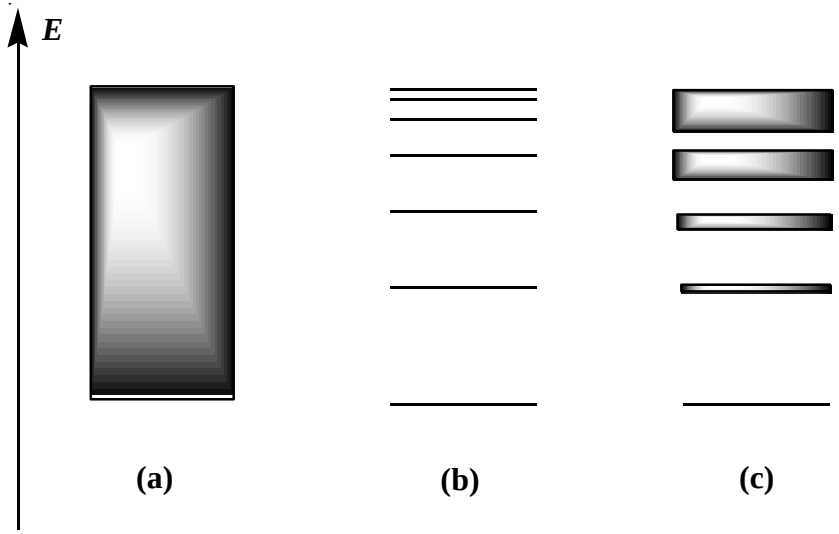


Energy states of an electron in (a) free space (b) a box (c) periodic lattice

Figure 3.1 Schematic representations of electron energy levels/states in (a) electron in free space; (b) electron in a confined box; (c) electron in a periodic (such as crystalline) lattice.

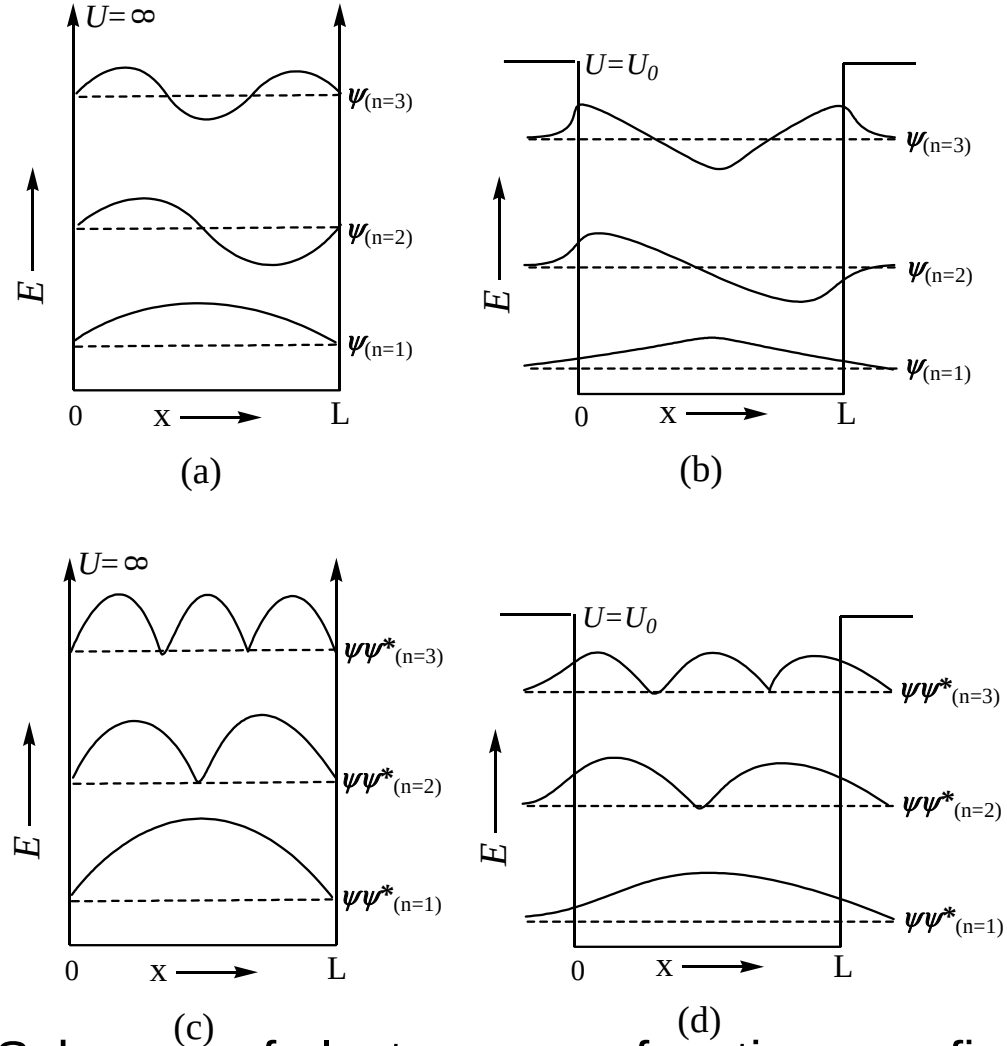


Figure 3.2 Schemes of electron wave functions confined in a 1-D size *L* potential well with (a) infinite height potential walls, and (b) finite height potential walls. Schemes of electron probability densities confined in a 1-D size *L* potential well with (c) infinite height potential walls and (d) finite height potential walls.

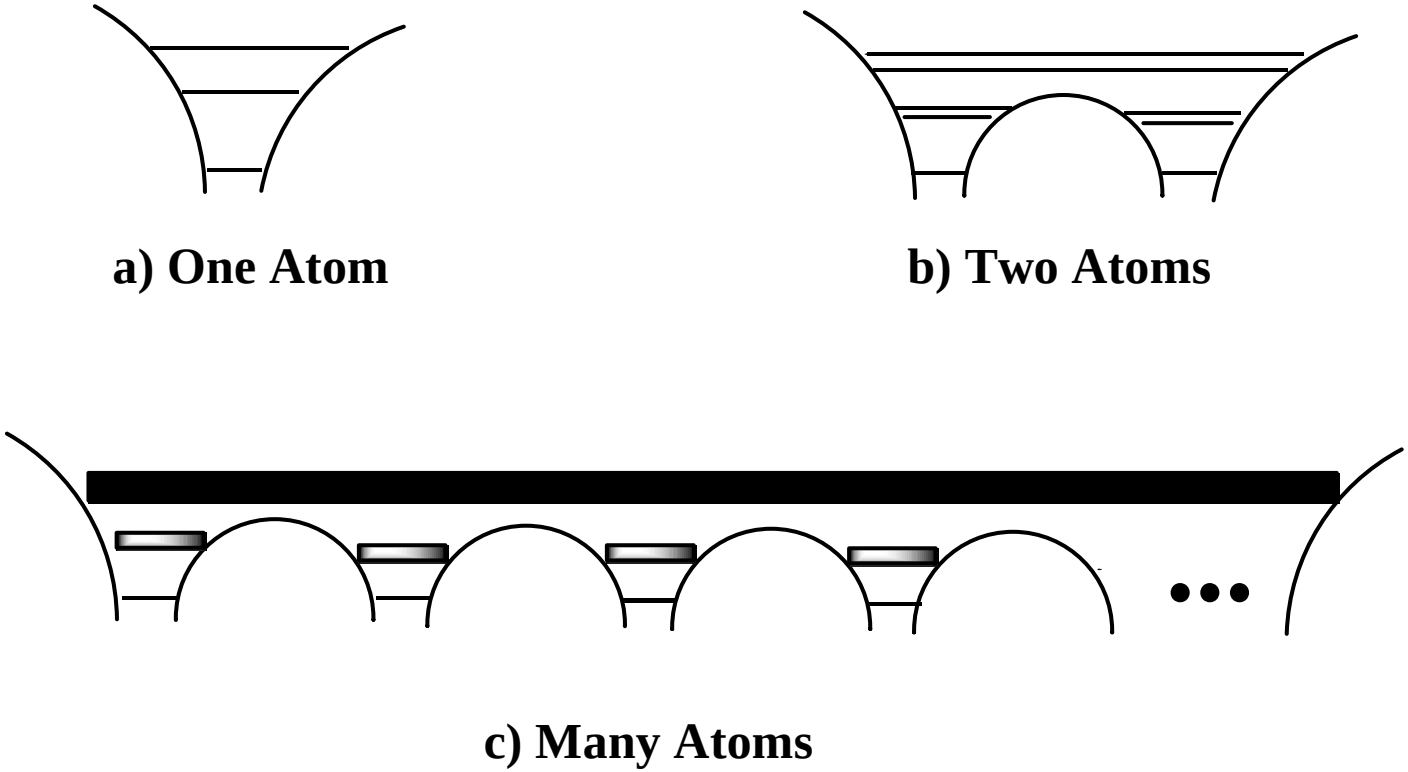


Figure 3.3 Schematic representations of atomic electronic potential surfaces and electron orbital levels in (a) a single atom; (b) two-atom molecule; (c) a many-atom periodic (such as crystalline) structure.

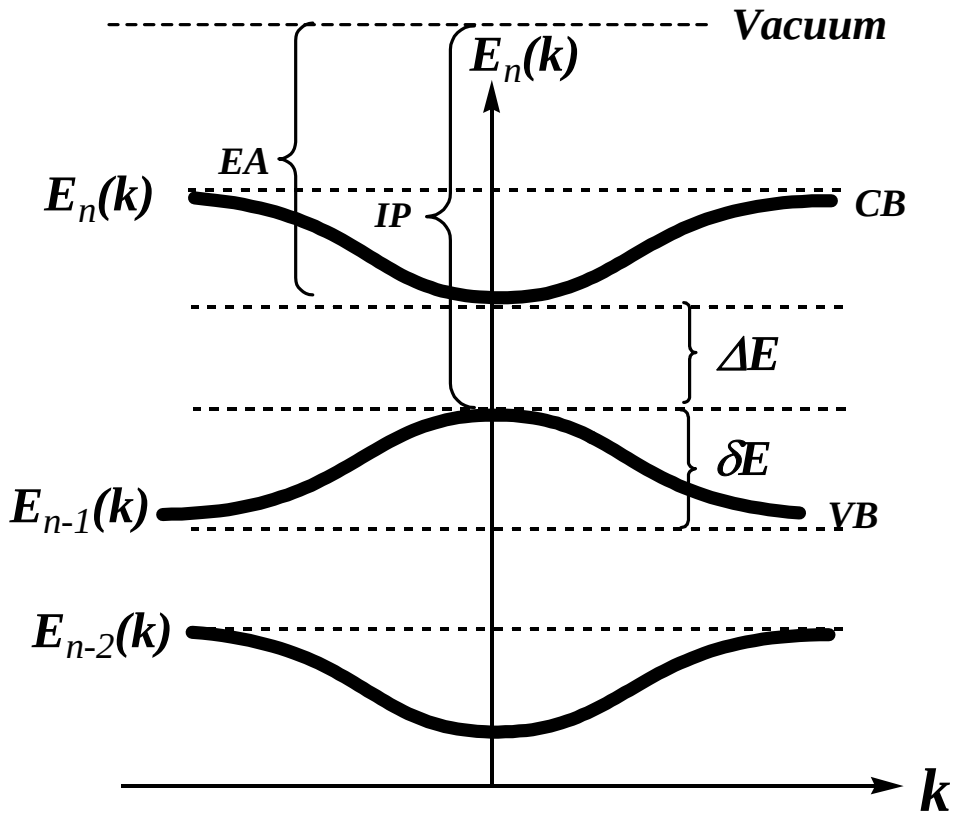


Figure 3.4 Schematic representations of electron energy $E_n(\boldsymbol{k})$ versus electron wave vector $\boldsymbol{k}$ in a periodic crystalline lattice where Bloch function is applicable. *CB* denotes conduction band, *VB* denotes valence band, *EA* denotes electron affinity, *IP* denotes ionization potential, ΔE denotes band-gap, and δE denotes band-width.

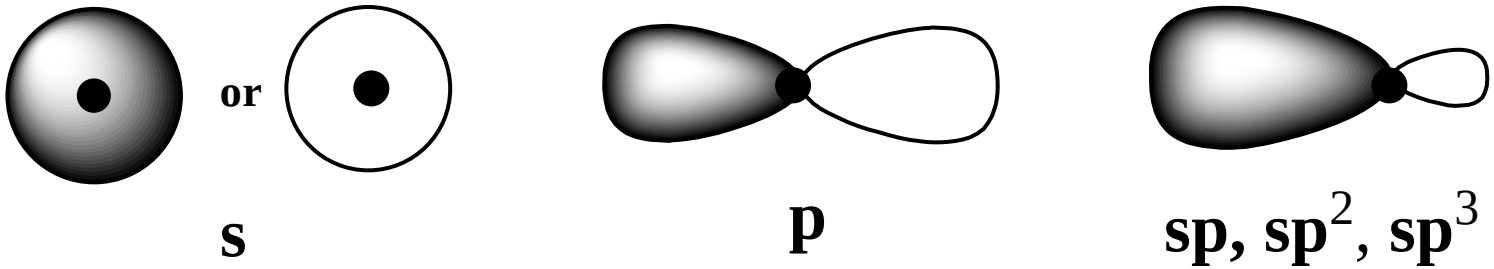


Figure 3. 5 Shapes of some representative atomic electron orbitals. The dark dot in the middle represents the nucleus. The two colors of the orbital lobes represent the positive and negative phases of the electron wave functions. The orbital shapes roughly represent the electron probability density in space.

