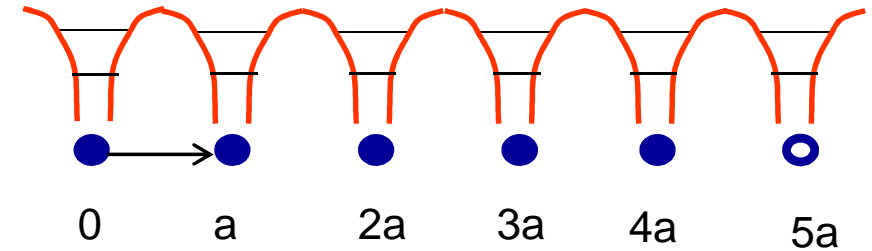


Modelo 1D com N orbitais independentes

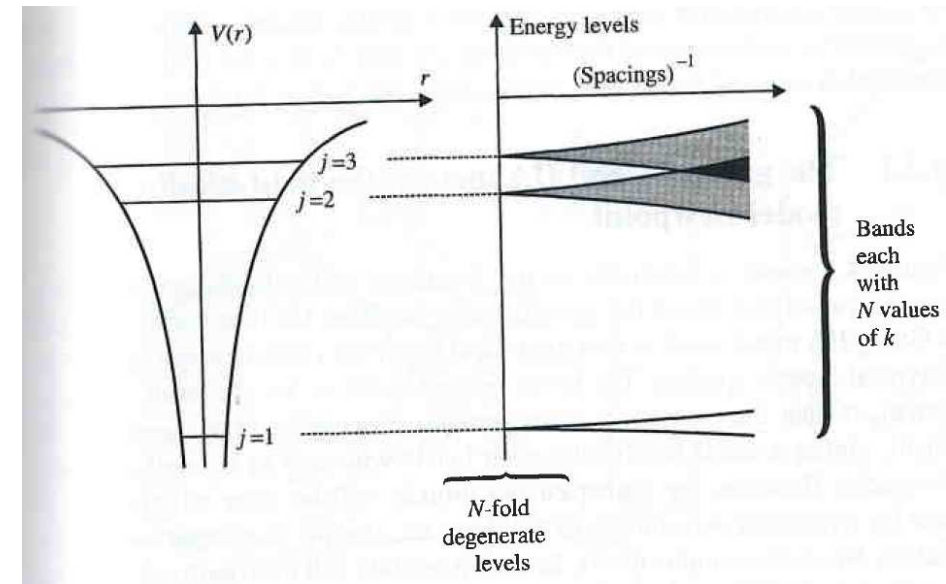
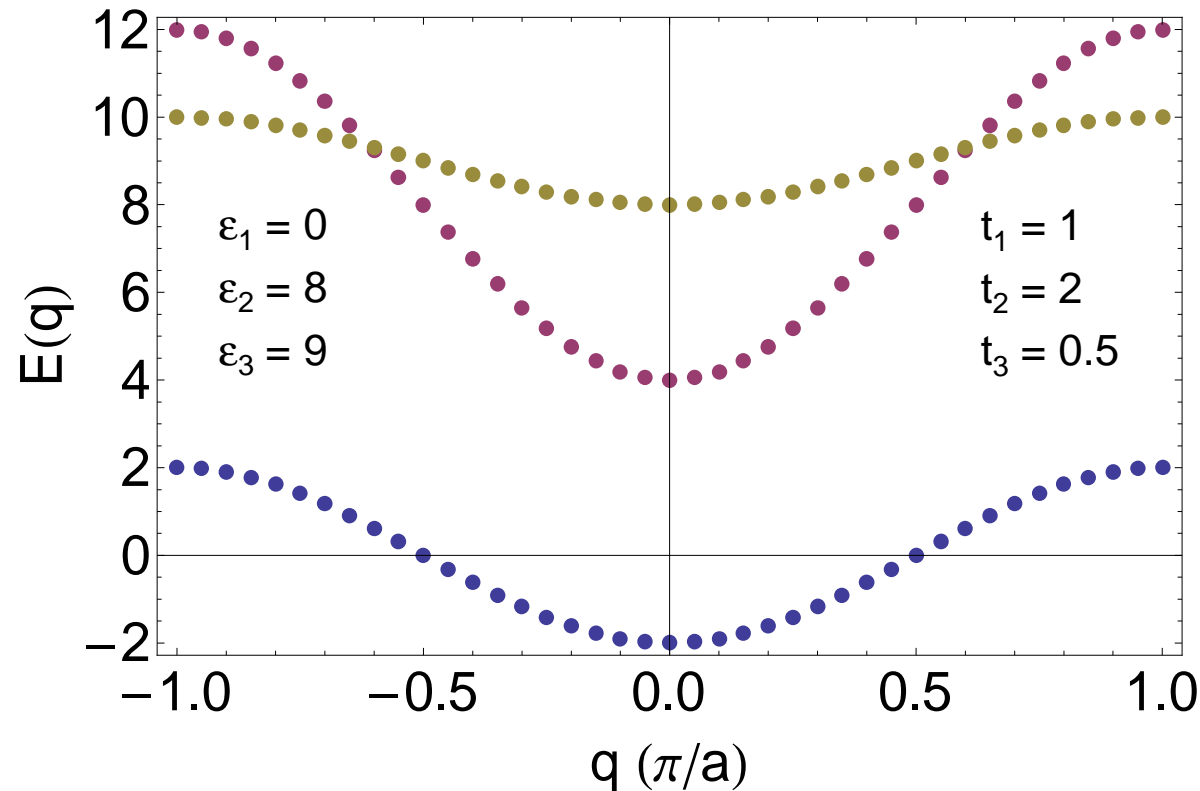
- Caso 1D com mais orbitais por sítio:

