Chem231B: Hw 4

February 26, 2020

BO Approx

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

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

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

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

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

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,

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

Hence, the purely electronic Hamiltonian is,

$$\begin{aligned}
\hat{H}_{el} &= \hat{T}_{el} + V(X, x) \\
&= \frac{p_x^2}{2} + \frac{1}{2}\omega_{el}^2(x - X)^2 + xX, \tag{5}
\end{aligned}$$

where p_x is electronic momentum operator and ω_{el} is the vibrational frequency. The Schödinger equation for the electronic part,

$$\hat{H}_{el}\phi_{el}(x) = E_{el,n}\phi_{el}(x) \tag{6}$$

$$\left(\frac{p_x^2}{2} + \frac{1}{2}\omega_{el}^2(x - X)^2 + xX\right)\phi_{el}(x) = E_{el,n}(X)\phi_{el}(x). \tag{7}$$

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 (7). Throughout this part, ω_{el} will be used. The energy levels $E_{el,n}(X)$ are determined for $n = 0, 1$ and then generalized to n levels. At $n = 0$,

$$\phi_{el,0}(x) = \left(\frac{\omega_{el}}{\pi}\right)^{\frac{1}{4}}e^{-\omega_{el}x^2/2} \tag{8}$$

$$\begin{aligned}
E_{el,0} &= \langle\hat{T}_{el}\rangle + \langle V(X, x)\rangle \\
&= \frac{\omega_{el}}{4} + \frac{\omega_{el}^2 X^2}{2} + \frac{\omega_{el}}{4} \\
&= \frac{\omega_{el}}{2} + \frac{\omega_{el}^2 X^2}{2} \tag{9}
\end{aligned}$$

Repeat for $n = 1$,

$$\phi_{\text{el},1}(x) = \left(\frac{\omega_{\text{el}}}{\pi}\right)^{\frac{1}{4}} \sqrt{2\omega_{\text{el}}} \, e^{-\omega_{\text{el}}x^2/2} \tag{10}$$

$$E_{\text{el},1} = \frac{3\omega_{\text{el}}}{2} + \frac{\omega_{\text{el}}^2 X^2}{2}. \tag{11}$$

Since $\omega_{\text{el}} = \sqrt{2}$ from Eqn (5), the electronic energy will be

$$\begin{aligned} E_{\text{el,n}}(X) &= \left(n + \frac{1}{2}\right)\omega_{\text{el}} + \frac{\omega_{\text{el}}^2 X^2}{2} \\ &= \left(n + \frac{1}{2}\right)\sqrt{2} + X^2 \end{aligned} \tag{12}$$

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.

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

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

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

$$\begin{aligned} E_{\nu,n} &= \left(\nu + \frac{1}{2}\right)\omega_{\text{nuc}} + \left(n + \frac{1}{2}\right)\sqrt{2} \\ &= \left(\nu + \frac{1}{2}\right)\sqrt{\frac{2}{m_p}} + \left(n + \frac{1}{2}\right)\sqrt{2} \end{aligned} \tag{14}$$

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

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

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

ν \ n	0	1
0	0.849	2.263
1	1.131	2.546
2	1.414	2.828
3	1.697	3.111
4	1.980	3.394
5	2.263	3.677
6	2.546	3.960
7	2.828	4.243
8	3.111	4.525
9	3.394	4.808
10	3.677	5.091

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

$$\omega_\pm^2 = 1 + \frac{1}{m} \pm \sqrt{1 - \frac{1}{m} + \frac{1}{m^2}} \tag{15}$$

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

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

$$\omega_+^2 = 1 + \frac{1}{m} + \sqrt{1 - \frac{1}{m} + \frac{1}{m^2}}$$
$$\approx 1 + \sqrt{\frac{m-1}{m}}$$
$$\approx 1 + 1$$
$$\omega_+ \approx \sqrt{2}.$$

For ω_-,

$$\omega_-^2 = 1 + \frac{1}{m} - \sqrt{1 - \frac{1}{m} + \frac{1}{m^2}}$$
$$\approx 1 + \frac{1}{m} - 1$$
$$\omega_- \approx \frac{1}{\sqrt{m}}$$

Close in agreement.

