

Chem231B: Hw 4

February 28, 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,

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

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

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

ω_{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 ν 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 (ν, n).

$\nu \backslash n$	0	1
0	0.830	2.244
1	1.075	2.489
2	1.319	2.734
3	1.564	2.979
4	1.809	3.224
5	2.054	3.469
6	2.299	3.713

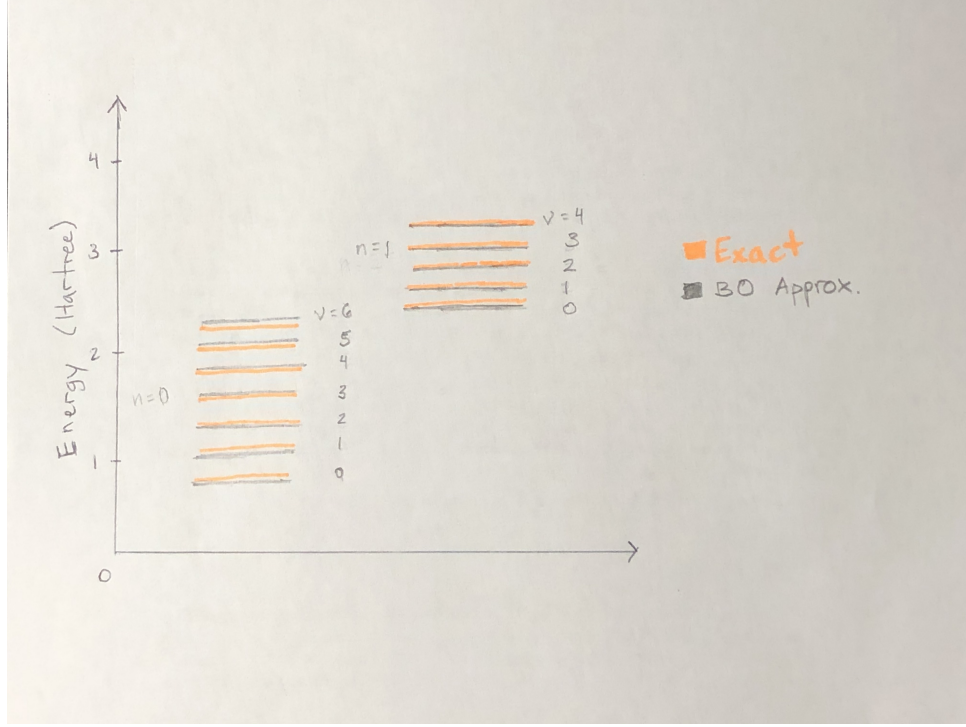


Figure 1: Energy spectrum of the exact and BO approximation energies for the electronic states (n) and vibrational states (ν). The mass of proton is $m = 25$.

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 $m \gg 1$, ω_+ is determined to be

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

For ω_- ,

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

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 (ν, n) .

$\nu \backslash n$	0	1
0	0.833	2.254
1	1.076	2.498
2	1.320	2.741
3	1.564	2.985
4	1.807	3.229
5	2.051	3.473
6	2.295	3.716

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 ν .

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

$\nu \backslash n$	0	1
0	0.361	0.456
1	0.163	0.361
2	0.038	0.283
3	0.048	0.218
4	0.111	0.163
5	0.159	0.116
6	0.196	0.074

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 (ν, n) .

$\nu \backslash n$	0	1
0	0.825	2.239
1	1.061	2.475
2	1.296	2.711
3	1.532	2.946
4	1.768	3.182
5	2.003	3.418
6	2.239	3.653

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

$\nu \backslash n$	0	1
0	0.828	2.249
1	1.062	2.483
2	1.297	2.718
3	1.532	2.952
4	1.766	3.187
5	2.001	3.422
6	2.235	3.656

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

$\nu \backslash n$	0	1
0	0.338	0.423
1	0.159	0.328
2	0.044	0.268
3	0.035	0.209
4	0.094	0.159
5	0.138	0.115
6	0.173	0.077

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.

H_2^+

The matrix elements in the calculation of the energy levels of 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 γ 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, ϵ_{\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.

