calculations in Hartree.

a) Just by staring at the numbers, can you spot two (large) typos in the table? One has a wrong digit, another has a misplaced decimal point. Correct them. Check the reduced mass results and convert into atomic units.

Incorrect vibrational frequency for  $D_2$  and equilibrium bond distance of  $H_2$ .

b) Given the results for  $v_e$ ,  $x_e$  and  $y_e$ , calculate the zero-point energy in each well.

$$E_{\text{vib}}(\nu) = hv_e[(\nu + \frac{1}{2}) - x_e(\nu + \frac{1}{2})^2 + y_e(\nu + \frac{1}{2})^3] \text{ for } \nu = 0, 1, \dots$$

Table 7: Vibrational zero point energies (ZPE) in Hartrees

Molecule	ZPE
$H_2$	0.00989
HD	0.00858
$D_2$	0.00704

c) Add your zero-point energies to each  $D_0$  to estimate  $D_e$ . What should you find, and do you find it?

Table 8: Well-depth ( $D_e$ ) in Hartrees

Molecule	$D_e$
$H_2$	0.174424
HD	0.174423
$D_2$	0.174434

The estimated  $D_e$  is identical to  $H_2$  well-depth is 0.174486 Hartrees.  $D_e$  is independent of mass.

d) Calculate the force constant for each well. What should you find, and do you find it?

Table 9: Force constant  $k$

Molecule	$k$
$H_2$	1.0184
HD	1.0204
$D_2$	1.0237

Independent of mass (almost).

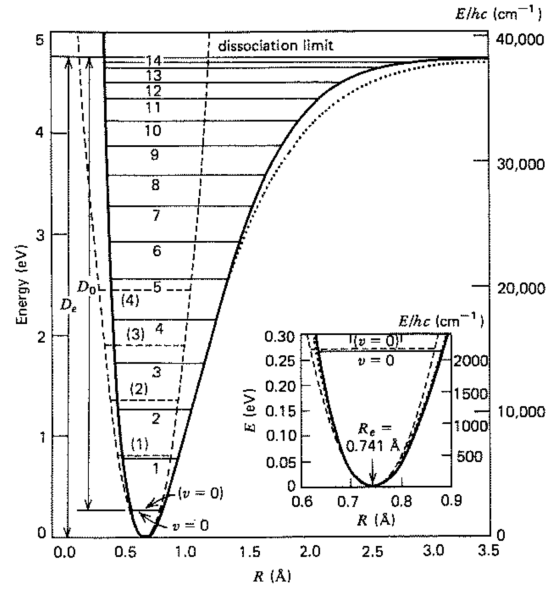
e) Using the spectroscopic formula for the energies, how many vibrational levels do you expect each well to bind?

Estimating with the Morse potential, the  $H_2$  has 14 vibrational levels. Since the mass changes, the vibrational states must change.

f) Repeat (e) assuming each well was purely parabolic.

8 vibrational states for the  $H_2$ .

g) For  $\text{H}_2$  only, plot the harmonic levels and the true levels.



h) Make the row of numbers for  $\text{T}_2$ .

Table 10: Vibrational constants for  $\text{T}_2$

Molecule	$\mu$ (amu)	$R_e$ (Angstrom)
$\text{T}_2$	1.5	0.7412

## Theoretical Approach to Diatomic Vibrations

The energy levels of a Morse potential  $V_0(\exp(-2\alpha(R - R_0)) - 2\exp(-\alpha(R - R_0)))$  are

$$\epsilon_n = -V_0 \left( 1 - \frac{\alpha(n + \frac{1}{2})}{\sqrt{2\mu V_0}} \right)^2 \quad (17)$$

where  $n$  takes all integer values from 0 up to where the term in brackets becomes negative, and  $\mu$  is the mass.

a) Find the minimum position and well-depth, and so relate  $V_0$  and  $R_0$  to quantities in molecular binding curves (if they had this shape).