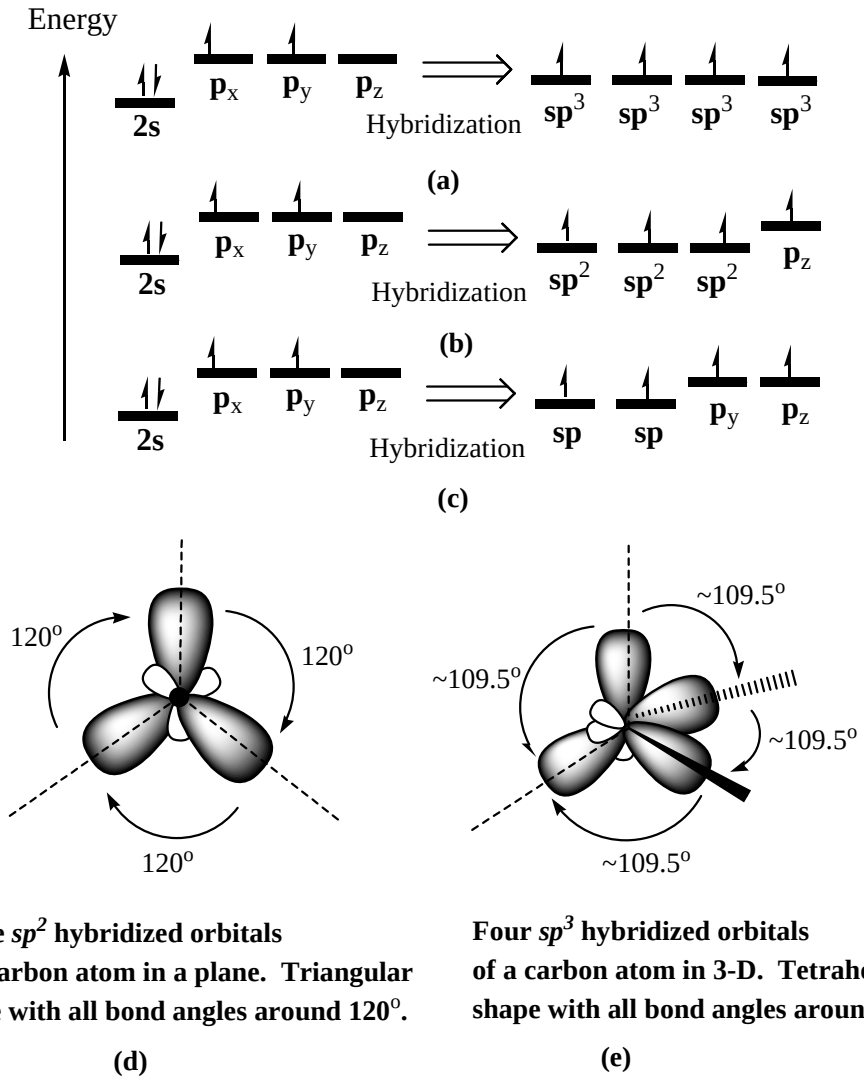


Figure 3. 6 Scheme of atomic orbital hybridizations in (a) sp^3 hybridization; (b) sp^2 hybridization; (c) sp hybridization; (d) shape of sp^2 hybridized orbitals; (e) shape of sp^3 hybridized orbitals.

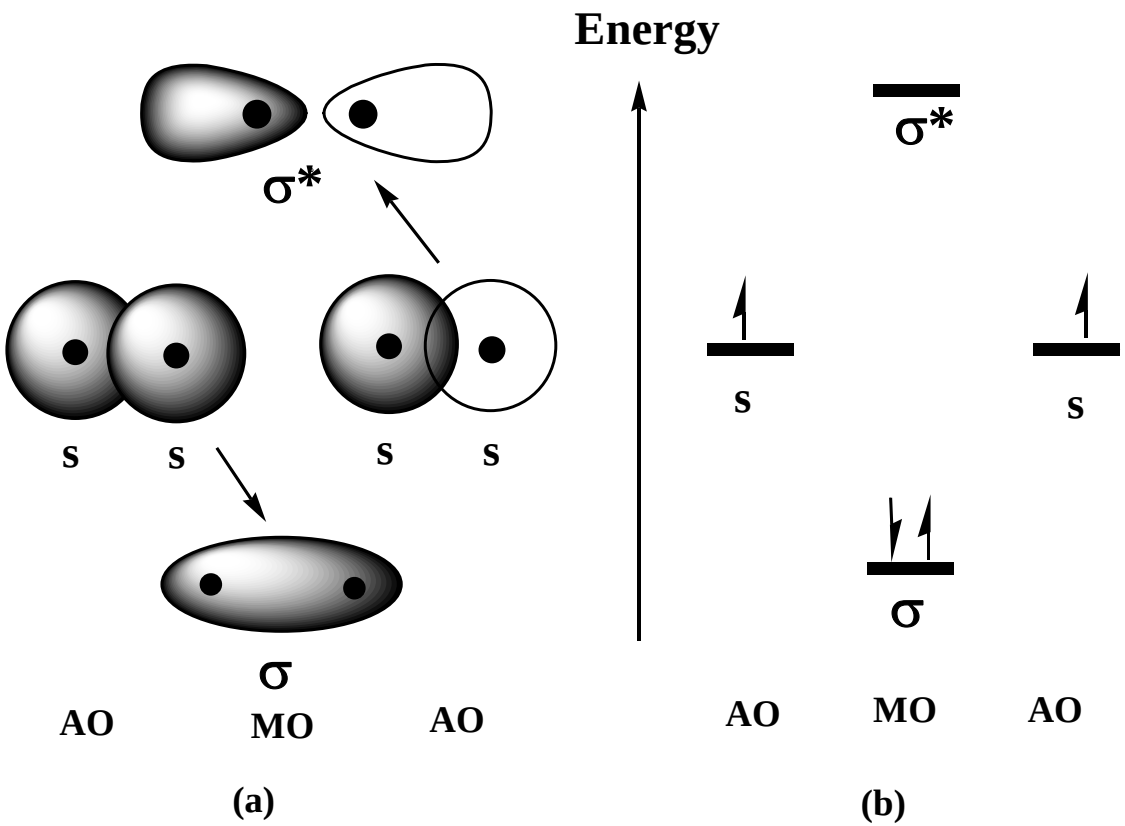


Figure 3. 7 Scheme of a pair of a σ type molecular orbitals (MOs) formed from the overlap of two s atomic orbitals (AOs) in (a) orbital shape representation and (b) orbital energy level representation.

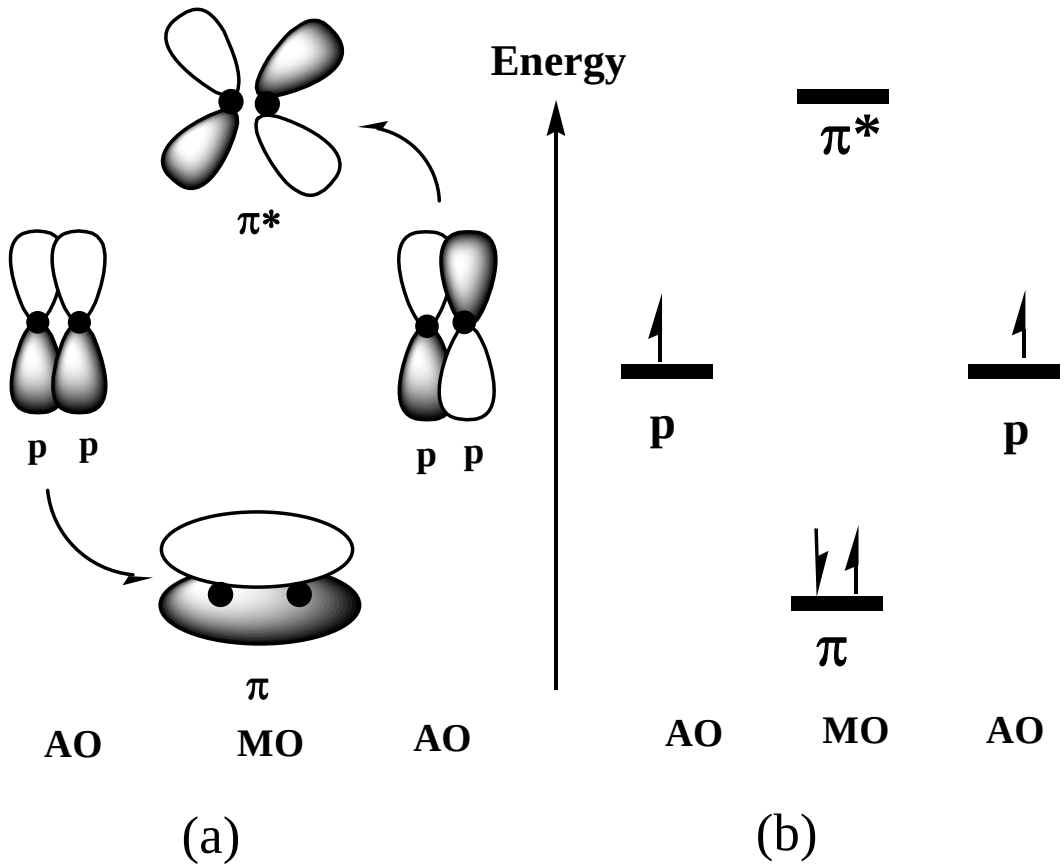


Figure 3. 8 Scheme of a pair of a π type molecular orbitals (MOs) formed from the overlap of two vertically aligned parallel p atomic orbitals (AOs) in (a) orbital shape representation and (b) orbital energy level representation.

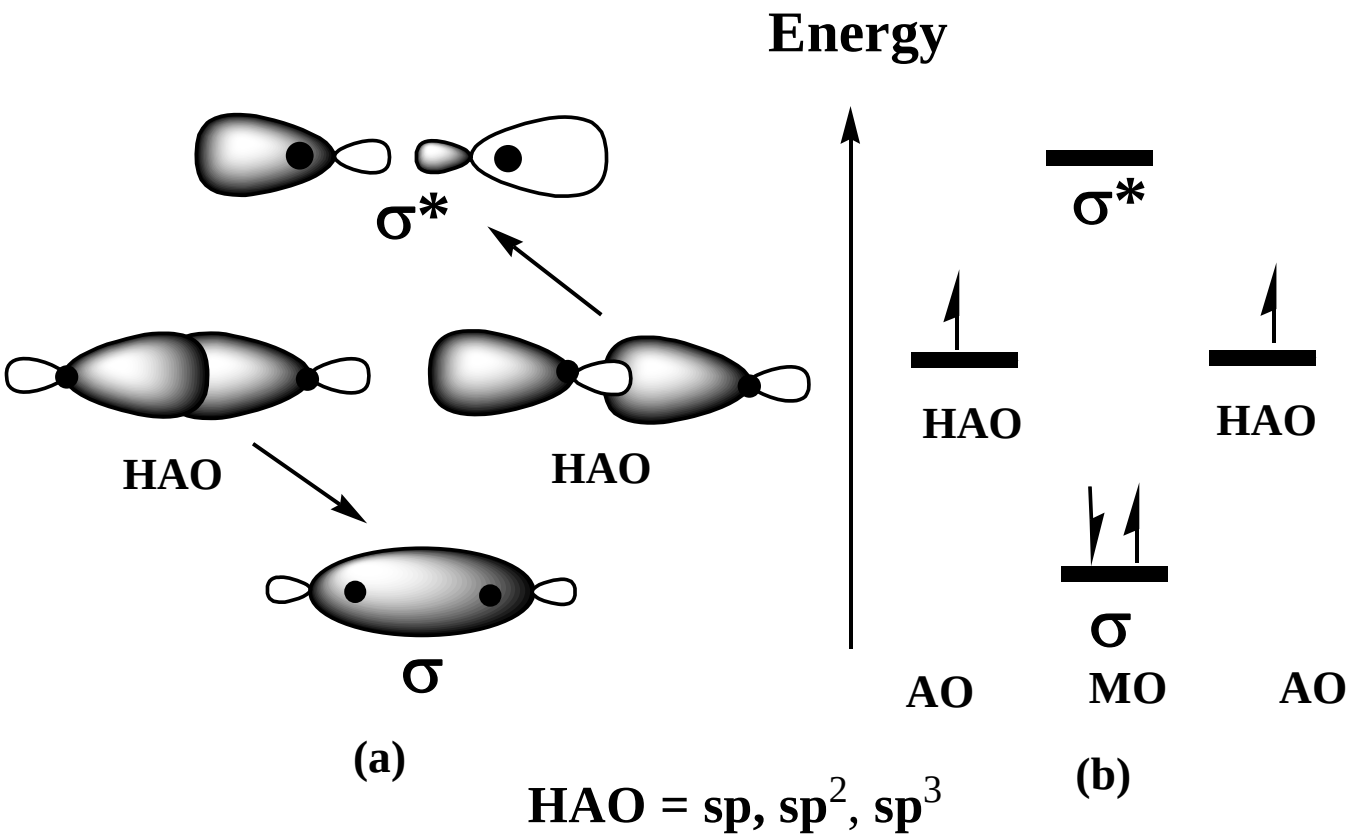
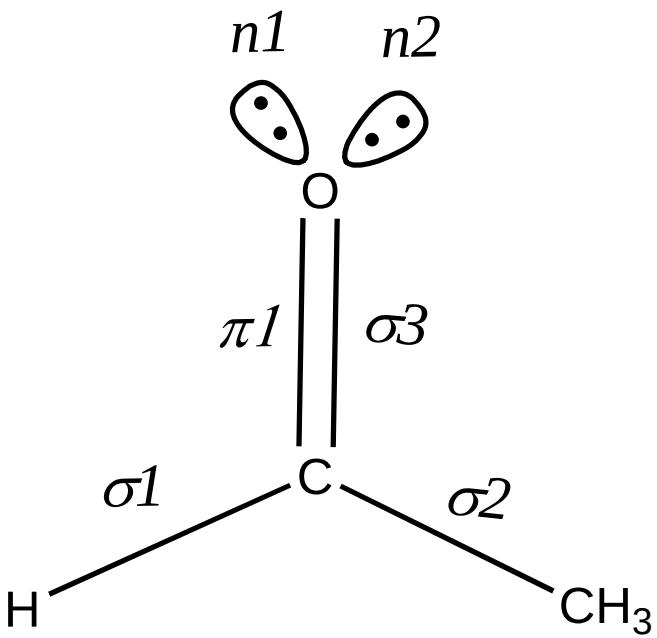
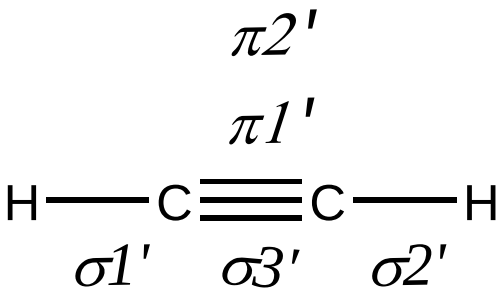