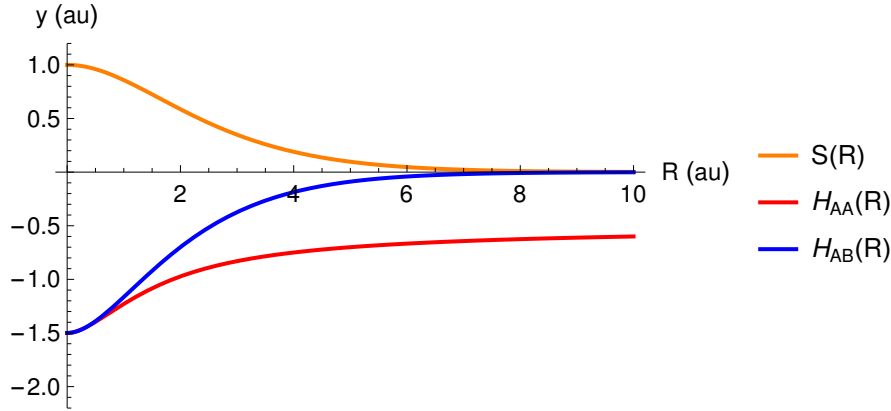


Figure 2: For $\gamma = 1$, the overlap ($S(R)$), the diagonal element of the Hamiltonian (H_{AA}), and the off-diagonal element of the Hamiltonian (H_{AB}) is shown as a function of R .

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.

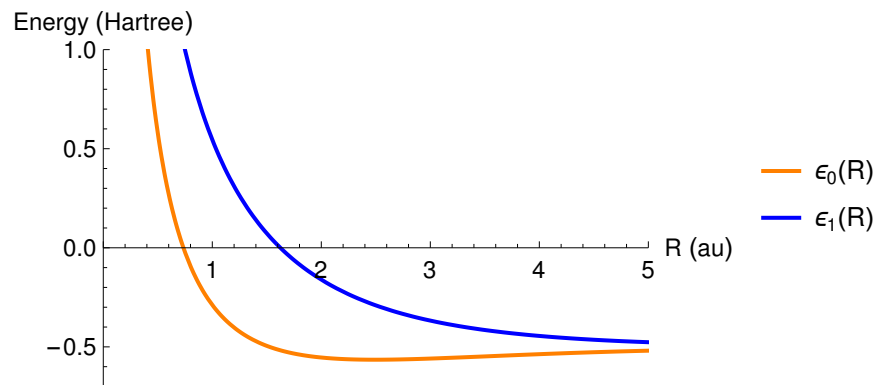


Figure 3: The ground state curve (ϵ_1) and first excited state curve (ϵ_0) are shown as a function of the distance between two H nuclei (R).

The well-depth D_e is approximately 0.55 Hartree and the bond length is approximately 2.5 au.

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).

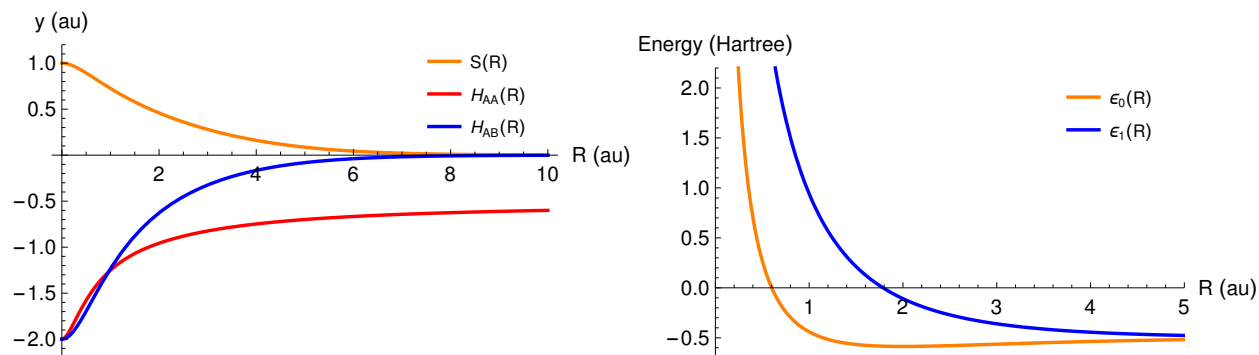


Figure 4: Side by side figures of the effect when $\gamma = 1 + 1/2^R$ on the $S(R)$, $H_{AA}(R)$, $H_{AB}(R)$, and energy curve of H_2^+ (left). The ground state (ϵ_1) and first excited state curves (ϵ_0) are shown (right).

Well-depth is approximately 0.1 Hartree and exact well-depth is 0.102 Hartree (google). Bond length is approximately 2.1 au and reported equilibrium bond length of H_2^+ is 2.0 ± 0.1 (DOI: 10.1063/1.1674078).

