HW #6 Answers Chem 1410

1. 2P 3d

\# arrangements = 6 × 10 = 60

possible states : $L = 3, 2, 1 \Rightarrow {}^3F, {}^1F, {}^3D, {}^1D, {}^3P, {}^1P$

arrangements = ${}^3F(21), {}^1F(7)\ {}^3D(15), {}^1D(5), {}^3P(9)\ {}^1P(3)$

Hund's rule #1 predicts the lowest energy state to be a triplet state. Hund's rule #2 predicts the ${}^3F$ state to be lowest in energy.

2. For the ground state the second order correction is (assuming atomic units)

$$-\frac{\gamma^2 |\langle 0|x|1\rangle|^2}{\omega} = -\frac{\gamma^2}{2\omega}$$

For the first excited state the second order correction is

$$-\frac{\gamma^2 |\langle 1|x|2\rangle|^2}{\omega} + \frac{\gamma^2 |\langle 1|x|0\rangle|^2}{\omega} = -\frac{\gamma^2}{\omega} + \frac{\gamma^2}{2\omega} = -\frac{\gamma^2}{2\omega}.$$

So the energy spacing between levels $|0\rangle$ and $|1\rangle$ is unchanged by the perturbation

Note that the total potential is

$$\tfrac{1}{2}kx^2 + \gamma x = \tfrac{1}{2}k\left(x^2 + 2\tfrac{\gamma}{k}x\right) = \tfrac{1}{2}k(x+\gamma)^2 - \tfrac{1}{2}k\gamma^2$$

So the γx term causes a shift in the potential but the curvature, and hence the frequency, is unchanged.