Figure 3. 9 Scheme of a pair of a σ type molecular orbitals (MOs) formed from the overlap of two horizontally aligned sp^n hybrid atomic orbitals (HAOs) in (a) orbital shape representation and (b) orbital energy level representation.

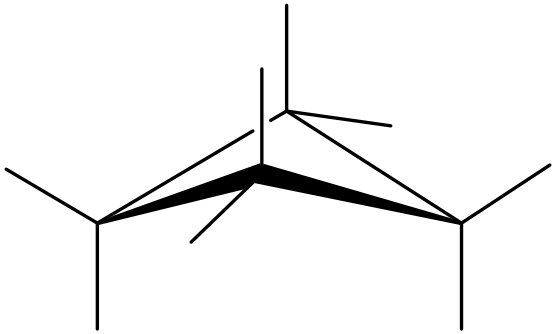


(a)

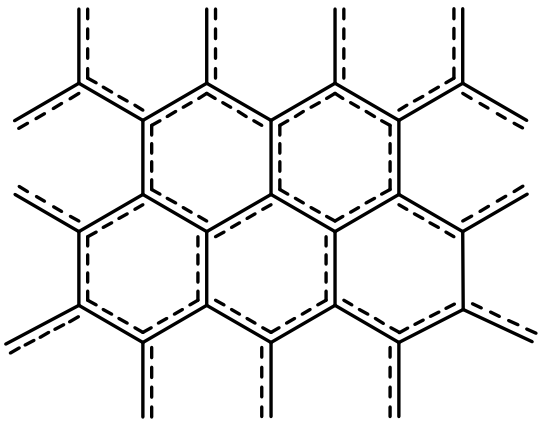


(b)

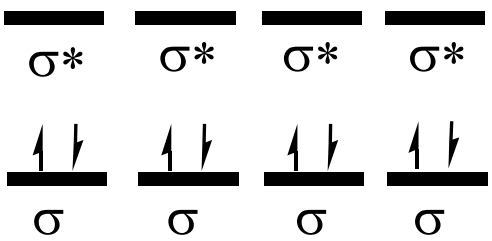
Figure 3. 10 Schematic chemical structure of (a) ethanal (ethyl aldehyde) and (b) ethyne (acetylene).



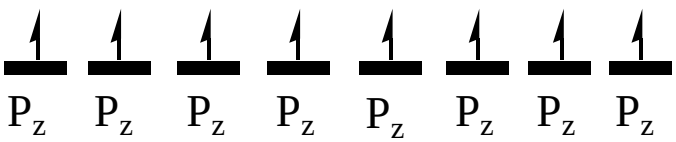
C-sp^3 + C-sp^3 --> C-C σ bonds in tetrahedral 3-D network



C-sp^2 + C-sp^2 --> C-C σ bonds in plane hexagnal style geometry. Vertical C-p_z orbitals can form a 2-D half-filled energy band



(a) Diamond



(b) Graphene/Graphite

Figure 3. 11 Schematic representations of atomic and molecular orbitals in (a) Diamond and (b) Graphene/Graphite.

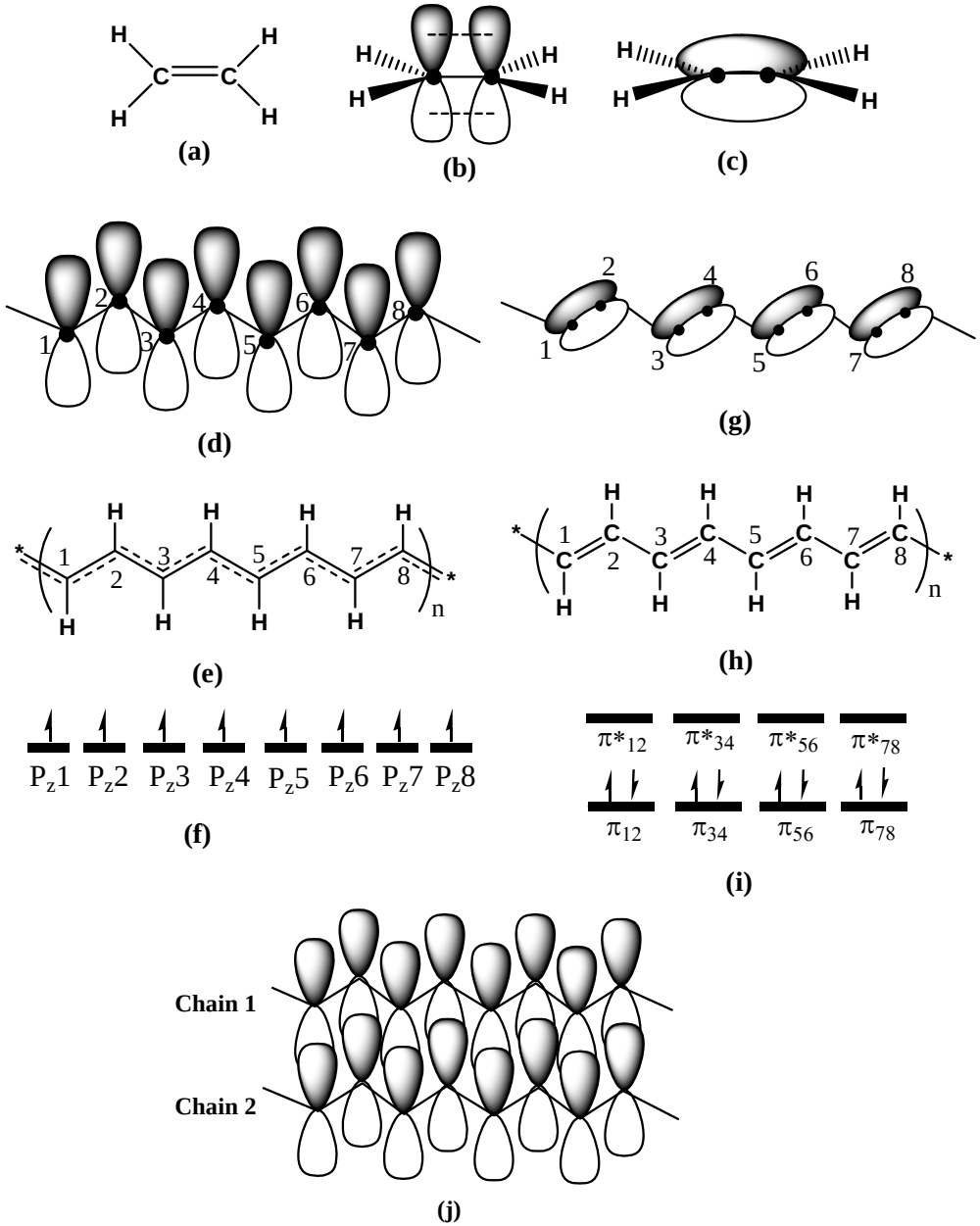


Figure 3. 12 Schematic representations of carbon-carbon double π bonds, represented in (a) chemical structure of ethene (or ethylene); (b) scheme a double bond formation by overlapping/coupling of two vertically aligned p_z orbitals at two adjacent carbon sites; (c) schematic shape of a π bonding orbital; (d) atomic p_z orbital representation of PA backbone; (e) chemical structure representation of PA assuming no 1-D Peierls distortion; (f) scheme of frontier orbitals and valence electron of PA assuming no Peierls distortion; (g) scheme of PA conjugated backbone showing π bonding orbitals; (h) chemical structure representation of PA assuming 1-D Peierls distortion applicable; (i) scheme of frontier orbitals and valence electron of PA assuming Peierls distortion; (j) atomic p_z orbital representation of two self-assembled and closely packed PA conjugated backbones.

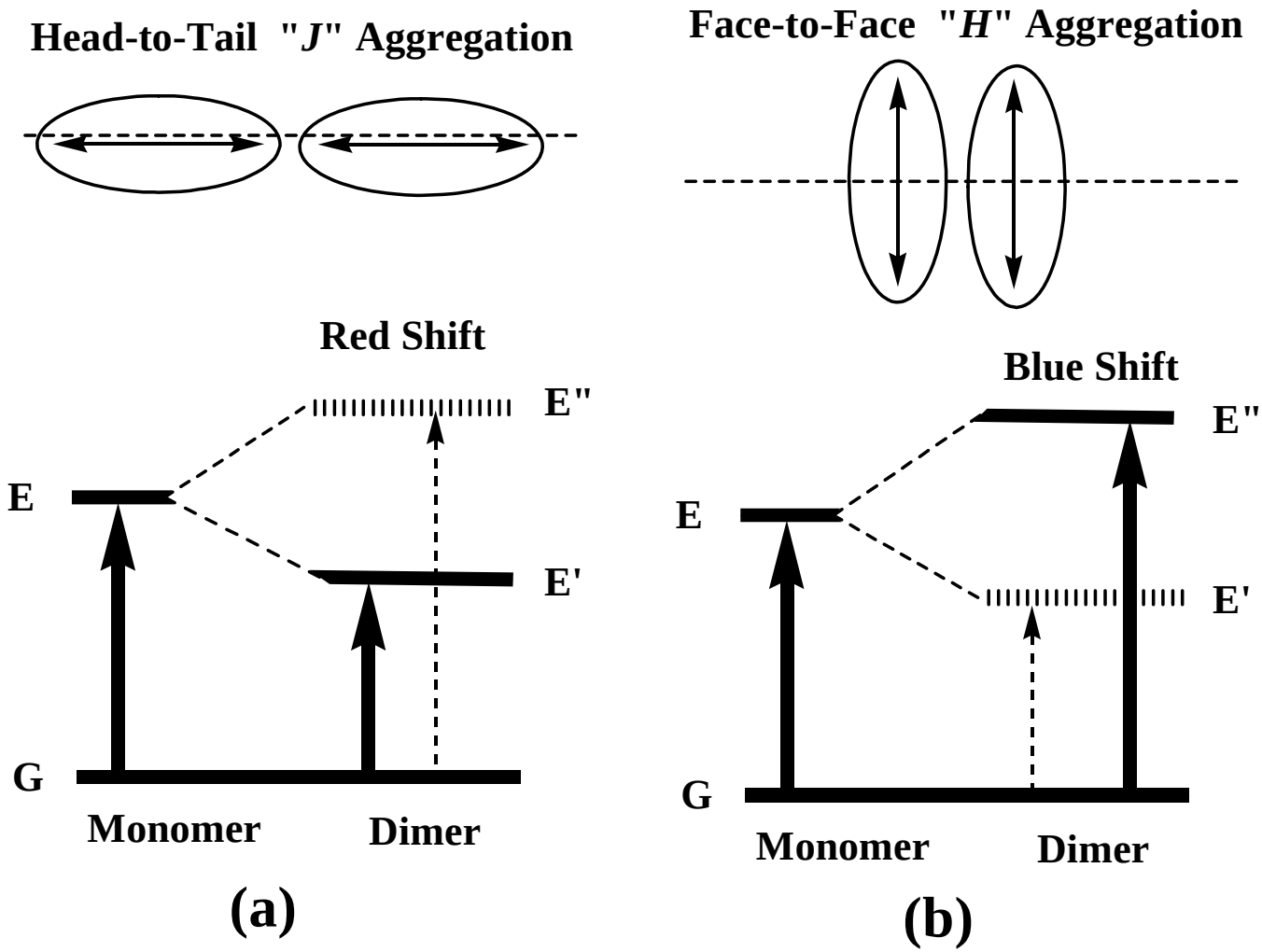


Figure 3.13 Molecular aggregates in (a) *J* type aggregates; (b) *H* type aggregates.

