Heterojunctions are at the heart of many modern semiconductor devices with tremendous societal impact: Light‐emitting diodes shape the future of energy‐efficient lighting, solar cells are promising for renewable energy, and photoelectrochemistry seeks to optimize efficiency of the water‐splitting reaction. Design of heterojunctions is difficult due to the limited number of materials for which band alignment is known, and the experimental and computational difficulties associated with obtaining this data. Band alignment based on branch‐point energies (EBP) is shown to be a good and efficient approximation that can be obtained using data from existing electronic‐structure databases. Errors associated with this approach are comparable to those of expensive first‐principles computational techniques and experiments. EBP alignment is then incorporated into a framework capable of rapidly screening existing online databases to design semiconductor heterojunctions. The method is showcased for five different prototype cases: Transport layers are successfully predicted for CdSe‐ and InP‐based LEDs, and for CH3NH3PbI3‐ and nanoparticle PbS‐based solar absorbers. In addition, Cu2O as a possible hole‐transport layer for solar cells is examined. The framework addresses the challenge of accomplishing fast materials selection for heterostructure design by tying together first‐principles calculations and existing online materials databases.