Quantum Mechanics and Spectroscopy
CHEM 3PA3
Assignment 22 **Name:** _____

1. For each of the systems listed below, list the type of special function(s) that appear in its eigenfunctions.

_____ Particle in a Box	A. Associated Laguerre Polynomials
_____ Harmonic Oscillator	B. Hermite Polynomials
_____ Rigid Rotor	C. Spherical Harmonics
_____ One-electron Atom	D. Trigonometric functions like sine and cosine

2. To a good approximation, the microwave spectrum of $H^{35}Cl$ consists of a series of equally spaced lines, separated by 6.26×10^{11} Hz. Calculate the bond length of $H^{35}Cl$.

3. The bond length of $^{12}C^{14}N$ is 117 pm and its force constant is 1630 Nm^{-1}. Predict the rotation-vibration spectrum of $^{12}C^{14}N$.

4. Draw an example for each type of molecule: **S** spherical top, **P** prolate symmetric top, **O** oblate symmetric top, or **A** asymmetric top.

5. Draw the molecular orbital diagram for SiH_4. You do not have to include the orbitals that are nonbonding. Indicate the forms of the molecular orbitals as a linear combination of atomic orbitals.

6. The three fundamental vibrations of CO_2 are observed at 1340 cm^{-1}, 667 cm^{-1}, and 2349 cm^{-1}, the second one being the bending mode. Determine the force constant of the CO stretching. *Hint.* Compute k for each stretching mode and take the mean value.

7. Consider the simplest possible representation of the bonding and antibonding wavefunctions in the H_2^+ molecule,

$$\psi_{bonding}(\mathbf{r}) \propto \phi_{1s}^A(\mathbf{r}) + \phi_{1s}^B(\mathbf{r}) \qquad \psi_{bonding}(\mathbf{r}) \propto \phi_{1s}^A(\mathbf{r}) - \phi_{1s}^B(\mathbf{r})$$

Here, $\phi_{1s}^A(\mathbf{r})$ and $\phi_{1s}^B(\mathbf{r})$ denote the 1s-hydrogenic wavefunctions centered on atoms A and B, respectively. Show that electron density accumulates in the region between the atoms in the bonding orbital and is depleted in the region between the atoms in the antibonding orbital by comparing the electron density of the bonding/antibonding wavefunctions,

$$\rho_{bonding}(\mathbf{r}) = |\psi_{bonding}(\mathbf{r})|^2 \qquad \rho_{antibonding}(\mathbf{r}) = |\psi_{antibonding}(\mathbf{r})|^2$$

to the "classical nonbonding density associated with noninteracting but overlapping hydrogen atoms,

$$\rho_{non}(\mathbf{r}) = \frac{1}{2}\left(\left|\phi_{1s}^A(\mathbf{r})\right|^2 + \left|\phi_{1s}^B(\mathbf{r})\right|^2\right).$$

I.e., compute and analyze $\rho_{bonding}(\mathbf{r}) - \rho_{non}(\mathbf{r})$ and $\rho_{antibonding}(\mathbf{r}) - \rho_{non}(\mathbf{r})$.