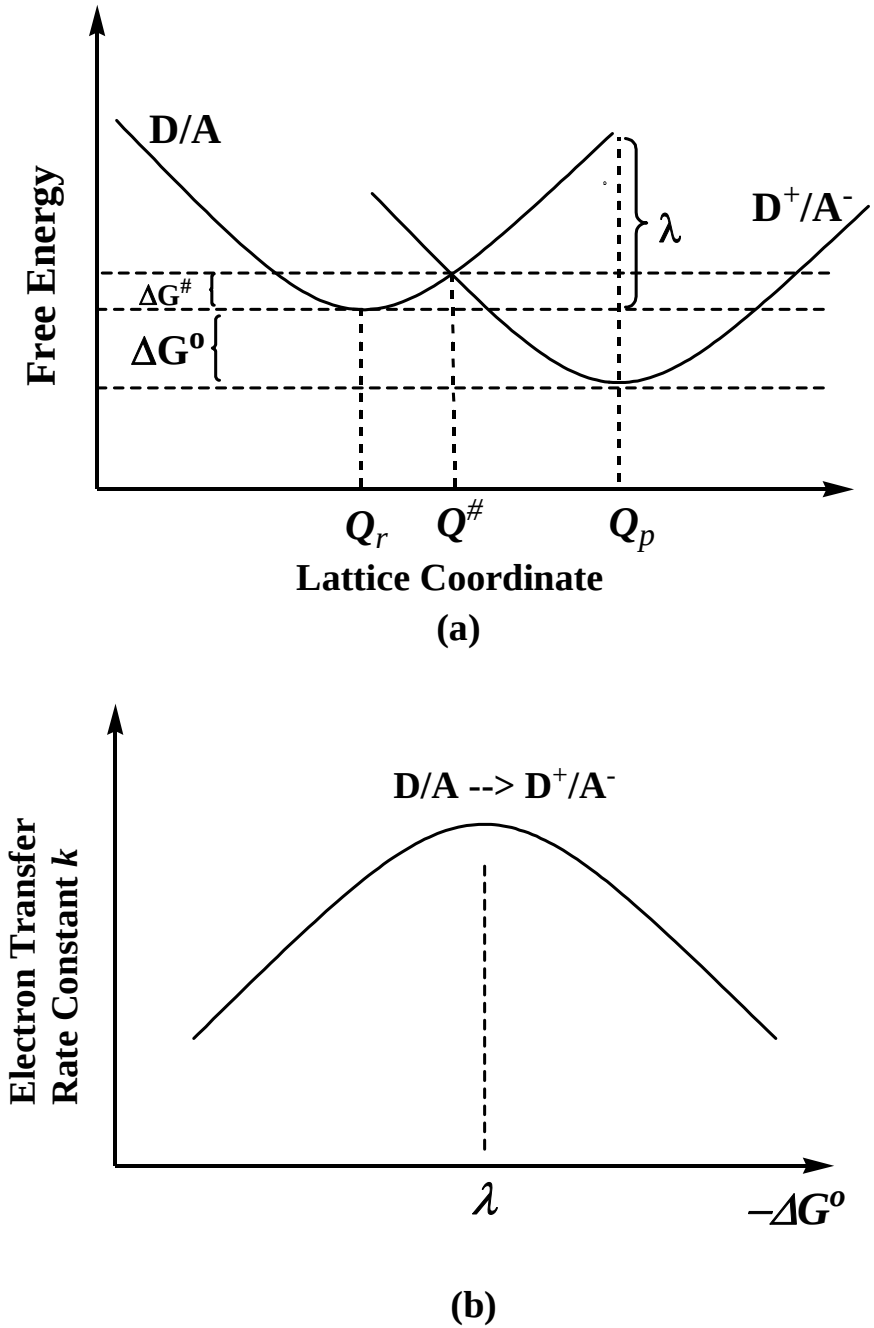
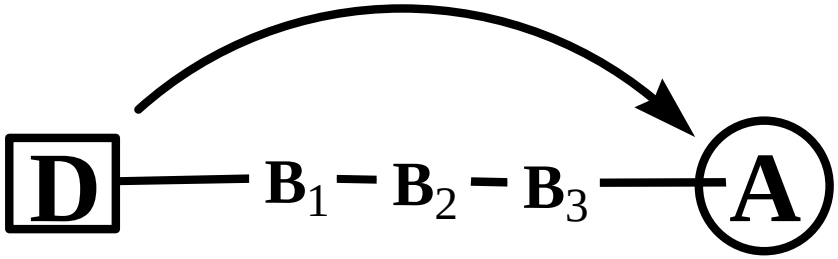


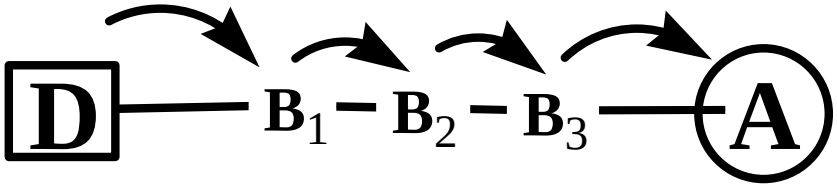
Figure 3. 14 Electron transfer from a donor to an acceptor represented by (a) free energy surface vs. lattice coordinate and (b) electron transfer rate constant vs. standard free energy change.



Superexchange: Coherent ET

$$k = k_o e^{-\beta r}$$

(a)



Hopping: Incoherent ET

$$k = k_o/r$$

(b)

Figure 3. 15 (a) Coherent electron transfer (super-exchange), and (b) incoherent electron transfer (hopping).

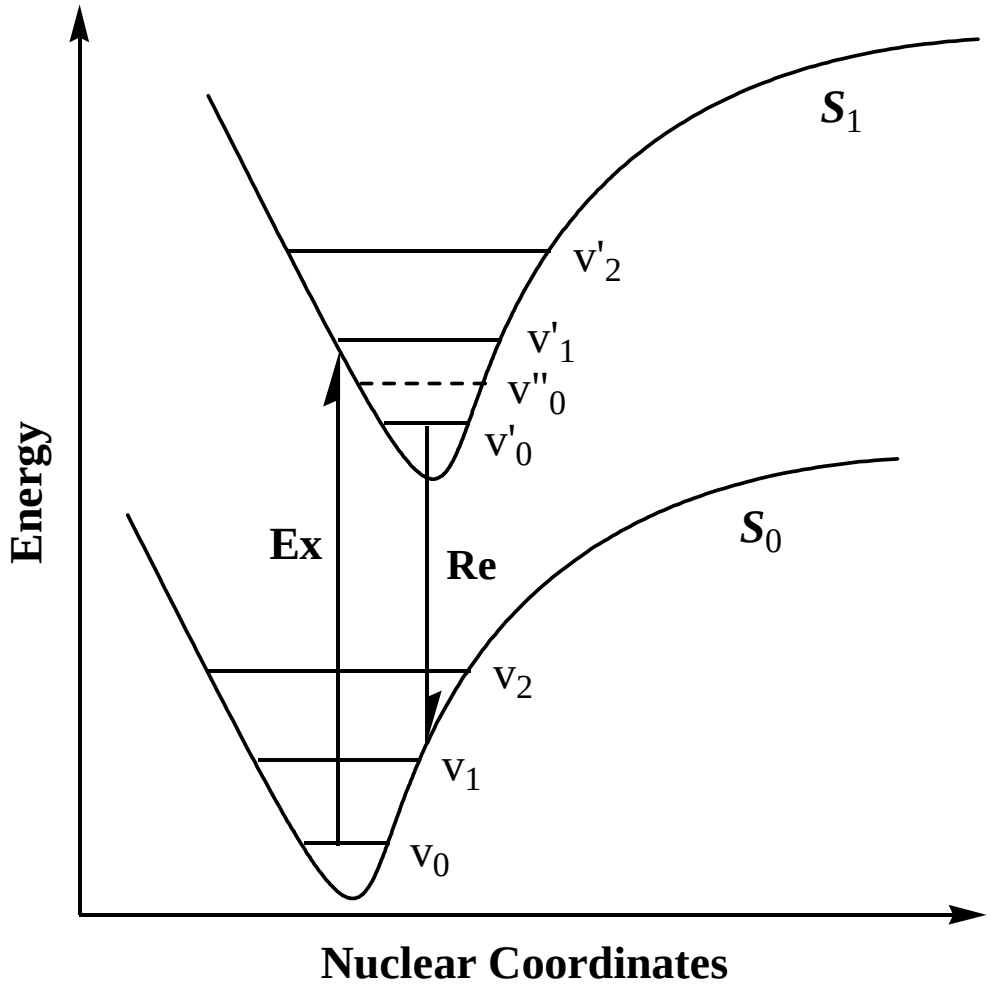


Figure 3. 16 Scheme of an idealized two-level model showing electronic excitation (Ex), recombination (or relaxation, Re), intra-molecular vibrational modes (v_n and v'_n) and an inter-molecular or aggregate vibrational mode (v''_0).

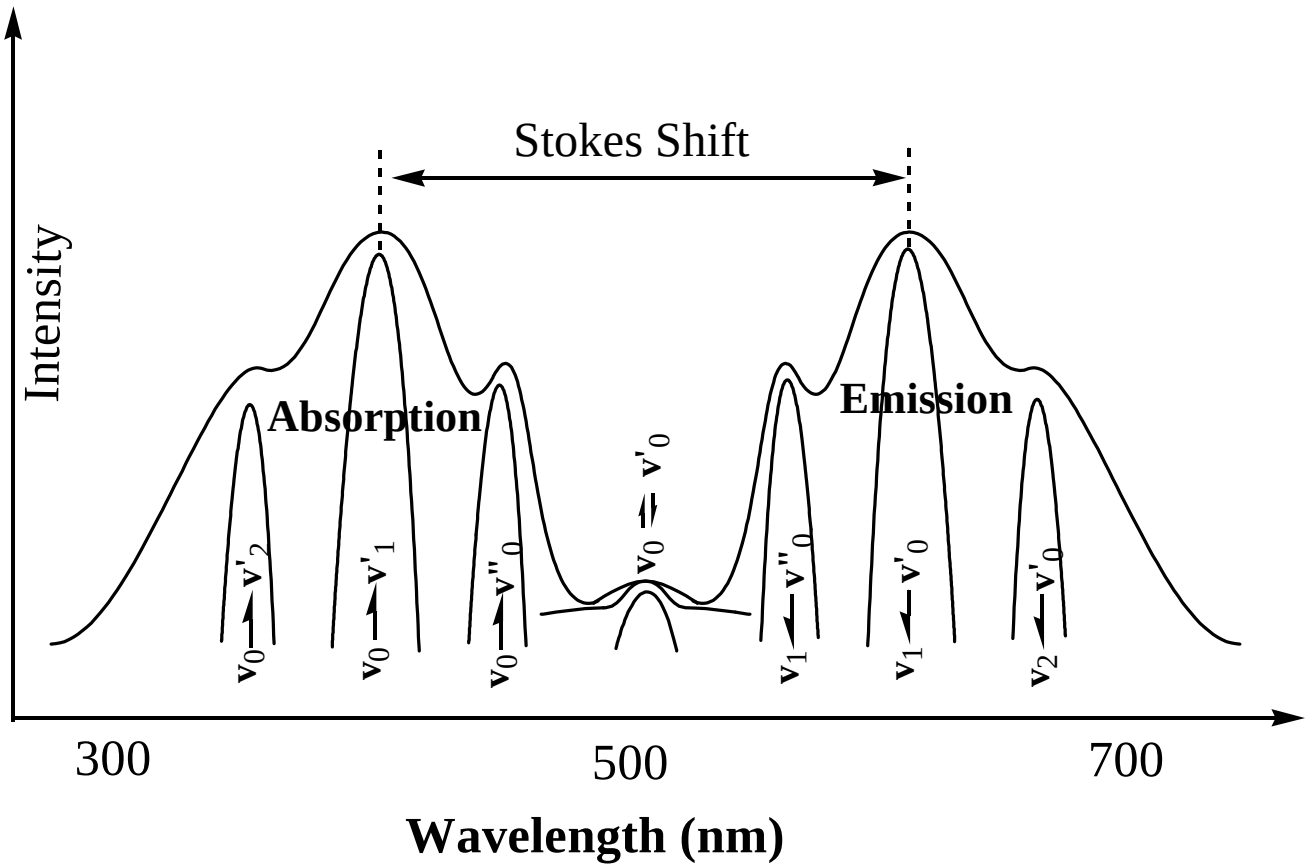


Figure 3. 17 Scheme of idealized optical absorption and fluorescence emission bands of a two level model, where the sharp component peaks due to intra- or inter-molecular vibrational modes are also indicated. For instance, $v_0 \rightarrow v'_1$ denotes an excitation transition from v_0 level to v'_1 level shown in FIGURE 3.16.

