Chapter 2

ENERGY BANDS AND BULK REFERENCES OF CRYSTALLINE SOLIDS

The alignment of energy bands at solid interfaces is of primary interest in this book. For small molecules in Chapter 1, the alignment of energy levels has been shown to be conveniently analyzed through the host–bath approach. For crystalline solids, the energy bands are their energy levels. Therefore, the alignment of energy bands at a solid interface can also be understood and analyzed through the same approach. A slight complication for the solid interfaces arises from the need to identify the hosts to represent the two crystals. While the definition of the host is unmistakable for small molecules before, there is some ambiguity and freedom in choosing the host for a solid. The formation of energy bands for a crystalline solid and available choices to select "model solid" as the host of the energy bands are discussed in this chapter. The extra step taken to employ a model solid allows the energy bands of a crystal to be referenced to the vacuum level, similar to the energy levels of an isolated molecule in Chapter 1. With the energy band positions of both crystals of an interface known with respect to the vacuum level, how they are aligned can be analyzed the same way as for the molecules. As is the case for molecules, the bath, which is the charge distribution of the interface after the removal of the two hosts, plays a crucial role in deciding the alignment condition.

2.1 Energy Bands of Crystalline Solids

In principle, all properties of an electronic system can be extracted from its wave function, which may be obtained through the Schrödinger equation. For a finite system such as a molecule, this process is straightforward, as described in Chapter 1. The same approach becomes impractical for solids, as the number of atoms in a solid is essentially infinite. Fortunately, the