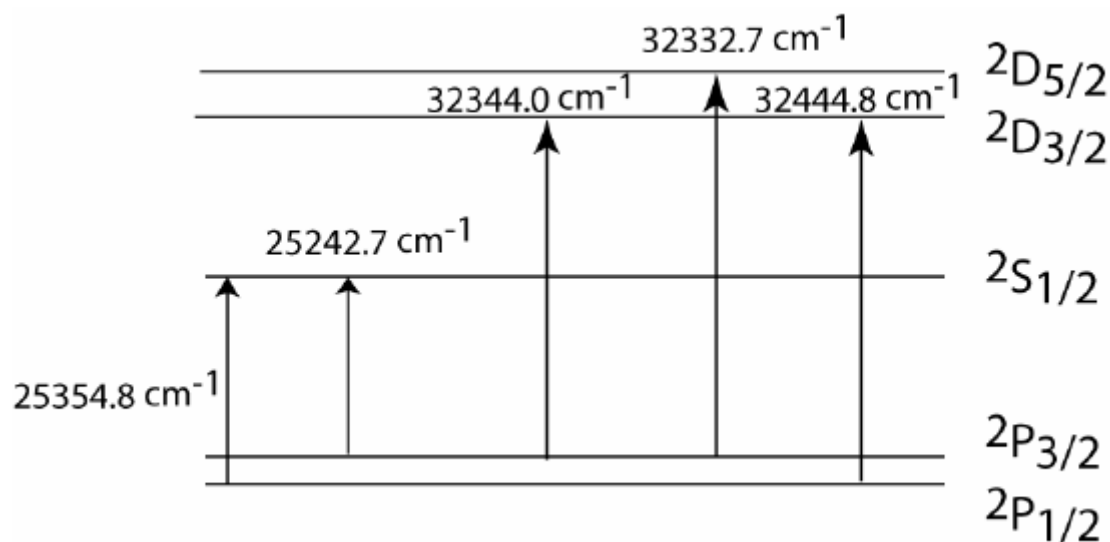


P11.14

The $\text{Al}[\text{Ne}](3s)^2(4s)^1$ configuration corresponds to a $^2S_{1/2}$ state. The $\text{Al}[\text{Ne}](3s)^2(3p)^1$ configuration contains two levels, $^2P_{1/2}$ and $^2P_{3/2}$. The $\text{Al}[\text{Ne}](3s)^2(3d)^1$ configuration contains two levels, $^2D_{3/2}$ and $^2D_{5/2}$. The relative order of these levels is $^2P_{1/2} < ^2P_{3/2} < ^2S_{1/2} < ^2D_{3/2} < ^2D_{5/2}$. In each case, the level with the smaller J value has the lower energy. The levels are sketched below (not to scale). With the information given, the most energetic transition must be $^2P_{3/2} \rightarrow ^2D_{5/2}$, and the least energetic $^2P_{3/2} \rightarrow ^2S_{1/2}$. The rest of the transitions can be assigned on the basis of the level spacings.

**Q12.1**

Atoms are much more massive than electrons. Therefore, the vibrational period (inverse frequency) of a molecule is significantly longer than the relaxation time needed for the much less massive electrons to adjust to the periodic changes in the nuclear positions. For this reason, the nuclear motion can be decoupled from the electron motion.

Q12.5

Imagine an undisturbed hydrogen atom separated from a bare proton by the distance R .

The energy of the total system is the energy of the atom, E_{1s} , plus the interaction energy between the two nuclei, $\frac{e^2}{4\pi\epsilon_0 R}$ and the energy of the electron on the H

atom interacting with the bare proton. Treating the electron as a diffuse electron charge, the last term is J . The sum of these three terms is H_{aa} .

Q12.7

ΔE_g and ΔE_u have the same expressions in the numerator. However, ΔE_g has $1 + S_{ab}$ in the denominator, whereas ΔE_u has $1 - S_{ab}$ in the denominator. Because $S_{ab} > 0$, $1 + S_{ab} > 1$, and $1 - S_{ab} < 1$. Therefore, $\Delta E_u > \Delta E_g$.

Q12.11

A molecular orbital is a one electron wave function that is delocalized over the whole molecule. A molecular wave function is an n electron wave function that is delocalized over the whole molecule.

Q12.12

a)

The amplitude of the wave function and therefore the probability density falls off as the distance from the nuclei increases. Therefore, contours of higher electron density lie closer to the molecule and will appear smaller in a contour plot.

b)

The neck shows that the electron density in the bonding region is smaller than the electron density near the nuclei.

c)

This image shows the distortion of the electron density from a spherically symmetric shape at a density greater than that found in the bonding region. It corresponds to one of the contours close to the nucleus in the image for the bonding MO in Figure 12.9. The same information is contained in Figure 12.8 where it is seen that for a given distance from a proton, the probability density is higher on the side of the proton towards the bond than on the side of the proton corresponding to the outside of the molecule.

d)

The density lies between 0.25 and 0.30 electrons/ a_0^3 because the neck is still visible at 0.25 electrons/ a_0^3 , but not at 0.30 electrons/ a_0^3 .