Quantum Chemistry
Exercises 3

1. Although the average displacement of a harmonic oscillator is zero, one can use the root mean square displacement, $\sqrt{\langle x^2 \rangle}$ as a measure of the vibrational amplitude. Use the expressions derived in class to calculate $\sqrt{\langle x^2 \rangle}$ for the *n*=0 state of the following molecules:

Molecule	$\tilde{\nu}$ **[cm^{-1}]**	l_0 **[Å]**
H_2	4.33×10^3	0.74
$^{35}Cl^{35}Cl$	5.60×10^2	1.99
$^{14}N^{14}N$	2.35×10^3	1.10

Compare $\sqrt{\langle x^2 \rangle}$ to the equilibrium bond length, l_0. What does this tell you about the rigid rotor approximation?

2. In the infrared spectrum of $H^{79}Br$ there is an intense line at 2600 cm^{-1}. Calculate the force constant of $H^{79}Br$ and its classical frequency of vibration.

3. Show that the Hamiltonian for the Harmonic oscillator can be written in terms of the raising and lowering operators,

$$\hat{a} = \sqrt{\frac{\mu\omega}{2}}\hat{x} + i\frac{\hat{p}_x}{\sqrt{2\mu\omega}}$$

and

$$a^{\dagger} = \sqrt{\frac{\mu\omega}{2}}\hat{x} - i\frac{\hat{p}_x}{\sqrt{2\mu\omega}}:$$

as

$$\hat{H} = \omega\hat{a}^{\dagger}\hat{a} + \tfrac{1}{2}\hbar\omega$$

4. Express the position operator $\hat{x}$ and momentum operator $\hat{p}_x$ in terms of the lowering and raising operators defined above.

5. Now we have some tools to help evaluate many of the integrals that one encounters in problems involving the quantum mechanical harmonic oscillator. One of these problems is the evaluation of average values.

Using the raising and lowering operators, find the average value of x^2 and the average value of p_x^2 for a harmonic oscillator in the state with $n = 2$.

6. You will see in the Spectroscopy course of next semester that IR light can only be absorbed by a molecule if the following integral is non-zero:

$$\int_{-\infty}^{\infty} \psi_n^*(x) x \psi_m(x)\, dx$$

Show, assuming that the wavefunctions are eigenfunction of the Harmonic oscillator, that this integral is non-zero only when $\Delta n = \pm 1$, as was assumed in class when discussing the IR absorption of molecules.