Let  $R' = R - R_0$  and find the minimum of Morse potential

$$\frac{dV(R')}{dR'} = -2\alpha V_0(e^{-2\alpha R'} - e^{-\alpha R'}) = 0. \quad (18)$$

Since the minimum of the Morse potential is 0 at  $R' = R - R_0 = 0$ , then  $V_0 = D_e$  implying  $R_0 = R_e$ .

b) Expand the Morse potential around its minimum, and so find a formula for  $\alpha$  in terms of the harmonic approximation to a molecular well. Substitute  $R' = R - R_e$ ,

$$\begin{aligned} V(R) &= V_0(e^{-2\alpha(R-R_0)} - 2e^{-\alpha(R-R_0)}) \\ &= D_e(e^{-2\alpha(R')} - 2e^{-\alpha(R')}) \\ &= D_e(1 - 2\alpha R' + 2\alpha^2 R'^2 - 2(1 - \alpha R' + \frac{1}{2}\alpha^2 R'^2)) \\ &= -D_e + D_e\alpha^2 R'^2 = -D_e + \frac{1}{2}kR'^2 \\ k &= 2\alpha^2 D_e \\ \alpha &= \sqrt{k/(2D_e)}. \end{aligned}$$

c) Deduce expressions for  $x_e$  and  $y_e$  for this well, in terms of the molecular properties.

$$\begin{aligned} \epsilon_n &= -D_e \left( 1 - \frac{\alpha(n + \frac{1}{2})}{\sqrt{2\mu D_e}} \right)^2 \\ &= -D_e(1 - \sqrt{\frac{2}{\mu D_e}}\alpha(n + \frac{1}{2}) + \frac{\alpha^2}{2\mu D_e}(n + \frac{1}{2})^2) \\ &= -D_e + \omega(n + \frac{1}{2})(1 - x_e(n + \frac{1}{2}) + y_e(n + \frac{1}{2})^2) \\ y_e &= 0 \\ \omega &= \sqrt{\frac{2D_e}{\mu}}\alpha \\ \omega x_e &= \frac{\alpha^2}{2\mu} \\ x_e &= \frac{\alpha}{\sqrt{8\mu D_e}}. \end{aligned}$$

d) From your expression for  $x_e$ , find a combination of  $D$ ,  $x_e$ , and  $\nu_e$  that should be mass independent, and use the data to check if it is. Compare with Morse result and comment.

Eliminate  $\alpha$  where  $\alpha^2 = \frac{\mu\omega^2}{2D_e}$ ,

$$\begin{aligned}\omega x_e &= \frac{\omega^2}{4D_e} \\ x_e &= \frac{\omega}{\sqrt{4D_e}}.\end{aligned}$$

e) How many levels does your Morse potential predict for  $\text{H}_2$ ? Compare with the perturbative answer and the harmonic approximation and comment.

$$\begin{aligned}\epsilon_e &= -D_e \left[1 - \frac{\omega}{2D_e} \left(x + \frac{1}{2}\right)\right]^2 \\ n_{\max} &= \frac{2D_e}{\omega} - \frac{1}{2} = \frac{x_e^{-1} - 1}{2} = 16 \times 9\end{aligned}$$

Morse predicts 16 levels and harmonic approximation predicts 8. The reality is 14.

f) Add the Morse levels to your plot of  $\text{H}_2$  levels, and compare with true levels.

Morse potential will be close but, not perfect at higher levels.

## General Problems about Diatomics from BRR

1. *Ionic bonds:* Use Table 7.3 to deduce the values of  $B$  and  $\rho$  used in Eq (7.43). Are they reasonable? How might you have found them without reverse engineering? Is the agreement between calculation and experiment accurate enough by quantum chemistry standards? Identify which components of a KS calculation are being approximated by the separate terms in Eq (7.44).

$$V_{\text{rep}}(R) = Be^{-R/\rho} \quad (19)$$

$$E(R) = -\frac{q_1q_2}{4\pi\epsilon_0 R} + V_{\text{rep}}(R) \quad (20)$$

$E(R)$  is the “ionic dissociation energy” taken from BRR and  $V_{\text{rep}}(R)$  is the Eq (7.43) or the Born–Mayer potential. With Table 7.3, we can reverse engineer from calculated  $D_e$  to fit the exponential. The constants  $B$  and  $\rho$  are determined 33.056 and 2.324, respectively.

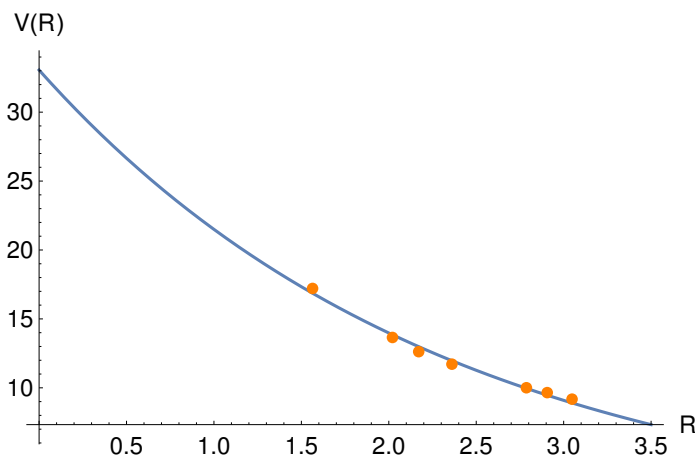


Figure 8: Exponential fit for the Born–Mayer potential to determine  $B$  and  $\rho$  from Eqn. (19).

