

bands about 2 eV below the Fermi surface and about 2 eV in width, while the 4s electron lies mainly in a band extending from about 10 eV below the Fermi surface to several electron volts above. The *s* and *d* bands hybridize together in the energy range where they intersect. Two calculations of the copper bands are displayed: LMTO and plane wave. The two agree in all essential respects. Optical experiments are in good accord with the prediction that an energy of around 2eV is needed to excite electrons from states at the top of the *d* band to states in the *s* band at the Fermi surface. The LMTO calculations are more rapid than the plane wave calculations, but cannot reliably be employed for complicated non-symmetrical unit cells where the plane wave method remains accurate.

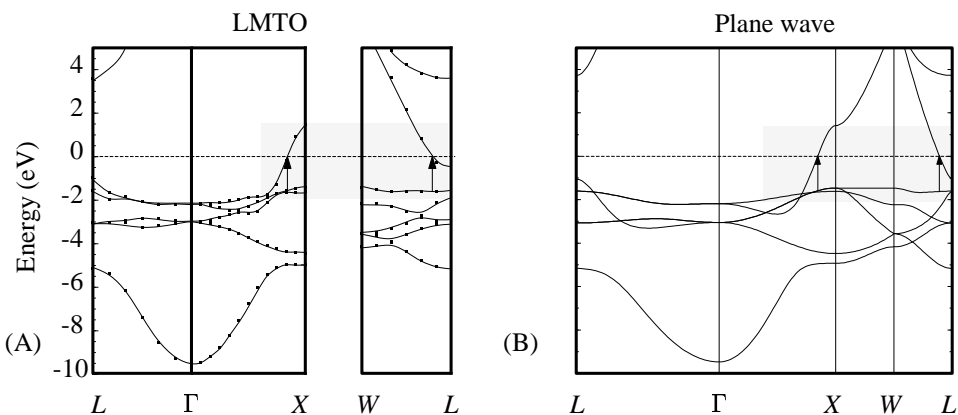


Figure 10.8. (A) Energy bands of copper, as calculated with the LMTO code of Skriver (1984). The calculation assumes that copper adopts the fcc structure, with a lattice constant of 3.61 Å, and also begins with information describing the electron density, so that all that remains to be done is to find energy bands in the presence of a known potential. This calculation is around 10 times faster than the calculation for copper with plane waves. Light absorption is dominated by the transition indicated by arrows in the gray box; the prediction that absorption sets in at around 2 eV is in reasonable agreement with data in Figure 23.8. (B) Energy bands of copper, as calculated with the plane-wave pseudopotential code VASP of Kresse and Hafner (1994) and Kresse and Furthmüller (1996). The calculation assumes that copper adopts the fcc structure, with a lattice constant of 3.61 Å. Not only the outer *s* electron but also 10 *d* electrons must be treated by the calculation. The 3*d* electrons are at a characteristic distance of less than 1 Å from the nucleus, and approximately 1000 plane waves are needed to capture simultaneously the extended *s* electron and tightly bound *d* electrons. This calculation has no adjustable parameters and would be preferred to LMTO if the two differed; the two agree in all important respects.

The elements of the second and twelfth columns of the periodic table could in principle be insulators, because from an atomic perspective, all electrons lie in closed shells, just having filled an *s* level. However, both band calculations and experiment agree that these elements form metals, in rough accord with the nearly free electron point of view. Instead of contracting to hug the Brillouin zone, the Fermi surface crosses in and out of it, leading in all cases to a metal. The elements of cubic symmetry (Ca, Sr, Ba) have two electrons per unit cell and are described by the second columns of Figures. 8.5 and 8.6. The elements with the hcp structure