H₂

a) Plot the HF binding energy of H₂, 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 γ as in H₂⁺.

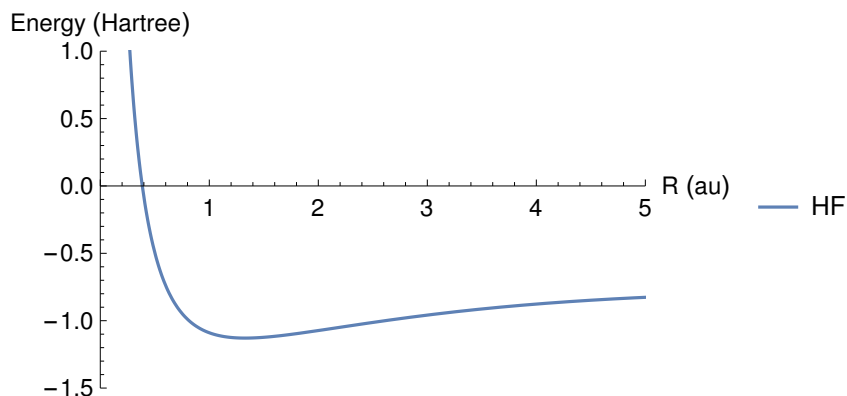


Figure 5: Apprxomiated HF binding energy of H₂ for $\gamma = 1$.

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 1.15 Hartree and the equilibrium bond distance is approximately 1.22 au. Accurate HF values for equilibrium bond distance and well-depth are 1.39 au and 1.13 Hartree, respectively.

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 H₂ 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.

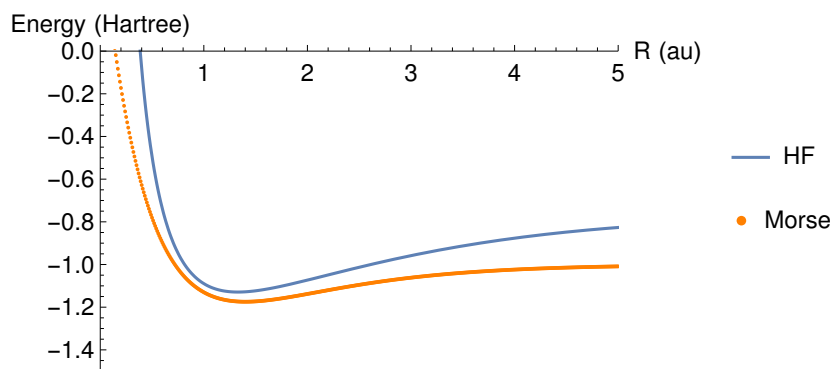


Figure 6: Morse potential corresponding to H₂ and HF binding energy of H₂ are shown.

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

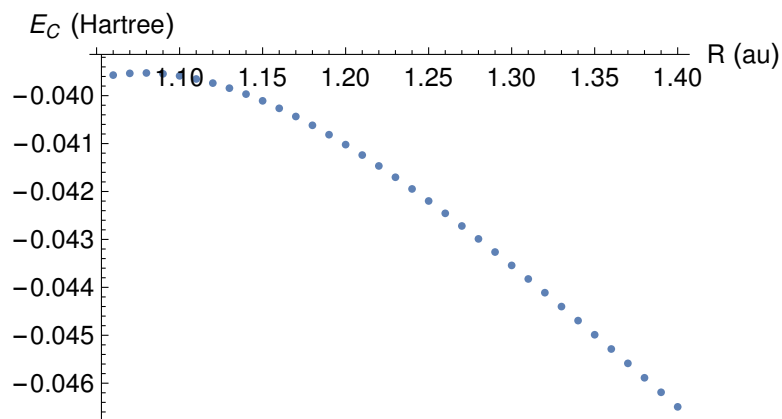


Figure 7: Difference between the Morse potential and HF curve of H_2 shown near the equilibrium bond length.

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 binding energy for H_2 approaches $-11/16$ Hartrees or -0.6875 Hartrees.

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 α_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 close e.g. H_2 well-depth is 0.174486 Hartrees.

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

Table 9: Force constant k

Molecule	D_e
H_2	1.0184
HD	1.0204
D_2	1.0237

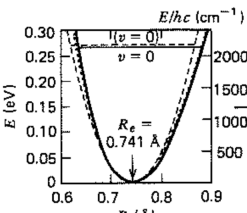
e) Using the spectroscopic formula for the energies, how many vibrational levels do you expect each well to bind?