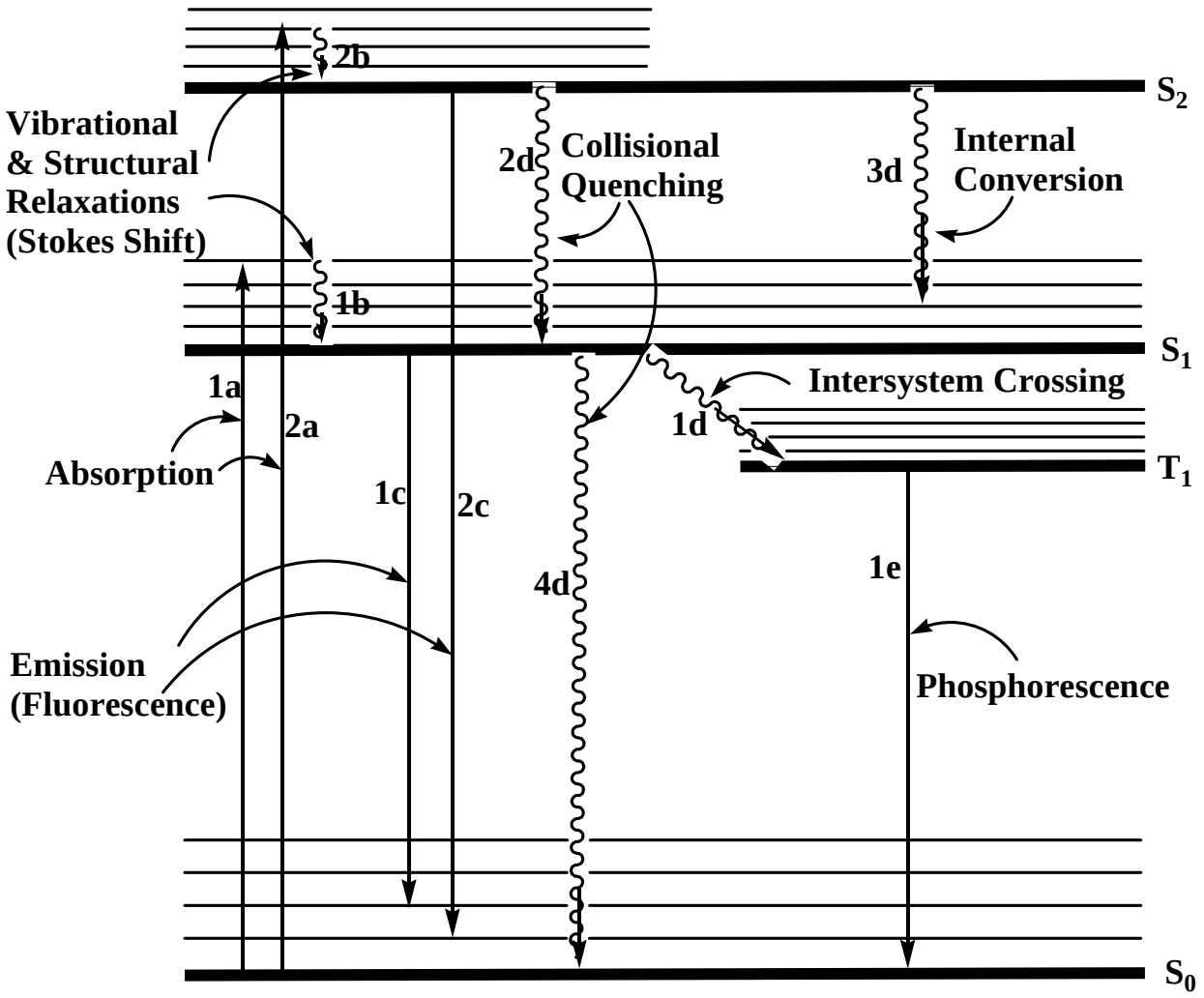


Figure 3. 18 Jablonski's diagram depicting major transitions of a material in energy regime.

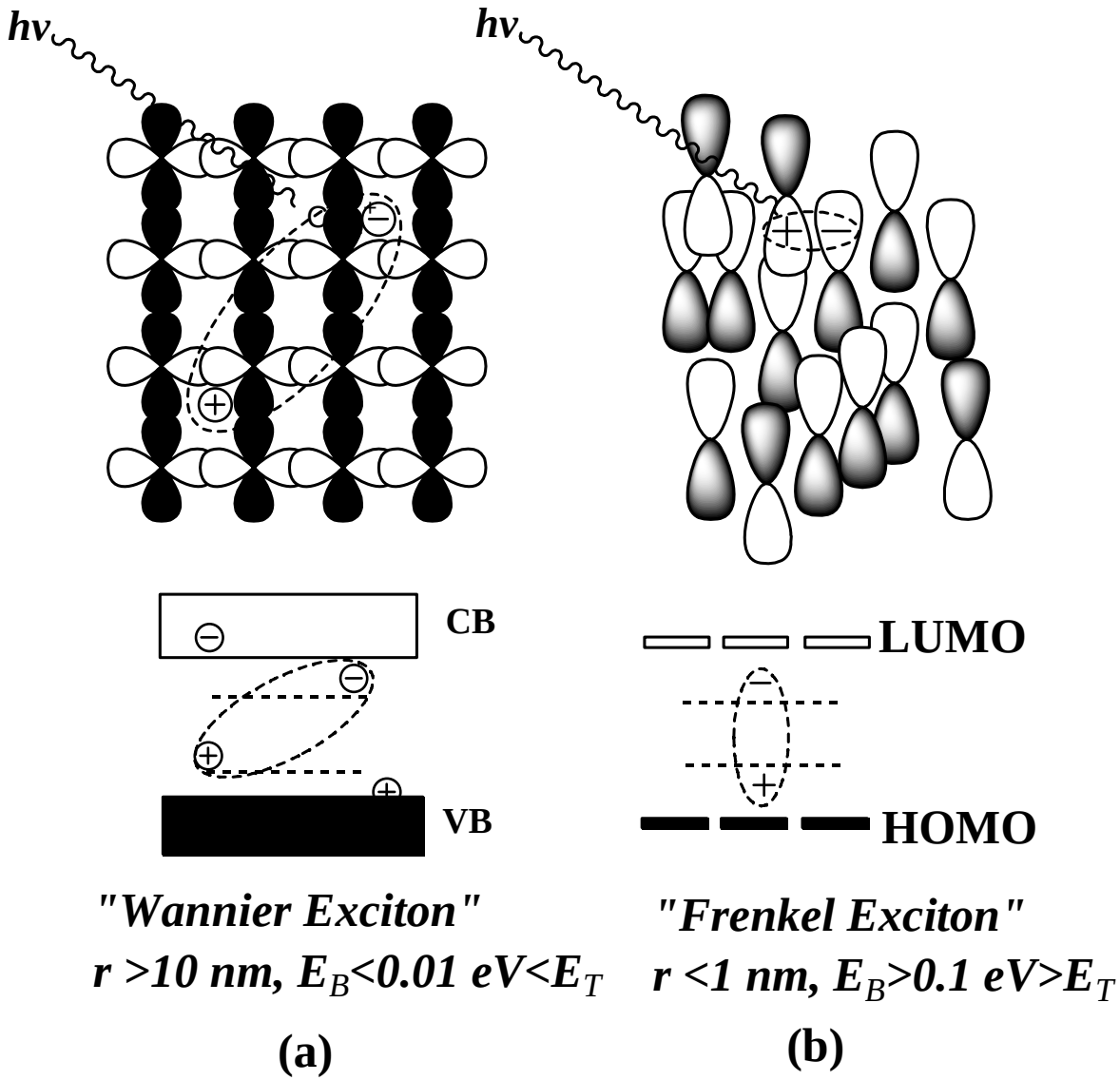


Figure 3. 19 Schematic representation of (a) Wannier-Mott type excitons; (b) Frenkel type excitons.

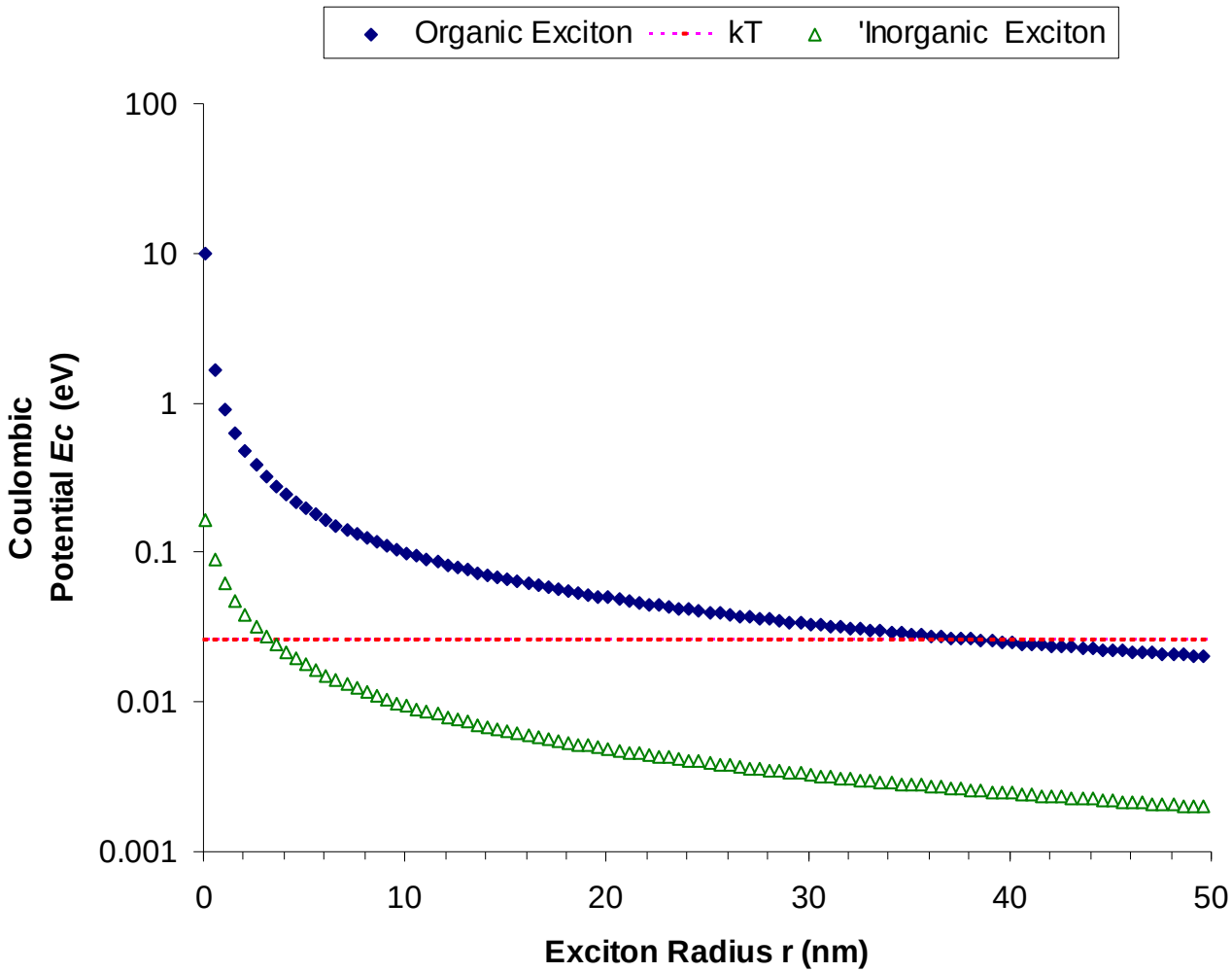


Figure 3. 20 Schemes of Coulombic potential (in absolute value) for typical Frenkel type excitons (diamonds) vs. Wannier-Mott type excitons (triangles).