Table 11: Ionic Bond Model and absolute difference between experiment and calculated in eV.

Molecule	Calc.	Obs.	Diff
LiF	7.9996	7.983	0.017
LiCl	6.513	6.648	0.135
NaCl	5.616	5.750	0.134
KF	5.993	6.036	0.043
KI	4.458	4.601	0.143
RbCl	4.835	4.917	0.082
CsCl	4.692	4.870	0.178

The error can be up to  $\sim 0.2$  eV, or  $\sim 3$  kcal/mol. It is fairly good for smaller ions within chemical accuracy of  $\sim 1$  kcal/mol. However, the model does not do “well” for large ions where errors can reach up to  $\sim 3$  kcal/mol based on quantum chemistry standards. In addition, this shows one can do very well with simple models and empirical parameters, but never know reliability or how to improve.

2. *Homonuclear diatomics:* Use Fig 7.14 to identify the error in a configuration in Table 7.5. Explain the labeling of the excited states in Table 7.6.

According to Fig 7.14, the molecular orbital configuration of  $N_2$  is incorrect and it should be:

$$\text{N}_2: \text{KK}(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$$

Molecular term symbols are defined

$$^{2S+1}\Lambda_{(g/u)}^{(+/-)}$$

where  $S$  is the total spin angular momentum,  $\Lambda$  is the total orbital angular momentum,  $g/u$  corresponds to symmetry of the electronic wavefunction with respect to inversion through this center, and  $+/-$  applies only to  $\Sigma$  states labeling symmetry of the wavefunction with respect to the reflection in a plane containing the nuclei.

3. *Electronegativity*: Read 7.7 and explain the spelling error in FONClBrISCHP.

Based on the Pauling scale, FONClBrISCHP has the incorrect order from most to least electronegative atoms. The Pauling order is FOCINBrISCHP but, electronegativity is not rigorous quantity.

4. *Potential energy surfaces*: Read 7.8 and explain the Massey criterion. When can curves cross and when do they not? If curves do not cross, can molecules change PES?

The Massey adiabatic criterion is the transition period ( $\Delta t$ ) at which the molecule on one potential energy surface (PES) encounters another PES within  $\Delta E$  over a range  $\Delta R$ . Yes, the molecule can change PES if the curves do not cross e.g. phosphorescence.

5. *Hydrides and isoelectronic series*: Read 7.9 and explain what is special about diatomic hydrides. Explain how hydrogen bonding upsets trends in boiling point data. Do problem 7.20.

Nearly all diatomic hydrides in the first row are highly reactive species that are observed mainly in high-temperature systems. Certain trends follow such as strength of bonding indicated by increasing  $D_e$ , shortening bond distances  $R_e$ , and increasing vibrational frequency  $\tilde{\nu}_e$  from LiH to HF. Typo on pg 220, the boiling trends where H<sub>2</sub>O boiling point is written 0.0°C but, H<sub>2</sub>O boils at 100°C. Hydrogen bonding

Problem 7.20) Predict dissociation energy, equilibrium internuclear distance  $R_e$ , and vibration frequency  $\tilde{\nu}_e$  by extrapolation from the data in Table 7.9.

The following results were roughly estimated with two points by linear regression between the observable and molar mass.

- a) At<sub>2</sub>:  $\tilde{\nu}_e = 22 \text{ cm}^{-1}$ ,  $R_e = 3.349 \text{ angstroms}$ ,  $D_0 = 0.79 \text{ eV}$ .
- b) DAt:  $\tilde{\nu}_e = 1705 \text{ cm}^{-1}$ ,  $R_e = 1.954 \text{ angstroms}$ ,  $D_0 = 1.81 \text{ eV}$ .
- c) Fr<sub>2</sub>:  $\tilde{\nu}_e = 12.72 \text{ cm}^{-1}$ ,  $R_e = 5.302 \text{ angstroms}$ ,  $D_0 = 0.41 \text{ eV}$ .