$$E_j(q) = \epsilon_j + \sum_n e^{inqa} \int \phi_j^*(x) \Delta V(x) \phi_j(x - na) dx$$

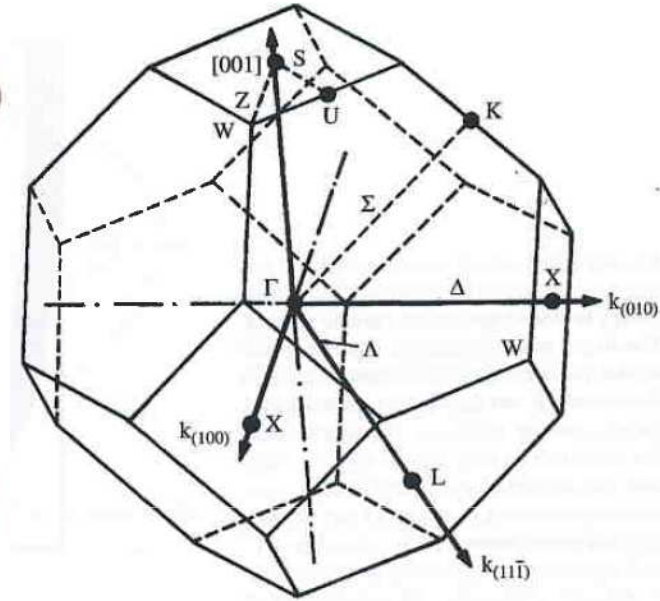
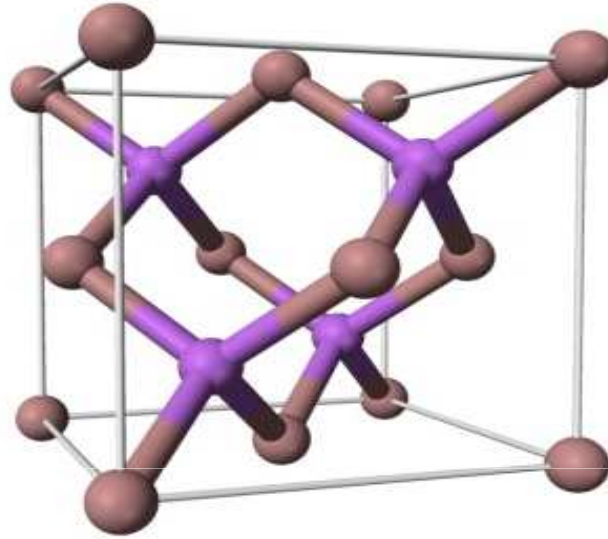
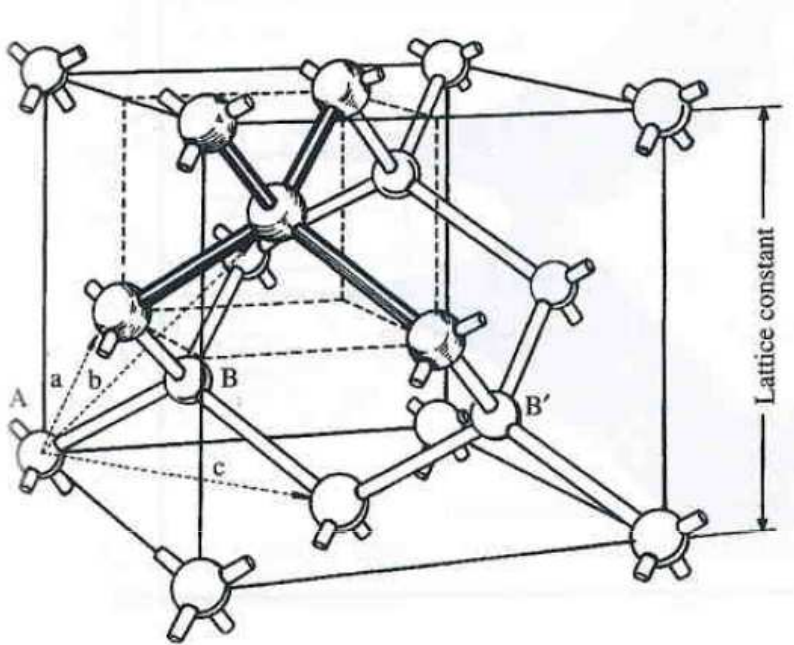
