

Chem231B: Hw 4

February 24, 2020

BO Approx

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

$$\hat{H}_{\text{el}} = \hat{T}_{\text{el}} + V(X, x) \quad (1)$$

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,

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

Hence, the purely electronic Hamiltonian is,

$$\begin{aligned} \hat{H}_{\text{el}} &= \hat{T}_{\text{el}} + V(X, x) \\ &= \frac{p_x^2}{2} + (x - X)^2 + xX, \end{aligned} \quad (3)$$

where p_x is momentum operator for the electron. The Schrödinger equation for the electronic part,

$$\hat{H}_{\text{el}}\phi_{\text{el}}(x) = E_{\text{el},n}\phi_{\text{el}}(x) \quad (4)$$

$$\left(\frac{p_x^2}{2} + (x - X)^2 + xX \right) \phi_{\text{el}}(x) = E_{\text{el},n}(X)\phi_{\text{el}}(x). \quad (5)$$

This looks like the harmonic oscillator problem but with an additional coupled xX term and proton position X in the $(x - X)^2$ term. The harmonic oscillator wavefunctions are solutions to Eqn (5). For convenience, we rewrite $(x - X)^2 = (1/2)(2)(x - X)^2$ and this shows that $\omega_{\text{el}} = \sqrt{2}$. Throughout the problem, ω_{el} will be used and substituted later. The energy levels $E_{\text{el},n}(X)$ are determined for $n = 0, 1$ and then generalized to n levels. At $n = 0$,

$$\phi_{\text{el},0}(x) = \left(\frac{\omega_{\text{el}}}{\pi} \right)^{\frac{1}{4}} e^{-\omega_{\text{el}}x^2/2} \quad (6)$$

$$\begin{aligned} E_{\text{el},0} &= \langle \hat{T}_{\text{el}} \rangle + \langle V(X, x) \rangle \\ &= \frac{\omega_{\text{el}}}{4} + \frac{\omega_{\text{el}}}{4}(1 + 2X^2\omega_{\text{el}}) \\ &= \frac{\omega_{\text{el}}}{2} + \frac{X^2\omega_{\text{el}}^2}{2}. \end{aligned} \quad (7)$$

Repeat for $n = 1$,

$$\phi_{\text{el},1}(x) = \left(\frac{\omega_{\text{el}}}{\pi}\right)^{\frac{1}{4}} \sqrt{2\omega_{\text{el}}} e^{-\omega_{\text{el}}x^2/2} \quad (8)$$

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

Therefore, $E_{\text{el},n}(X) = (n + \frac{1}{2})\omega_{\text{el}} + \frac{X^2\omega_{\text{el}}^2}{2}$.

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 totla energy of the system, $E_{\nu,n}$, where ν is the quantum number for proton vibrations.

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

$$\hat{H}\Psi(x, X) = E_{\text{tot}}\Psi(x, X) \quad (10)$$

$$\Psi(x, X) = \phi_{\text{el}}(x)\phi_{\text{nuc}}(X) \quad (11)$$

$$\hat{H} = \hat{T}_{\text{nuc}} + \hat{T}_{\text{el}} + V(X, x). \quad (12)$$

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

$$(\hat{T}_{\text{nuc}} + E_{\text{el},n}(X))\phi_{\text{el}}(x)\phi_{\text{nuc}}(X) = E_{\text{tot}}\phi_{\text{el}}(x)\phi_{\text{nuc}}(X). \quad (13)$$

Solutions of $\phi_{\text{nuc}}(X)$ for Eqn (13) is simply the harmonic oscillator wavefunctions. Similarly, in part a), the computation of E_{ν} for quantum number of proton vibrations $\nu = 0$ is shown,

$$\phi_{\text{nuc},0}(X) = \left(\frac{m\omega_{\text{nuc}}}{\pi}\right)^{\frac{1}{4}} e^{-m\omega_{\text{nuc}}X^2/2} \quad (14)$$

$$E_{\nu=0} = \frac{\omega_{\text{nuc}}}{4} + \frac{3\omega_{\text{el}}^2}{4m\omega_{\text{nuc}}}. \quad (15)$$

For $\nu = 1$, $E_{\nu=1}$ can be computed

$$\phi_{\text{nuc},1}(X) = \left(\frac{m\omega_{\text{nuc}}}{\pi}\right)^{\frac{1}{4}} \sqrt{2m\omega_{\text{nuc}}} e^{-m\omega_{\text{nuc}}X^2/2} \quad (16)$$

$$E_{\nu=1} = \frac{3\omega_{\text{nuc}}}{4} + \frac{3\omega_{\text{el}}^2}{4m\omega_{\text{nuc}}}. \quad (17)$$

Based on these, the total energy ($E_{\nu,n}$) is,

$$E_{\nu,n} = \left(\nu + \frac{1}{2}\right)\frac{\omega_{\text{nuc}}}{2} + \left(n + \frac{1}{2}\right)\omega_{\text{el}} + \frac{3\omega_{\text{el}}^2}{4m\omega_{\text{nuc}}}. \quad (18)$$

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

From earlier, $\omega_{\text{el}} = \sqrt{2}$ which means that $k = 2$. We can define $\omega_{\text{nuc}} = \sqrt{k/m} = \sqrt{2/m}$. The energy state (ν, n) is given by,

$$\begin{aligned} E_{\nu,n} &= \left(\nu + \frac{1}{2}\right)\frac{\sqrt{2}}{2\sqrt{m}} + \left(n + \frac{1}{2}\right)\sqrt{2} + \frac{3\sqrt{2}}{4\sqrt{m}} \\ &= \left(\nu + 2\right)\frac{\sqrt{2}}{2\sqrt{m}} + \left(n + \frac{1}{2}\right)\sqrt{2} \end{aligned} \quad (19)$$



Figure 1: Computed total energy levels ($E_{\nu,n}$) for given nuclear and electronic quantum numbers (ν, n). The first 11 nuclear states (ν) are plotted at given n .

Table 1: Reported total energy in Hartree ($E_{\nu,n}$) for given nuclear and electronic quantum numbers (ν, n).

$\nu \backslash n$	0	1
0	0.990	2.404
1	1.131	2.546
2	1.273	2.687
3	1.414	2.828
4	1.556	2.970
5	1.697	3.111
6	1.838	3.253
7	1.980	3.394
8	2.121	3.536
9	2.263	3.677
10	2.404	3.818

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).

$$V_{\text{rep}}(R) = Be^{-R/\rho} \quad (20)$$

Reverse engineering the data requires looking up the α_i polarizability of the i -th ion from doi:10.1063/1.1679747. Once obtaining those values, the “ionic dissociation energy” can be computed and an exponential fit can be arranged via mathematica. The constants B and ρ are XX and XX, respectively.

Figure 2: Exponential fit for the Born–Mayer potential to determine B and ρ from Eqn. (20)

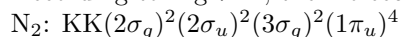
Table 2: Ionic Bond Model and absolute difference between experiment and calculated in eV.

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 FONClBrISCHP.

Based on the Pauling scale, FONClBrISCHP 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.

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