Today, we continue to solve some of the homework problems in class.

Let's take a look at problem 9.6. From the book:

9.6 An HCl molecule may rotate as well as vibrate. Discuss the difference in emission frequencies associated with these two modes of excitation. Assume that only $l \rightarrow l \pm 1$ transitions between rotational states are allowed. Assume the same for vibrational levels. For rotational levels assume $l \le 50$. Spring constant and moment of inertia may be inferred from the equivalent temperature values for HCl: $\hbar\omega_0 / k_B = 4150$ K; $\hbar^2 / 2Ik_B = 15.2$ K.

The rotational energy gap is much smaller than the vibrational energy gap. At room temperature (~300K), you can't excite HCl except at rotational state. At T<15.2 K you can't excite the rotational states.

The vibrational (thermal) energy of the rigid rotator is $E_n = \hbar\omega_0(n + \frac{1}{2})$.

The rotational energy of the rigid rotator is $E_l = \frac{\hbar^2 l(l+1)}{2I}$.

The vibrational energy is more than 10x the rotational energy.

If you write out the Hamiltonian

$\hat{H} = \frac{L^2}{2I}$ and $E_l = \frac{\hbar^2 l(l+1)}{2I}$

$I = 2Ma^2$ is the moment of inertia of a rotator

$$E_l - E_{l-1} = \frac{\hbar^2 l(l+1)}{2I} - \frac{\hbar^2 (l-1)l}{2I} = \frac{\hbar^2 l}{I} = \frac{\hbar^2 l}{2Ma^2} \qquad l = 0,1,2,...$$

Let's estimate this energy: $\frac{\hbar^2 l}{2Ma^2}$

Simplest way:the mass of a Hydrogen atom, a as Bohr radius. Define

$$\boxed{\square = \frac{\hbar^2}{2m_e a_0^2} = 13.6 \text{ eV}}$$

$$E_l - E_{l-1} = \frac{\hbar^2 l}{2Ma^2} = \frac{\hbar^2}{2m_e a_0^2}\frac{m_e l}{M} = \square \frac{m_e l}{M} = 13.6\frac{m_e l}{M} \text{eV} \sim 13.6 \cdot 10^{-3} l \square 10 \text{ meV can be ignored!}$$

Note:

Oxygen molecule: $M \uparrow 10\text{x} \quad E_l - E_{l-1} \square$ meV cool down.

Now let's look at problem 9.23. From the book:

9.23 Assume that a particle has an orbital angular momentum with z component $\hbar m$ and square magnitude $\hbar^2 l(l+1)$. (a) Show that in this state $\langle L_x \rangle = \langle L_y \rangle = 0$. (b) Show that $\langle L_x^2 \rangle = \langle L_y^2 \rangle = \frac{\hbar^2 l(l+1) - m^2\hbar^2}{2}$. [Hints: For part (a), use $\hat{L}_+$ and $\hat{L}_-$. For part (b), use $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$.]

Important relations for doing the homework:

$$\left.\begin{aligned}\hat{L}_+ &= \hat{L}_x + i\hat{L}_y \\ \hat{L}_- &= \hat{L}_x - i\hat{L}_y\end{aligned}\right\} \begin{aligned}\hat{L}_x &= \tfrac{1}{2}\left(\hat{L}_+ + \hat{L}_-\right) \\ \hat{L}_y &= -\tfrac{i}{2}\left(\hat{L}_+ - \hat{L}_-\right)\end{aligned}$$

Property

$$\hat{L}_\pm |l,m\rangle = \hbar\left[l(l+1) - m(m\pm 1)\right]^{1/2} |l,m\pm 1\rangle$$

$$\hat{L}^2 |l,m\rangle = \hbar^2 l(l+1) |l,m\rangle$$

$$\hat{L}_z |l,m\rangle = \hbar^2 m |l,m\rangle$$

and the orthogonality condition:

$$\langle l,m | l',m' \rangle = \delta_{ll'}\delta_{mm'}$$

Prove that:

$$\langle l,m | \hat{L}_x | l,m \rangle = 0$$

$$\tfrac{1}{2}\langle l,m | \hat{L}_+ + \hat{L}_- | l,m \rangle \to ?$$

Finally, let's look at problem 9.24. From the book:

9.24 The same conditions hold as in Problem 9.23. What is the expectation of the operator $\frac{1}{2}\left(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x\right)$ in the Y_l^m state?