$$t_j = - \int \phi_j^*(x) \Delta V(x) \phi_j(x \pm a) dx \quad (\text{Supondo } t_{ij} = 0!)$$



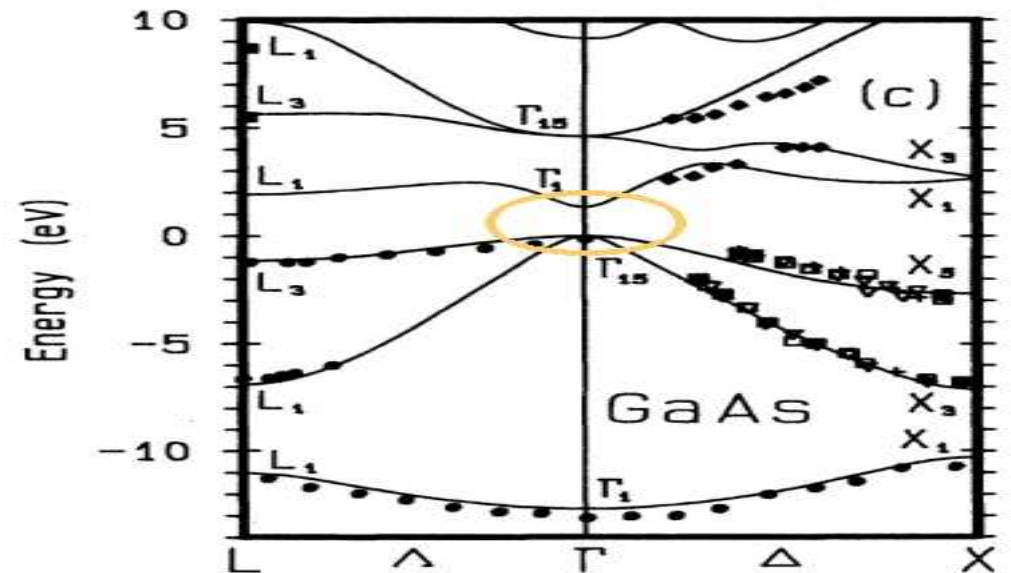
$$E_j(q) = \bar{\epsilon}_j - 2t_j \cos(qa)$$