Estimating with the Morse potential, the H_2 has 14 vibrational levels. This will be the same for the other isotopes.

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

8 vibrational states for the H_2 .

g) For H_2 only, plot the harmonic levels and the true levels.



h) Make the row of numbers for T_2 .

Table 10: Vibrational constants for T₂

Molecule	μ (amu)	R_e (Angstrom)
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 μ 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 α in terms of the harmonic approximation to a molecular well.

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

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

$$\begin{aligned} \epsilon_n &= -D_0 \left(1 - \frac{\alpha(n + \frac{1}{2})}{\sqrt{2\mu D_e}} \right)^2 \\ &= -D_e(1 - \sqrt{\frac{2}{\mu D_e}}\alpha(n + \frac{1}{2}) + \frac{\alpha^2}{2\mu D_e}(n + \frac{1}{2})^2) \\ &= -D_e + \omega(n + \frac{1}{2})(1 - x_e(n + \frac{1}{2}) + y_e(n + \frac{1}{2})^2) \\ y_e &= 0 \\ \omega &= \sqrt{\frac{2D_e}{\mu}}\alpha \\ \omega x_e &= \frac{\alpha^2}{2\mu} \\ x_e &= \frac{\alpha}{\sqrt{8\mu D_e}} \end{aligned}$$

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

e) How many levels does your Morse potential predict for H_2 ? Compare with the perturbative answer and the harmonic approximation and comment.

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

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

f) Add the Morse levels to your plot of 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 ρ 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 ρ are determined 33.056 and 2.324, respectively.

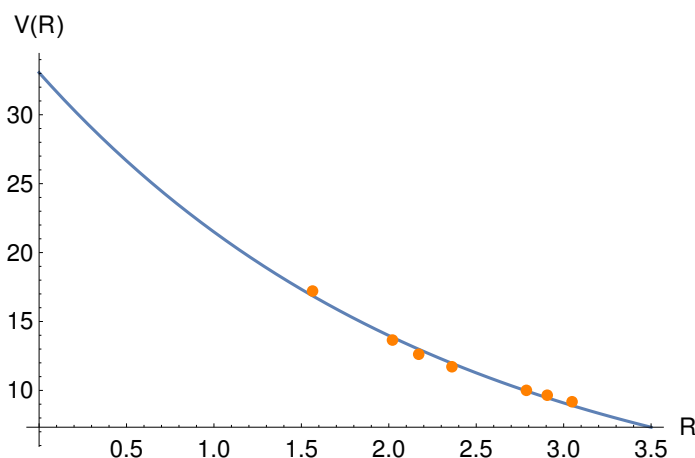


Figure 8: Exponential fit for the Born–Mayer potential to determine B and ρ from Eqn. (19).

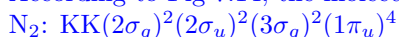
Table 11: Ionic Bond Model and absolute difference between experiment and calculated in eV.

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 ~ 0.2 eV, or ~ 3 kcal/mol. It is fairly good for smaller ions within chemical accuracy of ~ 1 kcal/mol. However, the model does not do “well” for large ions where errors can reach up to ~ 3 kcal/mol based on quantum chemistry standards.

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:



Molecular term symbols are defined

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

where S is the total spin angular momentum, Λ 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 Σ 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 FONCIBrISCHP.

Based on the Pauling scale, FONCIBrISCHP has the incorrect order from most to least electronegative atoms. The correct order is FOCINBrISCHP.

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 (Δt) at which the molecule on one potential energy surface (PES) encounters another PES within ΔE over a range ΔR . 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 H₂O boiling point is written 0.0°C but, H₂O 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.

Extrapolated results with linear regression between the observable and molar mass.

- a) At₂: $\tilde{\nu}_e = 22 \text{ cm}^{-1}$, $R_e = 3.349 \text{ angstroms}$, $D_0 = 0.79 \text{ eV}$.
- b) DAt: $\tilde{\nu}_e = 1705 \text{ cm}^{-1}$, $R_e = 1.954 \text{ angstroms}$, $D_0 = 1.81 \text{ eV}$.
- c) Fr₂: $\tilde{\nu}_e = 12.72 \text{ cm}^{-1}$, $R_e = 5.302 \text{ angstroms}$, $D_0 = 0.41 \text{ eV}$.