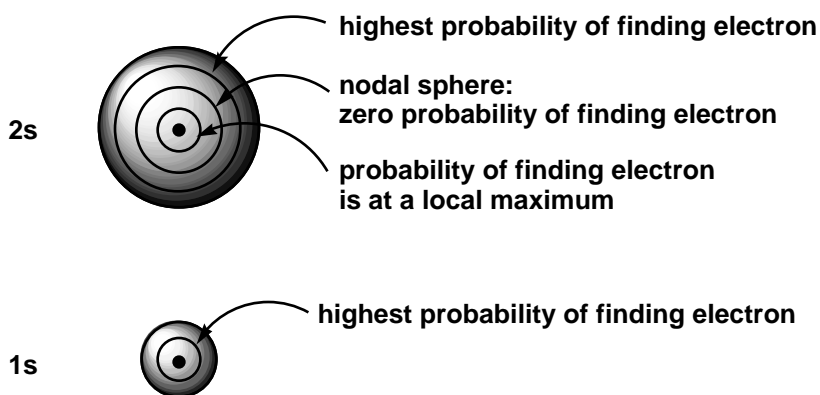
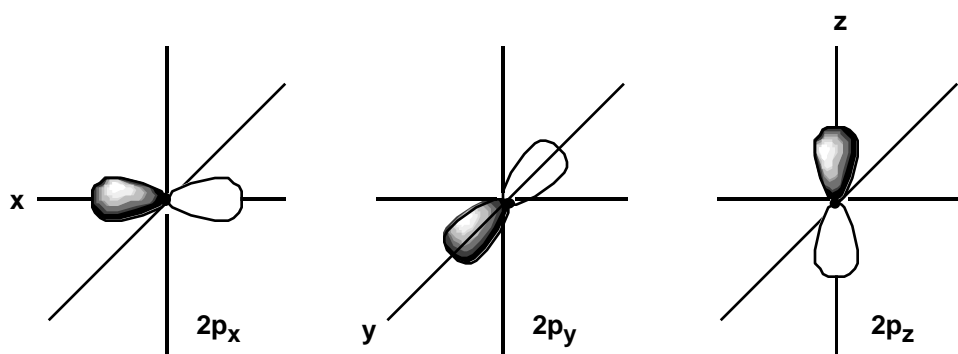


**Addendum**

The ideas just delineated can be extended nicely to rationalize the bonding in the important diatomic molecules of the second row of the periodic table — molecular nitrogen, molecular oxygen, and molecular fluorine — as well as the existence of neon as single atoms. In addition to the underlying 1s orbital, the atomic orbitals for this row (those having principle quantum number 2) are as follows:

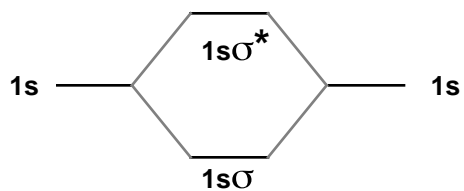
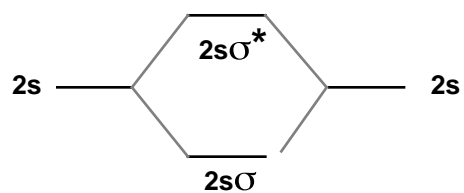
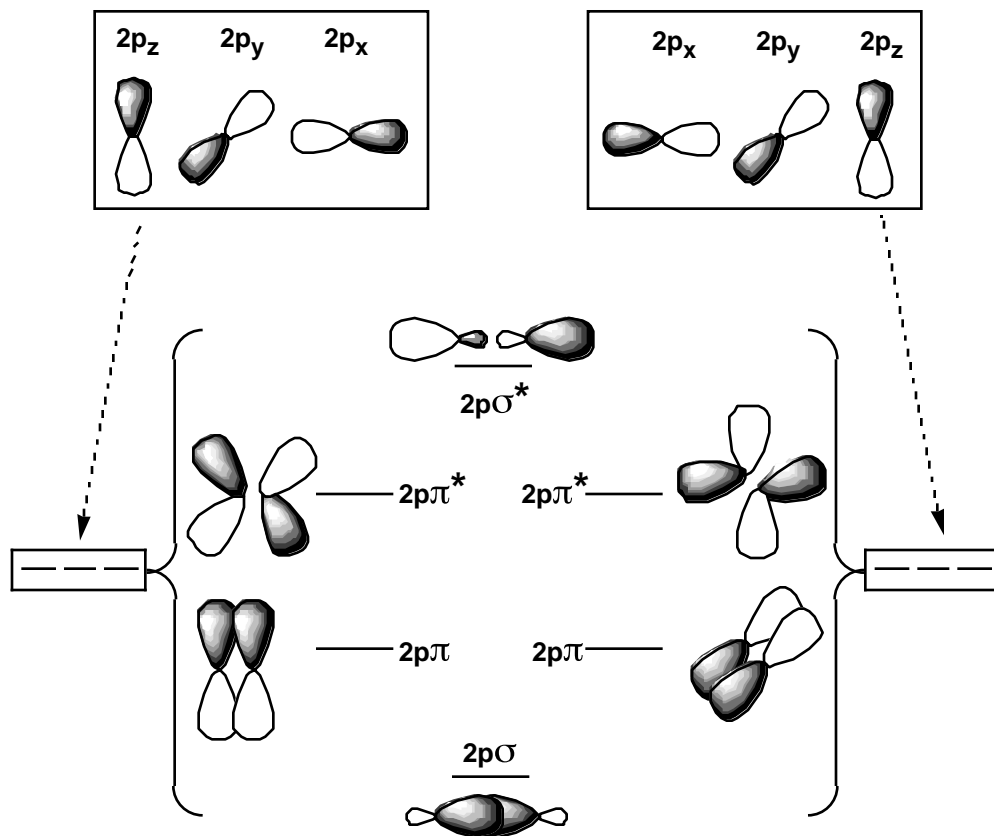


**atomic orbitals for second row elements**

The 2s orbital is spherical. Then, lying at somewhat higher energy, there are three 2p orbitals of elongated form, oriented along orthogonal axes. All of these orbitals have one node. (Remember what this says about their energy relative to the 1s orbital, which has no node.) The node in the 2s orbital is in the form of a nodal

sphere where there is effectively zero probability of finding an electron, on either side of which the probability rises. The nodes in the 2p orbitals are more easily depicted. Again, they represent points of effectively zero probability of finding an electron, where there is a phase change.