Modelos 3D: diamante e blenda de zinco

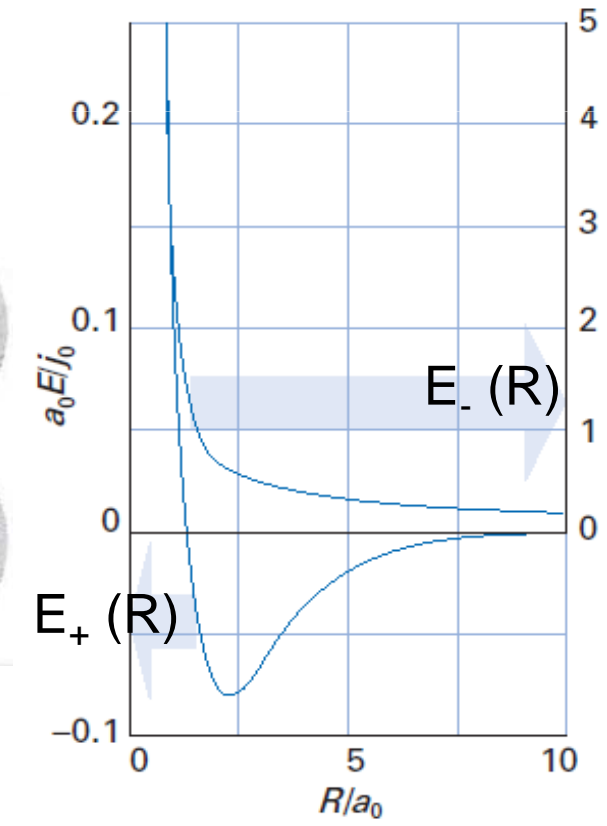
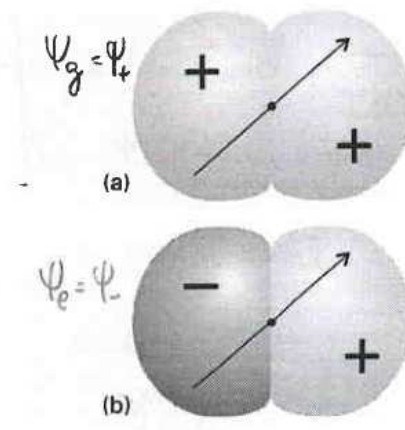
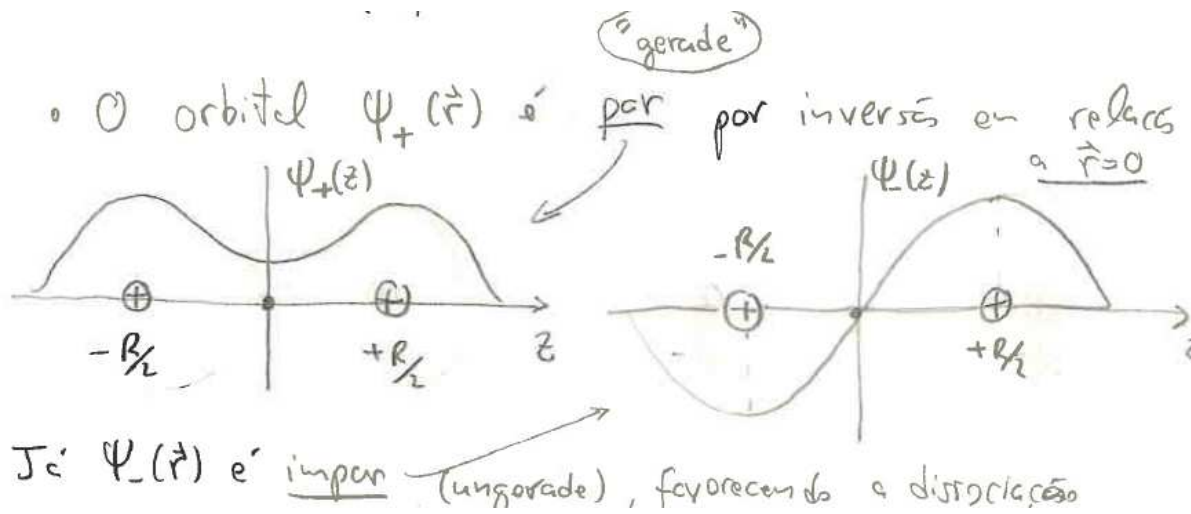
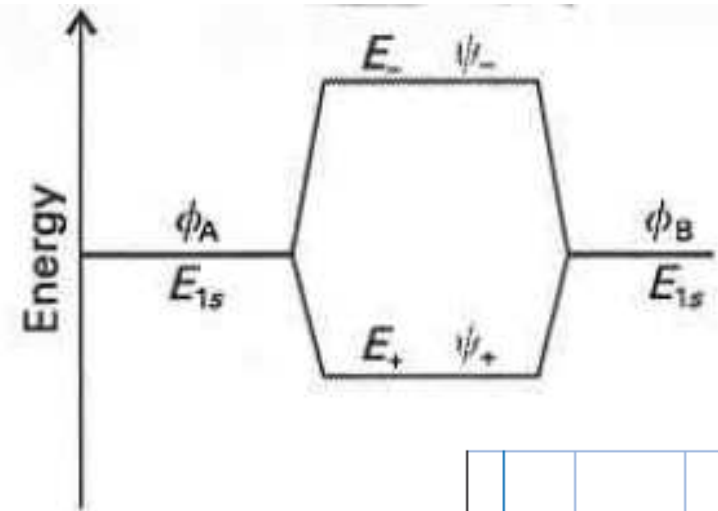