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 coupled harmonic oscillator in Hartree $(E_{n',n})$ for $m = 25$ and states (n', n).

n' \\ n	0	1
0	1.040	3.061
1	1.099	3.120
2	1.159	3.179
3	1.218	3.239
4	1.278	3.298
5	1.337	3.358
6	1.396	3.417
7	1.456	3.476
8	1.515	3.536
9	1.574	3.595
10	1.634	3.654

Accuracy of BO energies depends where you are on in the spectrum. For instance, the lowest energy state (0,0) is an error of $\sim 20\%$ and the next energy state (1,0) is approximately $\sim 3\%$ error.
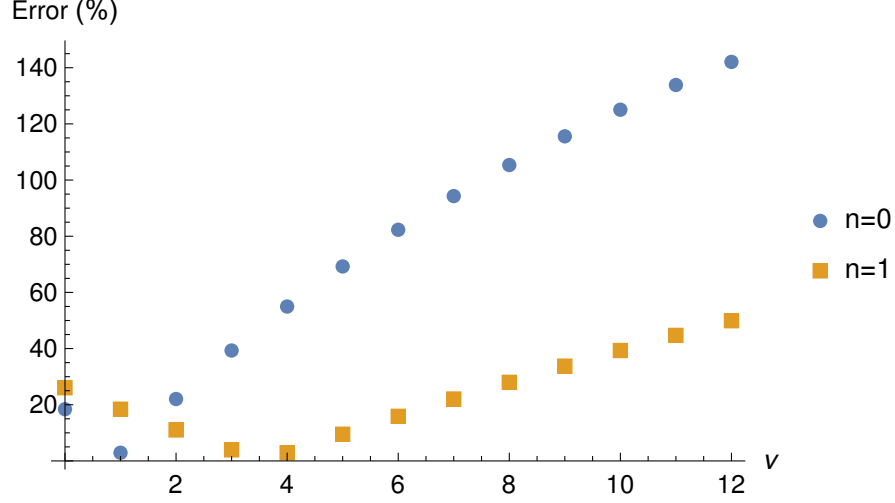
Figure 1: Percent errors between the exact and BO approximation energies for the electronic states (n) and vibrational states (ν). The mass of proton is $m = 25$.

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

ν $\diagdown$ n	0	1
0	0.843	2.257
1	1.115	2.530
2	1.388	2.802
3	1.660	3.074
4	1.932	3.346
5	2.204	3.618
6	2.476	3.890
7	2.748	4.163
8	3.021	4.707
9	3.293	4.979
10	3.565	5.251

Within BO approximation, there are near degeneracies between the high vibrational states $(\nu = 5, 6, 7, 8, 9)$ of the ground state $(n = 0)$ and the vibrational states $(\nu = 1, 2, 3, 4)$ of the first excited state $(n = 1)$.
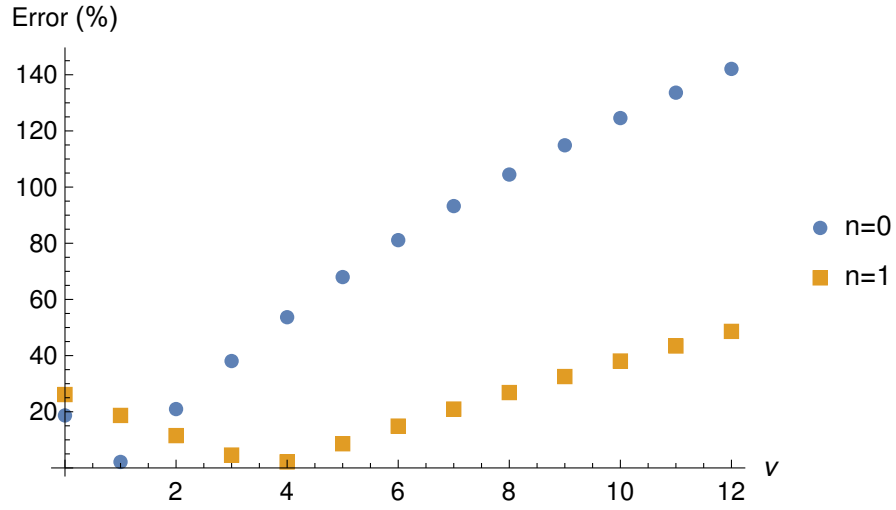
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Figure 2: Percent errors between the exact and BO approximation energies for the electronic states (n) and vibrational states (ν). The mass of proton is $m = 27$.

