Answers to Exercise 5.1
Band Theory: An Extension of Molecular Orbital Theory

1.

(a) The band theory term that is equivalent to **molecular orbital** is **state**. These two terms are equivalent because they both describe the wavefunction of an electron in a species with multiple electrons, and they are both made by linear combination of atomic orbitals. In both cases, the wavefunction may be delocalized over all the atoms. In the case of an MO, the electrons are delocalized over a molecule. For a state in a solid, the electrons are delocalized over the entire crystal.

(b) The band theory term that is equivalent to **HOMO** is **Fermi level**. In both cases, the concept described is the highest orbital/state occupied by electrons in the ground state of the molecule/solid. There are some slight differences in usage between these terms. The HOMO is an orbital, i.e. a wavefunction. The Fermi level is usually understood to denote the energy of the highest occupied state rather than the state itself.

Because each wavefunction/state is associated with an energy, the last distinction is a bit picky.

2. A band is a collection of states* that are extremely close in energy.

When a set of atomic orbitals of a solid (metal, semiconductor or insulator) combine to make a set of states, a large number of states are formed with very similar energies. These states behave as a continuum, so they are collectively called a band.

A solid may contain more than one band. There will usually be core bands and bands formed from valence orbitals, e.g. the 1s core band and 2s band in lithium. As in MO theory, the core bands are of little interest for most purposes. The conduction properties of solids, for example, depend almost entirely on the bands formed from valence orbitals. Even within the valence shell, there can be multiple bands.

* *Recall that states are equivalent to molecular orbitals. A state can be considered to be a 'molecular orbital for the whole solid'.*

3. Yes and no. It is of course possible to talk about the lowest energy unoccupied state when the material is in its ground state. That state would be the LUMO.

In metals, the LUMO would have essentially the same energy as the HOMO since the states are so close together.

In semiconductors and insulators, the HOMO is the top of the valence band, and the LUMO is the bottom of the conduction band. Indirectly then, the LUMO is discussed when we bring up the band gap, which is the difference in energy between the HOMO and LUMO.