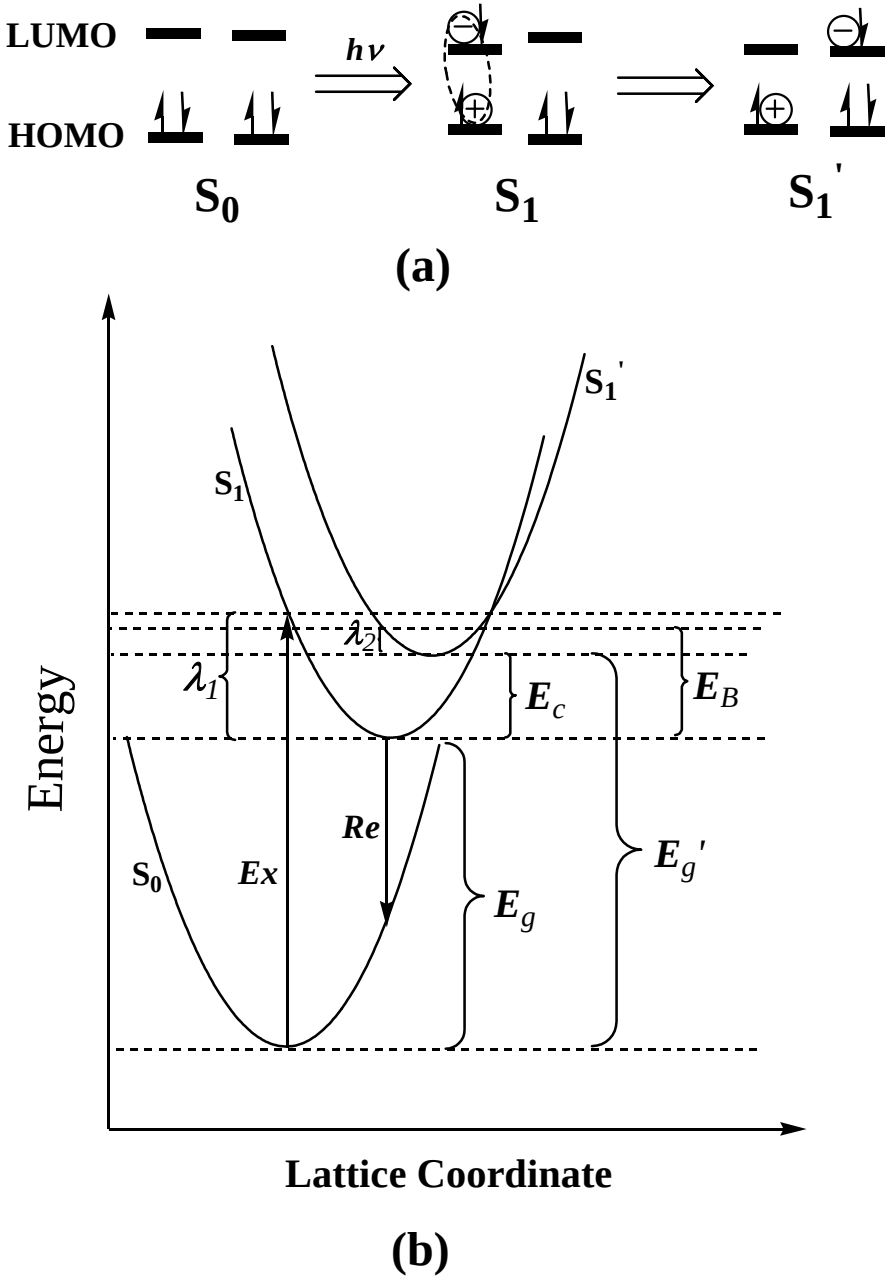


FIGURE 3.21
Scheme of photoelectric carrier generation processes in (a) frontier orbital representation; (b) free energy surface representation.

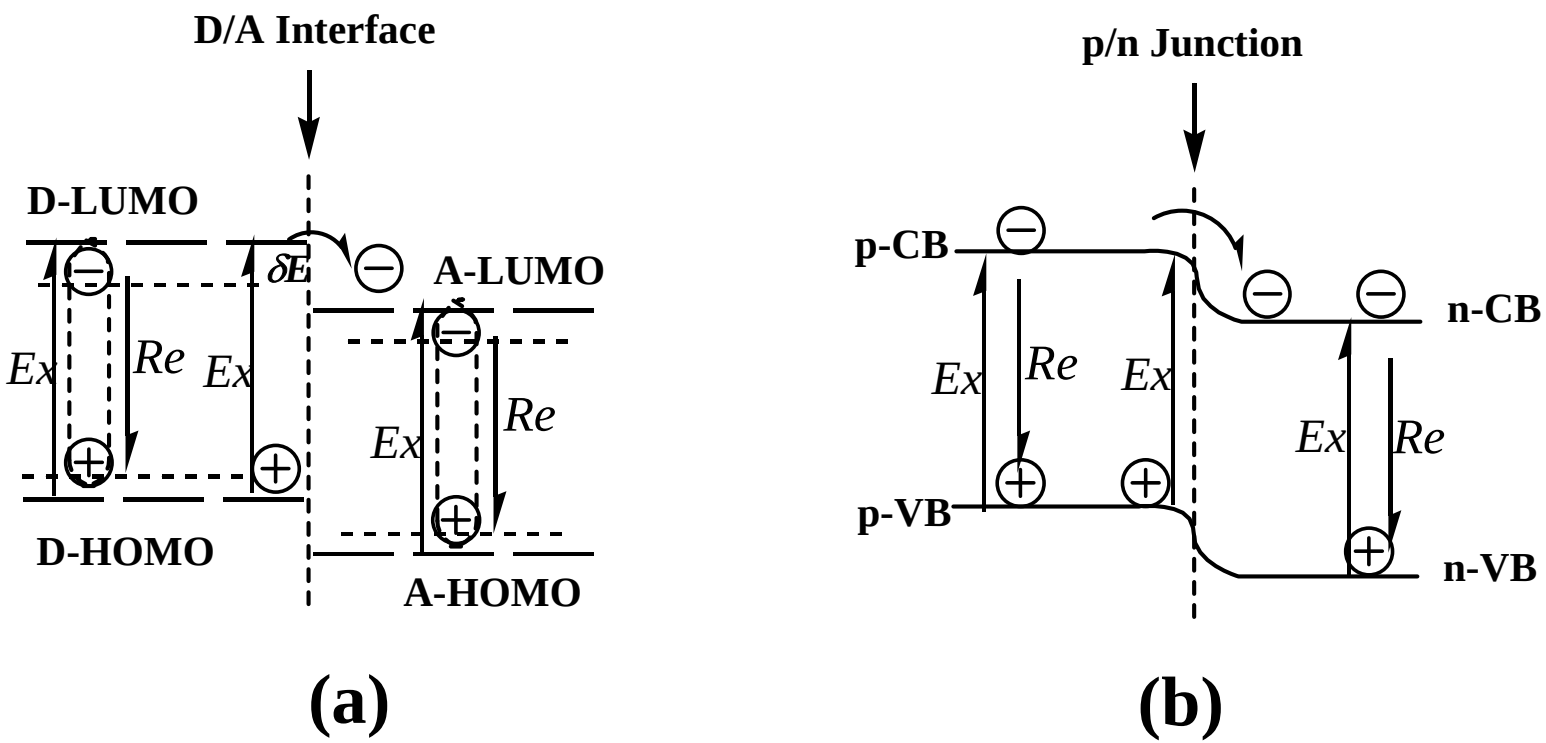


Figure 3. 22 Schemes of electron (charge) transfers at (a) a donor/acceptor (D/A) interface and (b) a p/n junction. Ex denotes excitation, and Re denotes exciton recombination.

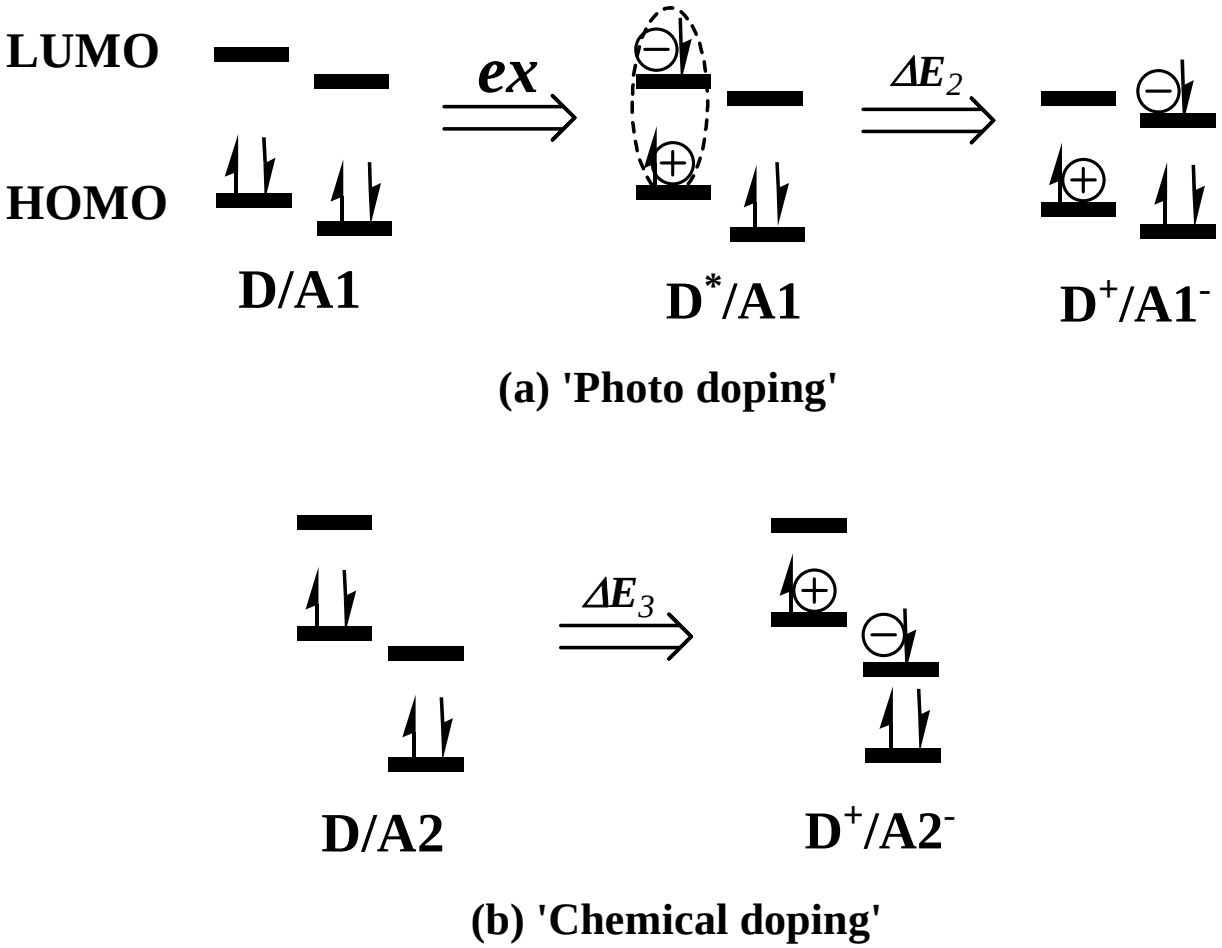


Figure 3. 23 Schemes of frontier orbitals and electron transfers of (a) photo doping and (b) chemical doping

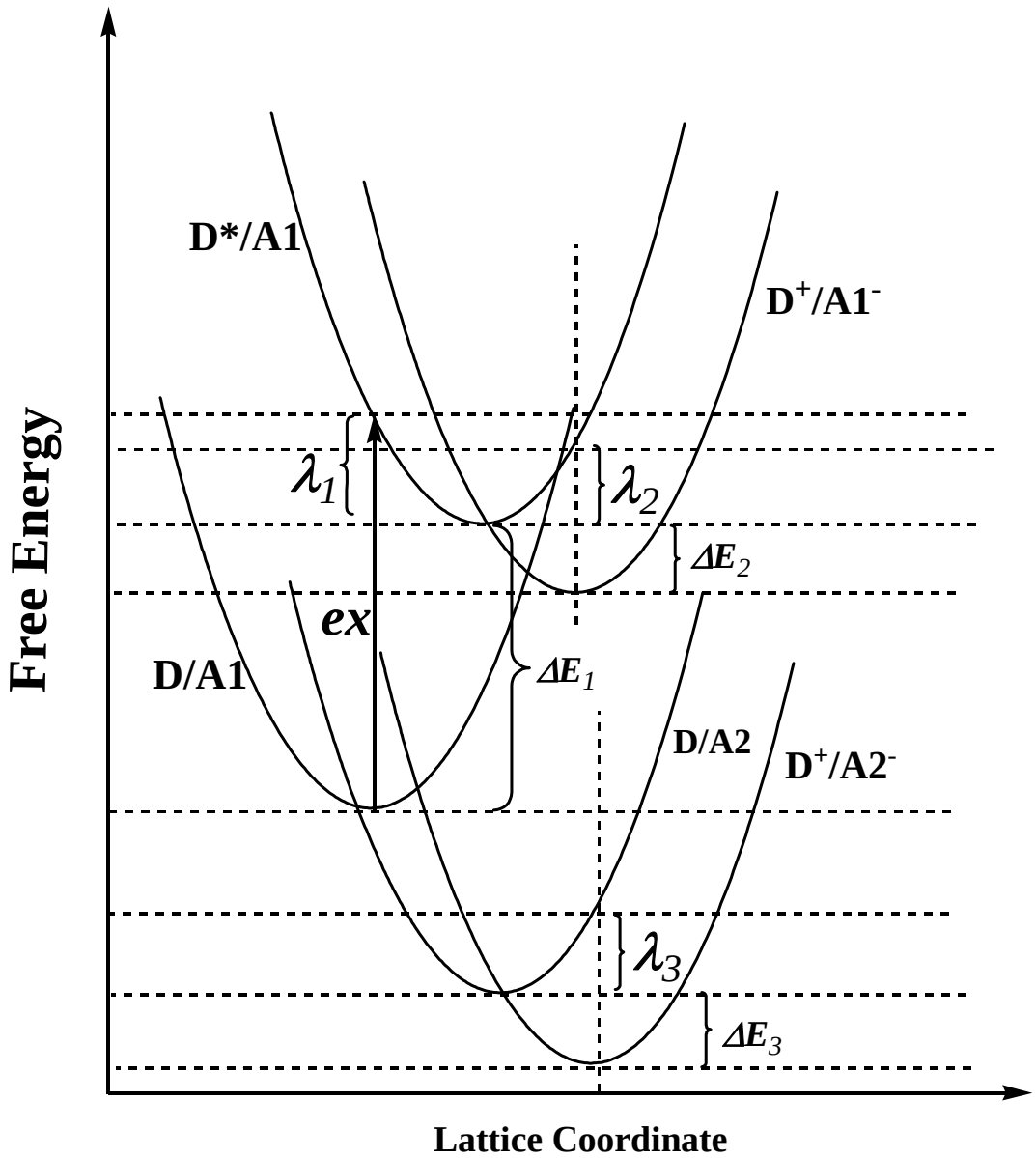


Figure 3. 24 Schemes of free energy surfaces and electronic transitions of photo doping (D/A1 → D*/A1 → $D^+/A1^-$) and chemical doping (D/A2 → $D^+/A2^-$)