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, $\epsilon_\pm$

Bonding orbital energy is defined

$$\epsilon_+ = \frac{H_{AA} + H_{AB}}{1 + S_{AB}}. \tag{16}$$

Antibonding orbital energy is defined

$$\epsilon_- = \frac{H_{AA} - H_{AB}}{1 - S_{AB}} \tag{17}$$

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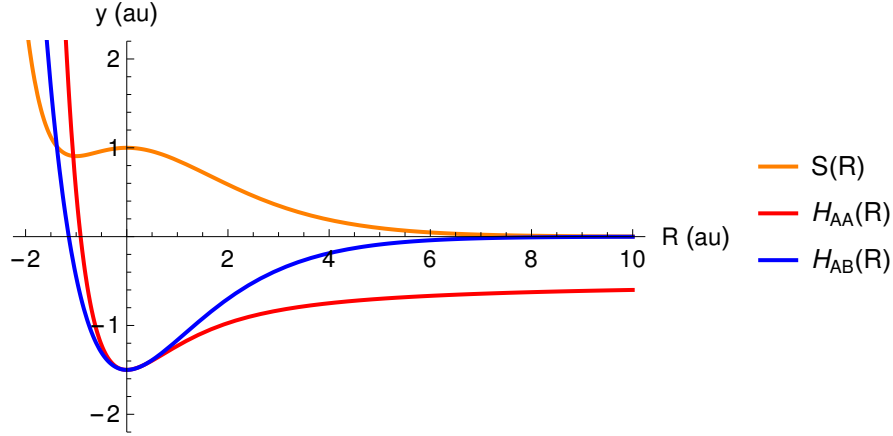

Figure 3: For $\gamma = 1$, the overlap $(S(R))$, the diagonal element of the Hamiltonian (H_{AA}), and the off-diagonal element of the Hamiltonian (H_{AB}) is shown as a function of R.

At $R \to \infty$, 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 $R \to \infty$. At $R \to 0$, 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.
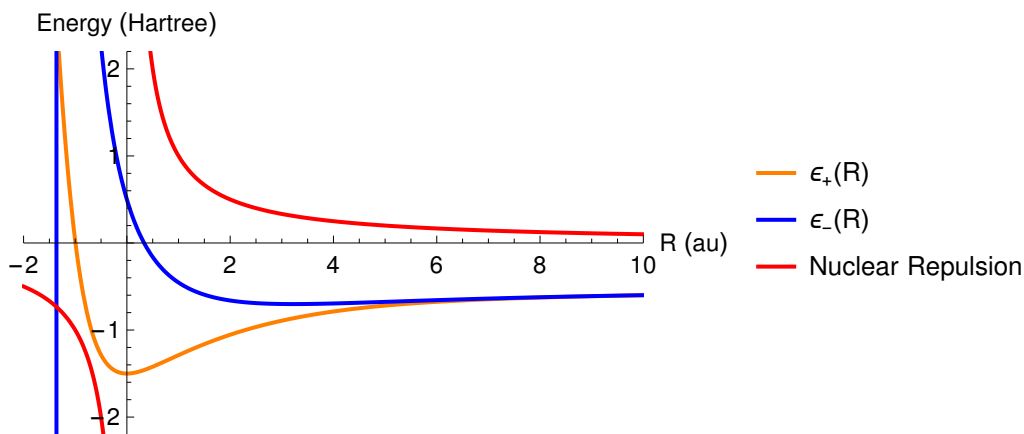
Figure 4: The nuclear repulsion, the bonding orbital (ϵ_+), and antibonding orbital energies (ϵ_-) are shown as a function of the distance between two H nuclei (R).

The well-depth D_e is approximately 1.0 Hartree and the bond length is approximately 1.5 au.

d) Repeat ($b + c$) using $\gamma = 1 + 1/2R$, 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).
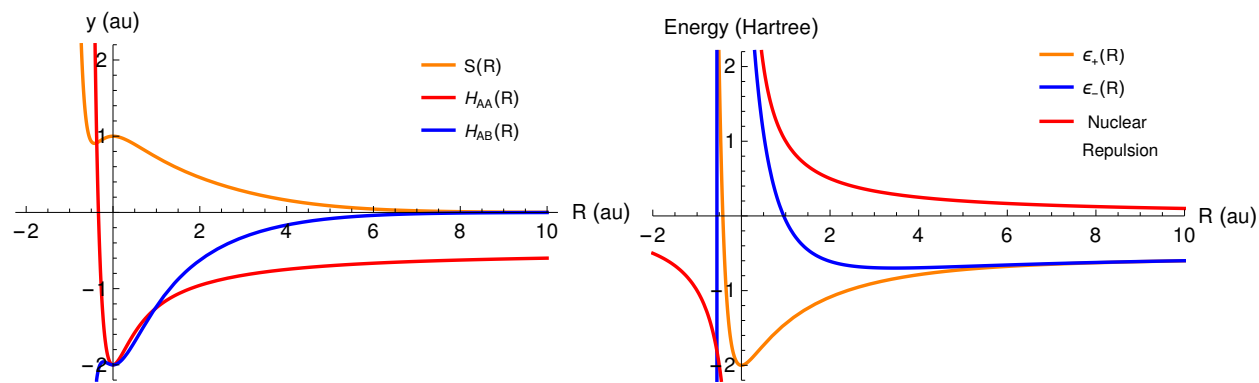

Figure 5: Side by side figures of the effect when $\gamma = 1 + 1/2R$ on the energy curve of H_2^+.