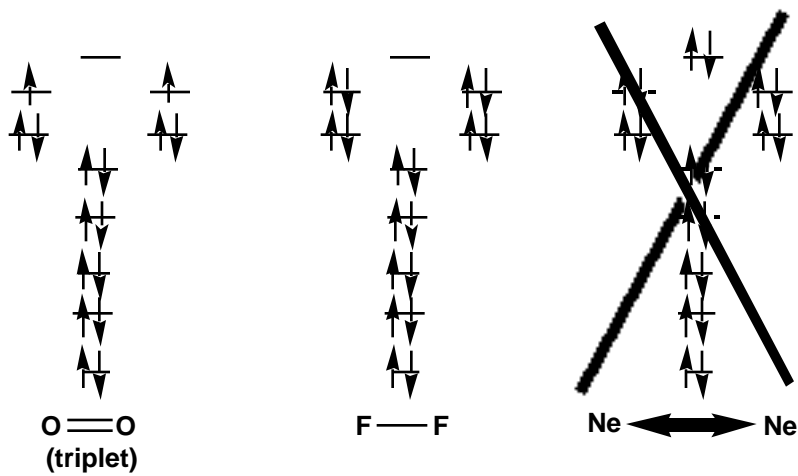
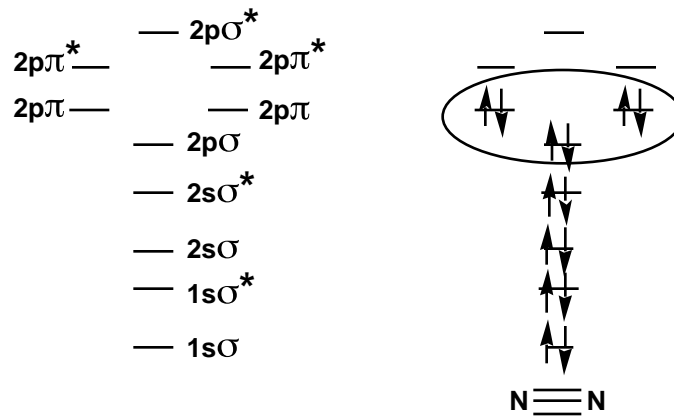
Consider now what happens when two sets of atomic orbitals for the second row elements are brought together and mixed. The two 1s orbitals once again mix to give  $1s$  and  $1s^*$  orbitals. Likewise, the two 2s orbitals mix to give  $2s$  and  $2s^*$ . From the six 2p atomic orbitals we make six new delocalized molecular orbitals. Imagine bringing together the two arrays of  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbitals along the x-axis. By mixing the  $2p_x$  orbitals in end-on fashion, in-phase and out-of-phase, with the same axial symmetry of overlap that yields  $1s$  and  $2s$  from 1s and 2s orbitals, we produce  $2p$  (bonding) and  $2p^*$  (antibonding) molecular orbitals. Note, now, that the two sets of  $2p_y$  and  $2p_z$  orbitals have been brought together edge-on. Again, these can be mixed in-phase and out-of-phase to yield molecular orbitals having lateral symmetry, different from the axial symmetry of the orbitals, and called  $2p$  (bonding) and  $2p^*$  (antibonding). There are two sets of each, perpendicular to one another, reflecting the orthogonality of the original p orbitals:



**construction of orbitals for second row diatomic molecules from atomic orbitals for second row elements**

As before, we are now in a position to fill these orbitals with electrons. Starting with molecular nitrogen we have fourteen electrons to deal with — seven

contributed by each nitrogen atom. Filling from the bottom, we arrive at the scheme shown below. Nitrogen has a triple bond, as a result of its filled  $2p$  and  $2p$  orbitals (circled). The antibonding  $2p^*$  and  $2p^*$  orbitals are left empty. Note that the low-lying  $1s$ ,  $1s^*$ ,  $2s$ , and  $2s^*$  orbitals are all filled. Here, antibonding cancels bonding; in fact, these are nonbonding lone pairs. However, the molecule is held together extremely strongly by the triple bond. Moving on in the periodic table, each oxygen atom brings with it one more electron than in nitrogen. Hence, in molecular oxygen two electrons must go into the  $2p^*$  antibonding orbitals. The net result is some loss of bonding relative to nitrogen, but molecular oxygen still has a net of four bonding electrons. According to Hund's Rule, the two antibonding electrons are placed separately, in the energetically degenerate  $2p^*$  orbitals. In fact, oxygen behaves in a manner characteristic of molecules having two unshared electrons, called diradicals. Proceeding to molecular fluorine, both of the  $2p^*$  orbitals now must be filled completely; there is only one net filled bonding orbital remaining, effectively the  $2p$ . Finally, with neon we reach again the circumstance where, because all of the orbitals must be filled, a net bonding gain no longer exists; instead, electron repulsion takes its toll, and neon, like helium, occurs in nature as single atoms:



electron filling of orbitals for second row diatomic molecules