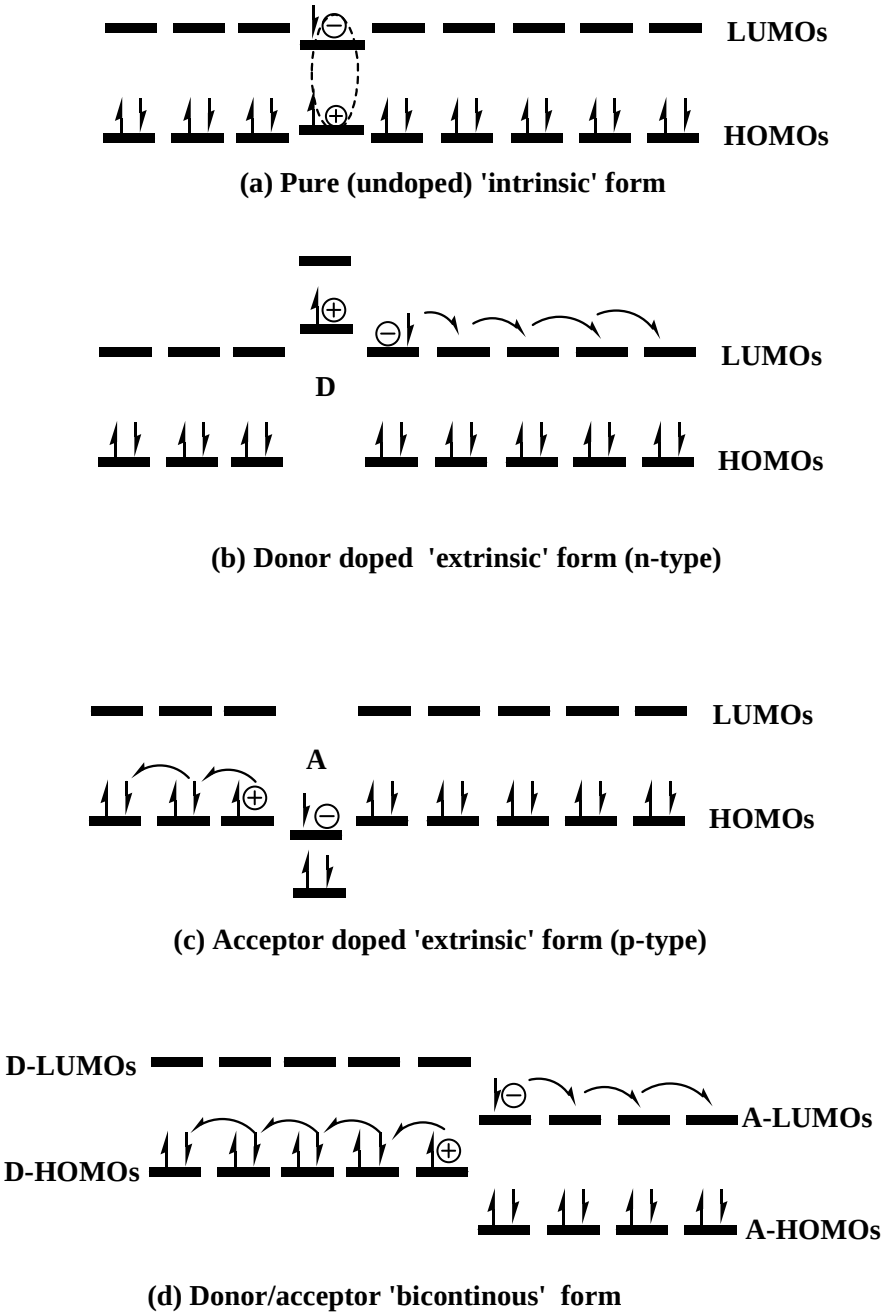


Figure 3. 25 Frontier orbitals and electron transfer schemes of organic/polymeric semiconductors and conductors in (a) pure (intrinsic) form; (b) donor (n-type) doped form; (c) acceptor (p-type) doped form; (d) donor/acceptor (p/n) junction form.

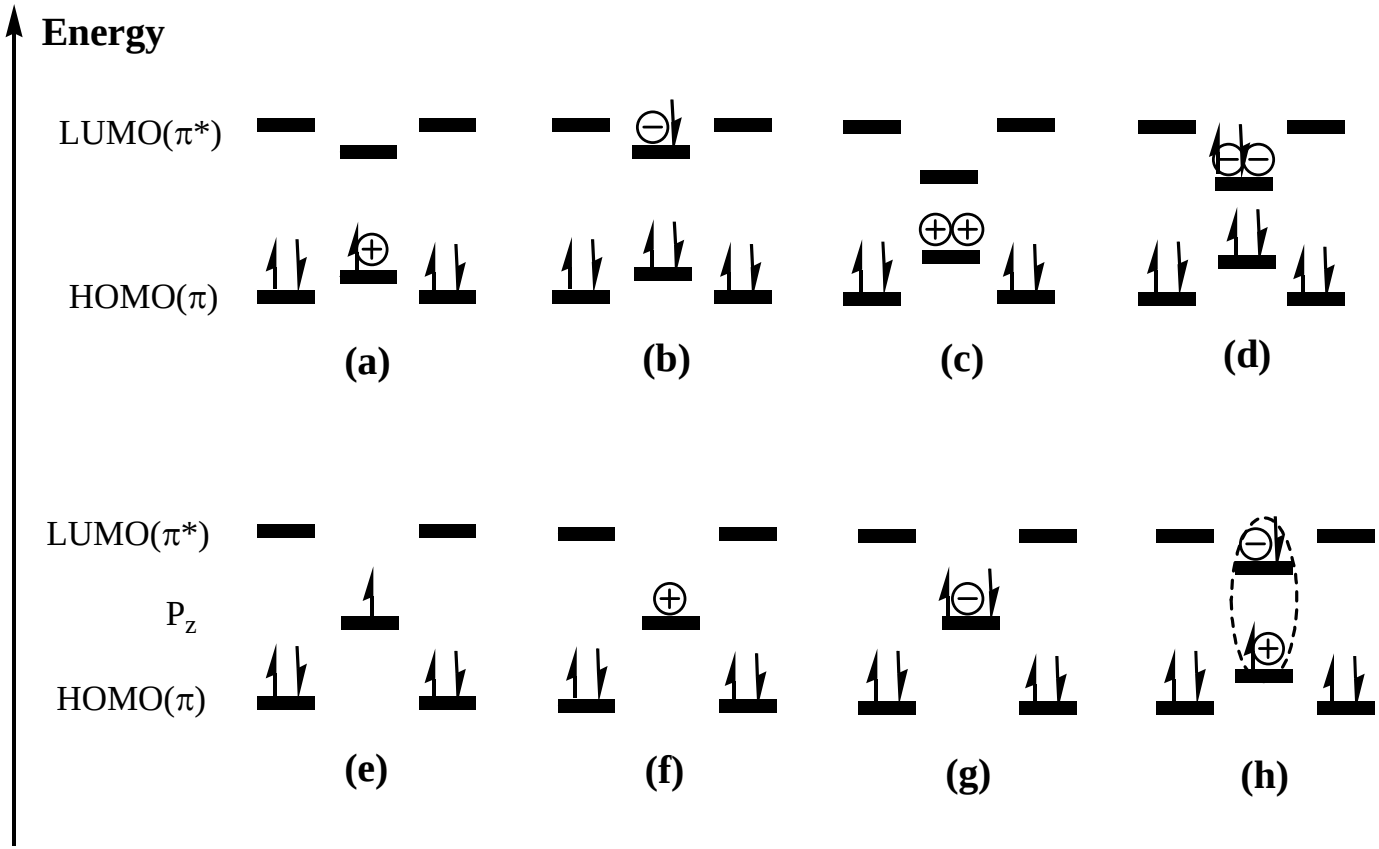


Figure 3. 26 Frontier orbital schemes of representative carriers: (a) positive (hole) polaron; (b) negative (electron) polaron; (c) positive (hole) bipolaron; (d) negative (electron) bipolaron; (e) neutral soliton; (f) positive (hole) soliton; (g) negative (electron) soliton; (h) exciton polaron.

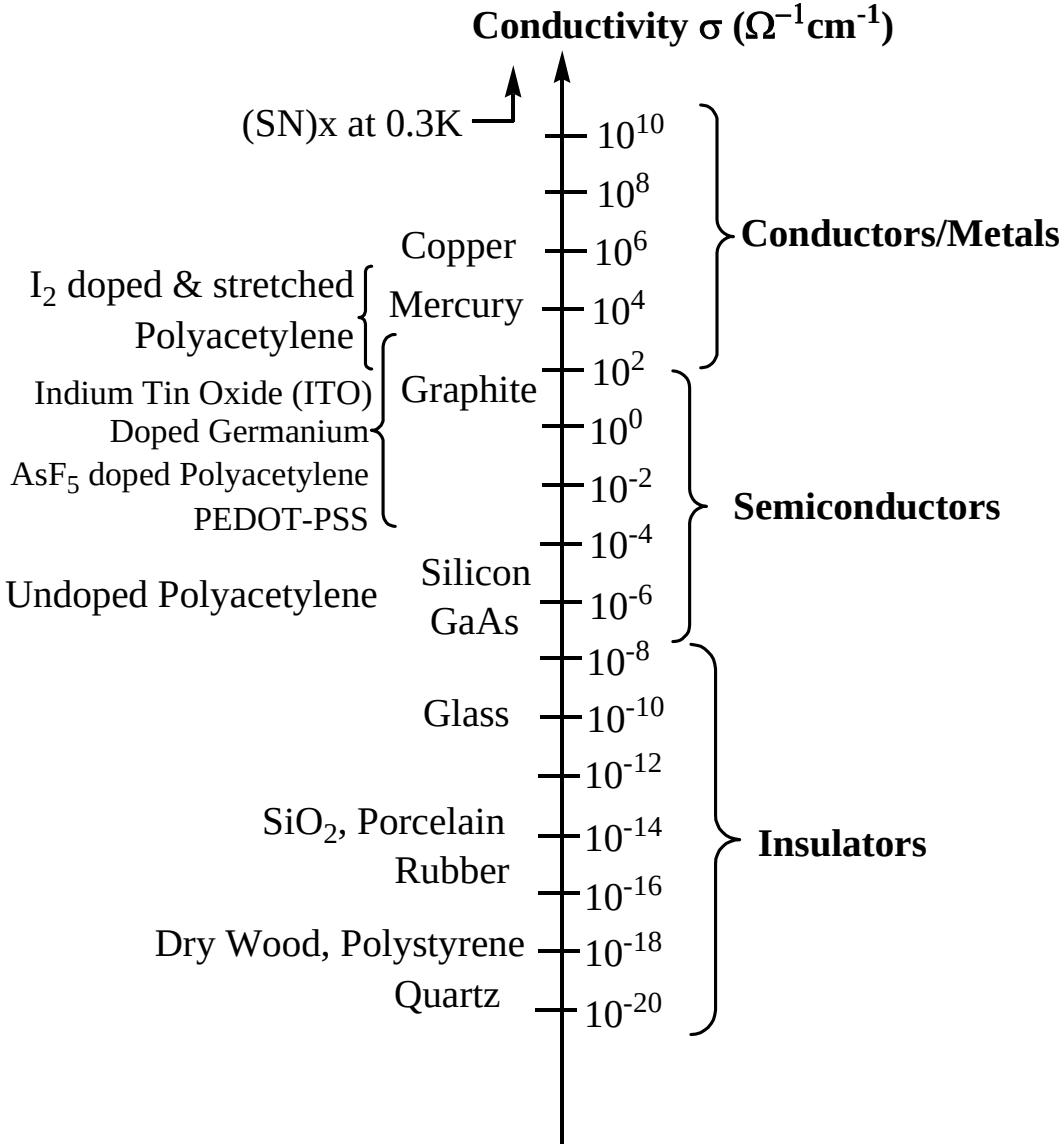


Figure 3. 27 Room temperature conductivity (σ) of various materials.