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H$_2$

a) Plot the HF binding energy of H$_2$, 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 H$_2^+$.
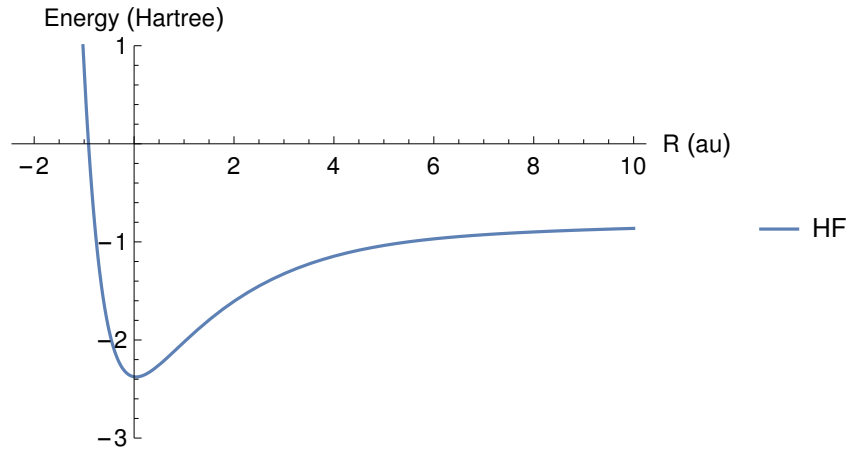

Figure 6: Apprxominated HF binding energy of H$_2$ for $\gamma = 1$.

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).

$$V_{\text{rep}}(R) = Be^{-R/\rho} \tag{18}$$

$$E(R) = -\frac{q_1 q_2}{4\pi\epsilon_0 R} + V_{\text{rep}}(R) \tag{19}$$

$E(R)$ 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.
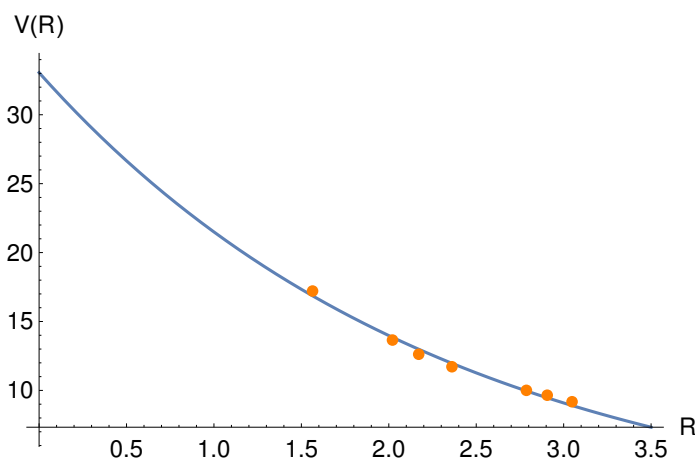

Figure 7: Exponential fit for the Born–Mayer potential to determine B and ρ from Eqn. (18).

Table 4: 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:
N_2: $KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$
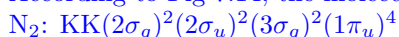
Molecular term symbols are defined

$$^{2S+1}|\Lambda|_{(g/u)}^{(+/-)}$$

where S is the total spin angular momentum, Λ is the total orbital angular momentum, g/u corrpondes to symmetry of the electronic wavefunction with repect 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 FOClNBrISCHP.

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 reative 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 $\tilde{v}_e$ from LiH to HF. Typo on pg 220, the boiling trends where H_2O boiling point is written $0.0°C$ but, H_2O boils at $100°C$. Hydrogen bonding

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

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

a) At_2: $\tilde{v}_e = 22$ cm^{-1}, $R_e = 3.349$ angstroms, $D_0 = 0.79$ eV.
b) DAt: $\tilde{v}_e = 1705$ cm^{-1}, $R_e = 1.954$ angstroms, $D_0 = 1.81$ eV.
c) Fr_2: $\tilde{v}_e = 12.72$ cm^{-1}, $R_e = 5.302$ anstroms, $D_0 = 0.41$ eV.