$$\hat{L}_x\hat{L}_y = \tfrac{-i}{4}\left(\hat{L}_+ + \hat{L}_-\right)\left(\hat{L}_+ - \hat{L}_-\right) = \tfrac{-i}{4}\left(\hat{L}_+^{\,2} - \hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+ - \hat{L}_-^{\,2}\right)$$

$$\hat{L}_y\hat{L}_x = \tfrac{-i}{4}\left(\hat{L}_+ - \hat{L}_-\right)\left(\hat{L}_+ + \hat{L}_-\right) = \tfrac{-i}{4}\left(\hat{L}_+^{\,2} + \hat{L}_+\hat{L}_- - \hat{L}_-\hat{L}_+ - \hat{L}_-^{\,2}\right)$$

add $\to \tfrac{-i}{4}\left(2\hat{L}_+^{\,2} - 2\hat{L}_-^{\,2}\right)$

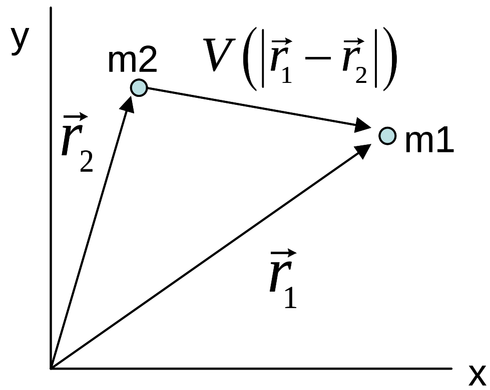
$$\tfrac{1}{2}\left(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x\right) = \tfrac{-i}{4}\left(\hat{L}_+^{\,2} - \hat{L}_-^{\,2}\right)$$

$$\therefore \langle l,m | \tfrac{1}{2}\left(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x\right) | l,m \rangle = \tfrac{-i}{4}\langle l,m | \hat{L}_+^{\,2} - \hat{L}_-^{\,2} | l,m \rangle$$

where $\langle l,m | \hat{L}_+^{\,2} | l,m \rangle = \langle l,m | \hat{L}_+ | l,m+1 \rangle = 0$, etc.

Now we start discussing the 2 particle problem.

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V\left(\left|\vec{r}_1 - \vec{r}_2\right|\right)$$



In classical mechanics, the 2-particle problem use center of mass
$(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2) \rightarrow (\vec{r}, \vec{p}, \vec{R}_{CM}, \vec{P}_{total})$

This is classical mechanics:

$\vec{r} = \vec{r}_1 - \vec{r}_2$	relative coordinate of the total momentum
$\vec{p}_{rel} = \frac{m_1 \vec{p}_1 - m_2 \vec{p}_2}{m_1 + m_2}$	relative momentum
$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}$	
$\hat{\mathcal{P}}_{total} = \hat{p}_1 + \hat{p}_2$	the total momentum

$$\hat{H} = \underbrace{\frac{\hat{\mathcal{P}}^2}{2M}}_{\hat{H}_{CM}} + \underbrace{\frac{\hat{p}_{rel}^2}{2\mu} + V(\vec{r})}_{\hat{H}_{rel}}$$

$\hat{H}_{CM}$ = Center of Mass for Particle in free space This is the kinetic energy of the system

$\hat{H}_{rel}$ = Relative Hamiltonian

μ = reduced mass $= \frac{m_1 m_2}{m_1 + m_2}$

M = total mass $= m_1 + m_2$

For the transformed system, the order of these operators can't change:

$[\hat{r}_{1j}, \hat{p}_{1j}] = i\hbar$ and $[\hat{r}_{2j}, \hat{p}_{2j}] = i\hbar$ $\quad j = 1, 2, 3, \ldots$

$[\hat{r}_j, \hat{p}_j] = i\hbar$ and $[R_j, \hat{p}_j] = i\hbar$

$[r, R] = [r, P] = [p, P] = 0$

$$\hat{H} = \underbrace{\frac{\hat{\mathcal{P}}^2}{2M}}_{\hat{H}_{CM}=\text{Center of Mass for Particle in free space}} + \underbrace{\frac{\hat{p}_{rel}^2}{2\mu} + V(\vec{r})}_{\hat{H}_{rel}=\text{Relative Hamiltonian}}$$

$$\hat{H} = \hat{H}_{CM} + \hat{H}_{rel}$$

$$\left[\hat{H}_{CM}, \hat{H}_{rel}\right] = 0 \quad \therefore \quad E = E_{CM} + E_{rel} \quad \text{and} \quad \psi = \varphi_{CM}(R)\varphi_{rel}(r)$$

$$\left.\begin{array}{l} \hat{H}_{CM} = \frac{\hat{\mathcal{P}}^2}{2M} \\ \varphi_k = Ae^{-\vec{k}\cdot\vec{R}} \\ E_k = \frac{\hbar^2 k^2}{2M} \end{array}\right\} \text{VERY SIMPLE!}$$

1 particle moves freely
1 particle moves in a potential

The Schrodinger equation is:

$$\left[\frac{\hat{p}_{rel}^2}{2\mu} + V(\vec{r})\right]\psi_{rel}(\vec{r}) = E_k \psi_k(\vec{r})$$

If we use spherical coordinates, we can write very easily into this:

$$\left[\frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2} + V(\vec{r})\right]\psi_{rel}(\vec{r}) = E_k \psi_k(\vec{r})$$

$\psi_{rel}(\vec{r}) = R(r)Y_l^m(\theta,\phi)$ can simplify the problem

$$\left[\frac{\hat{p}_r^2}{2\mu} + \underbrace{\frac{\hbar^2 l(l+1)}{2\mu r^2} + V(\vec{r})}_{\text{effective potential}}\right]R(r) = E_k R(r)$$