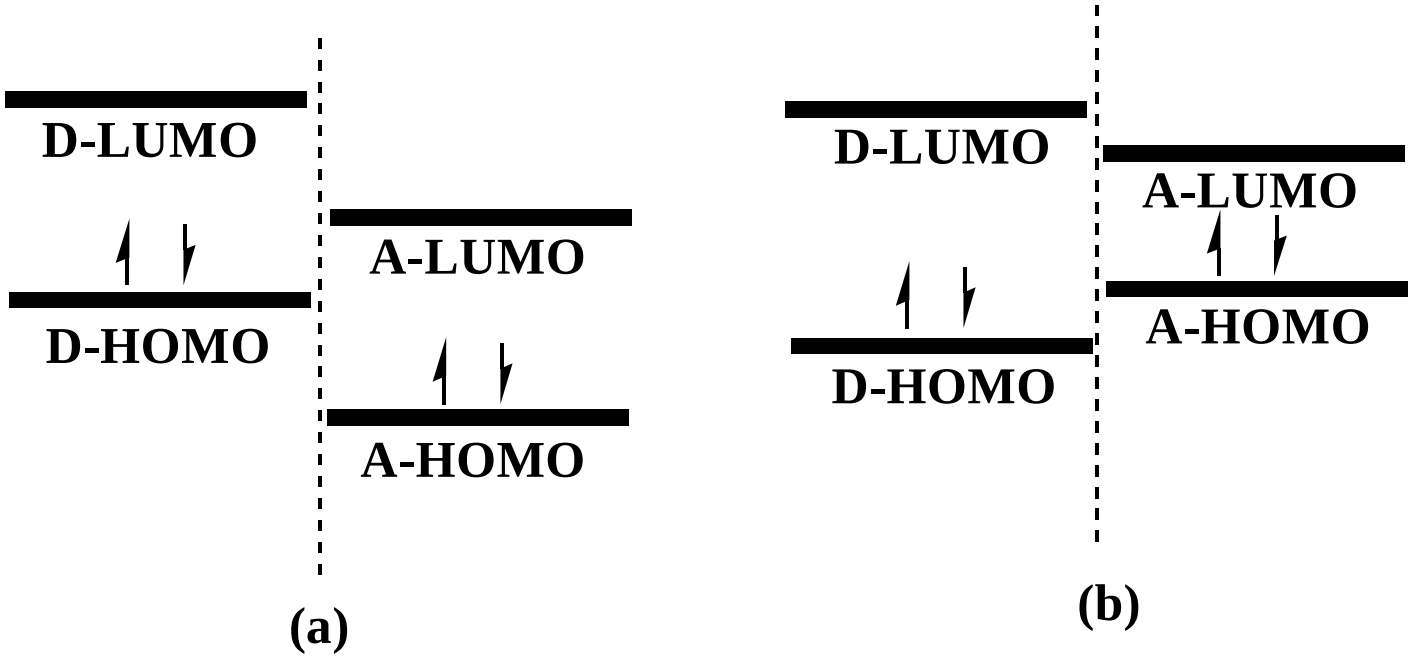


Figure 3. 28 Frontier orbital energy level representations for a typical (a) electron transfer and (b) energy transfer between two different materials. *D* denotes a donor and *A* denotes an acceptor.

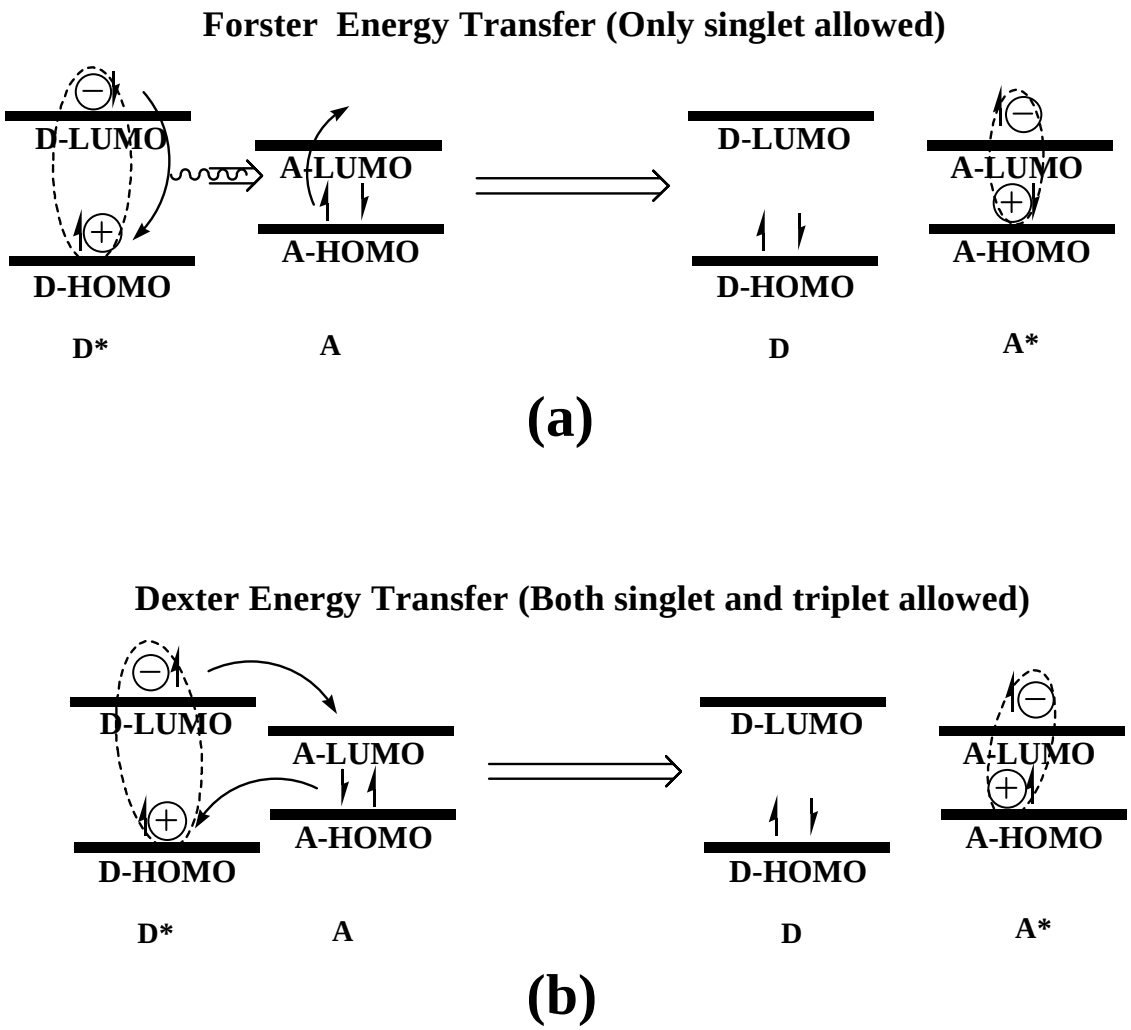


Figure 3. 29 Schemes of (a) Förster energy transfer and (b) Dexter energy transfer.

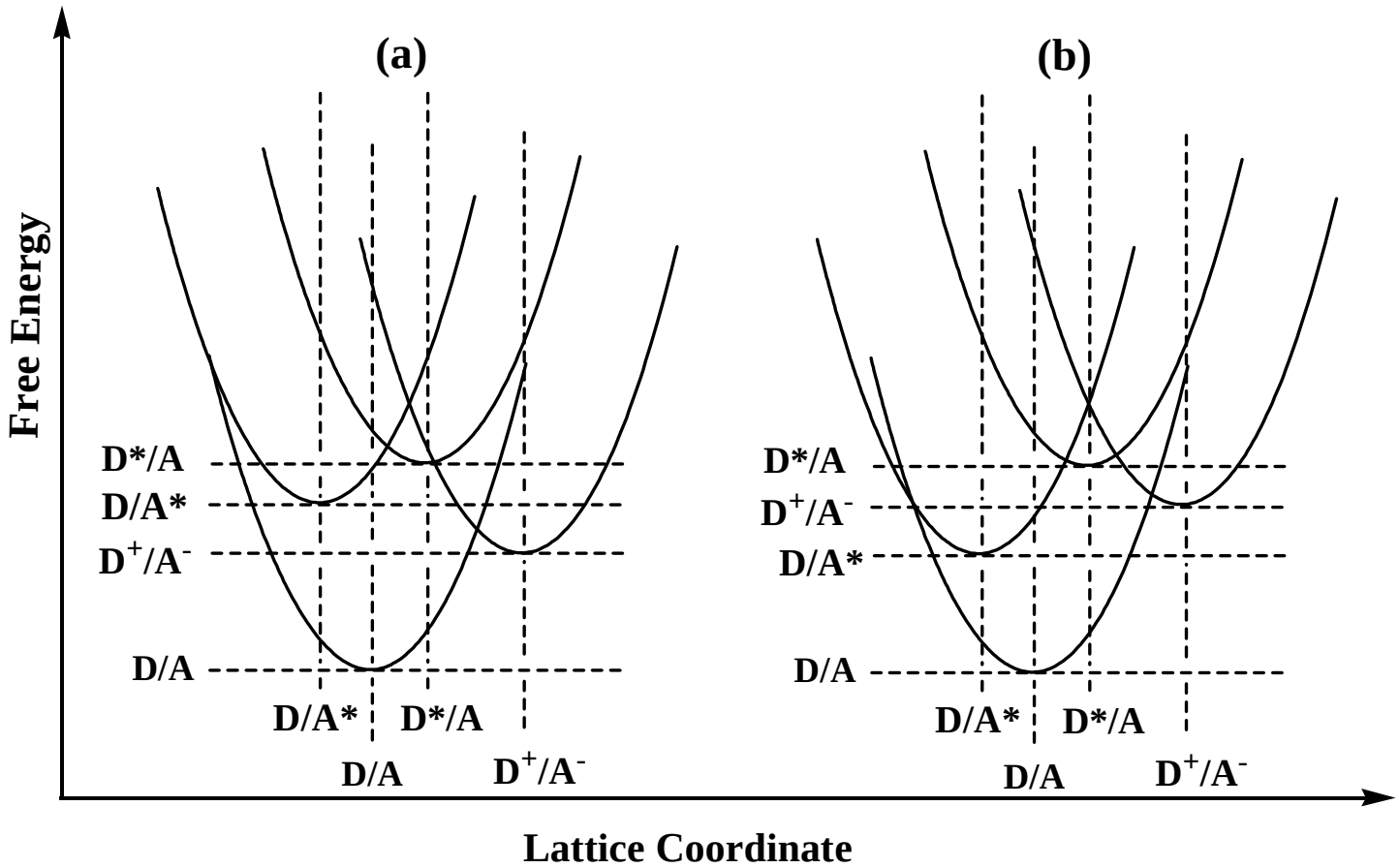


Figure 3. 30 Free energy surface schemes of a D/A pair in (a) charge transfer and (b) energy transfer scenarios.

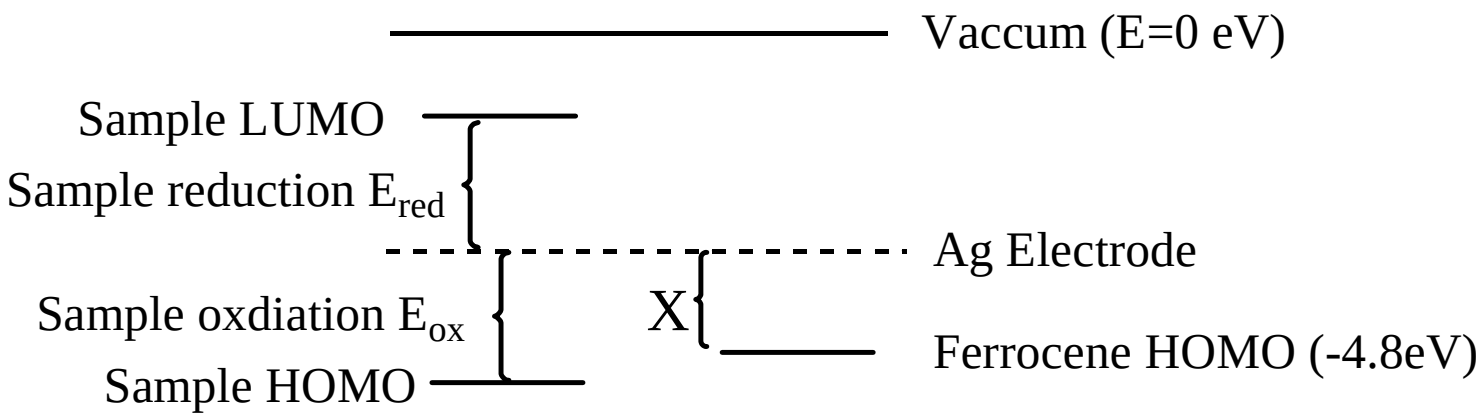


Figure 3. 31 Energy level scheme of cyclicvoltammetry (CV).