

Chem231B: Hw 4

February 19, 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,

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

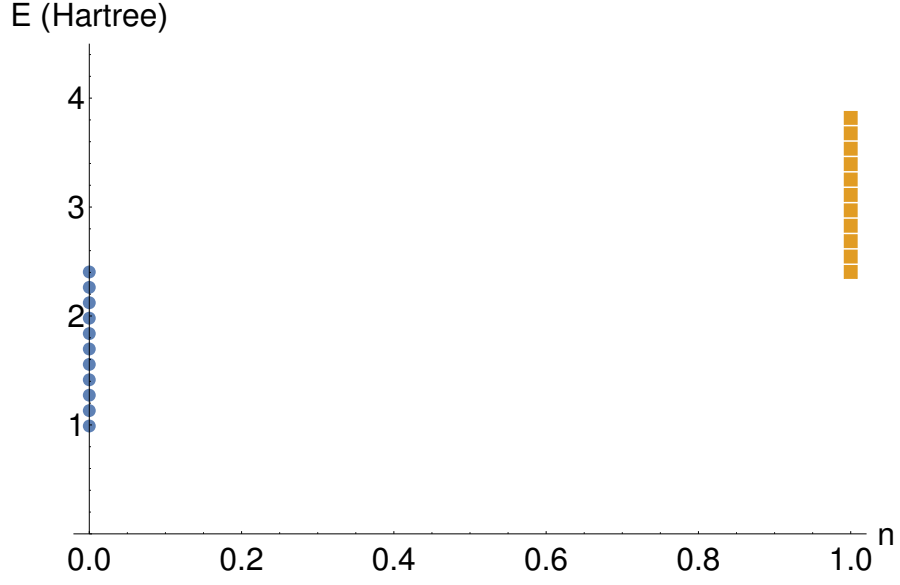


Figure 1: Computed total energy levels ($E_{\nu,n}$) for given nuclear and electronic quantum numbers (ν, n). The first 11 nuclear states (ν) are plotted at given n .

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