- Rede fcc com **dois átomos** na base.
- Se os dois átomos forem iguais: estrutura tipo **diamante** (C, Si, etc.)
- Se os dois átomos forem diferentes: estrutura tipo **blenda de zinco** (zincblende): semicondutores III-V e II-VI como **GaAs**, InAs, HgTe, CdTe, GaSb,...



Linear combination of atomic orbitals (LCAO)

- Base de dois átomos: LCAO nos dará os “orbitais” que entram no tight-binding.
- Separamos em estados *ligantes* e *não-ligantes*.
- Exemplo para molécula de H_2^+ (notas escaneadas)



Hibridização sp^3 : C, Si, Ge

- LCAO para carbono: $2s^2 2p^2 \rightarrow sp^3$
- Estados ligantes tipo s (σ) e p (π).
- Gap entre os estados preenchidos/não preenchidos.

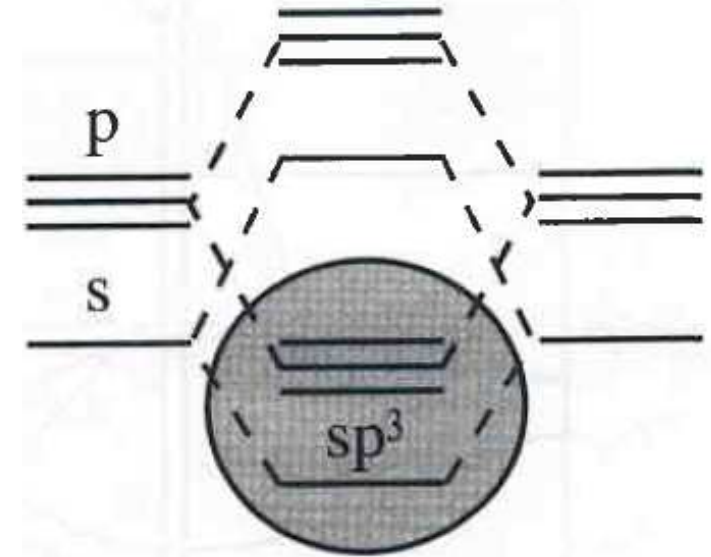
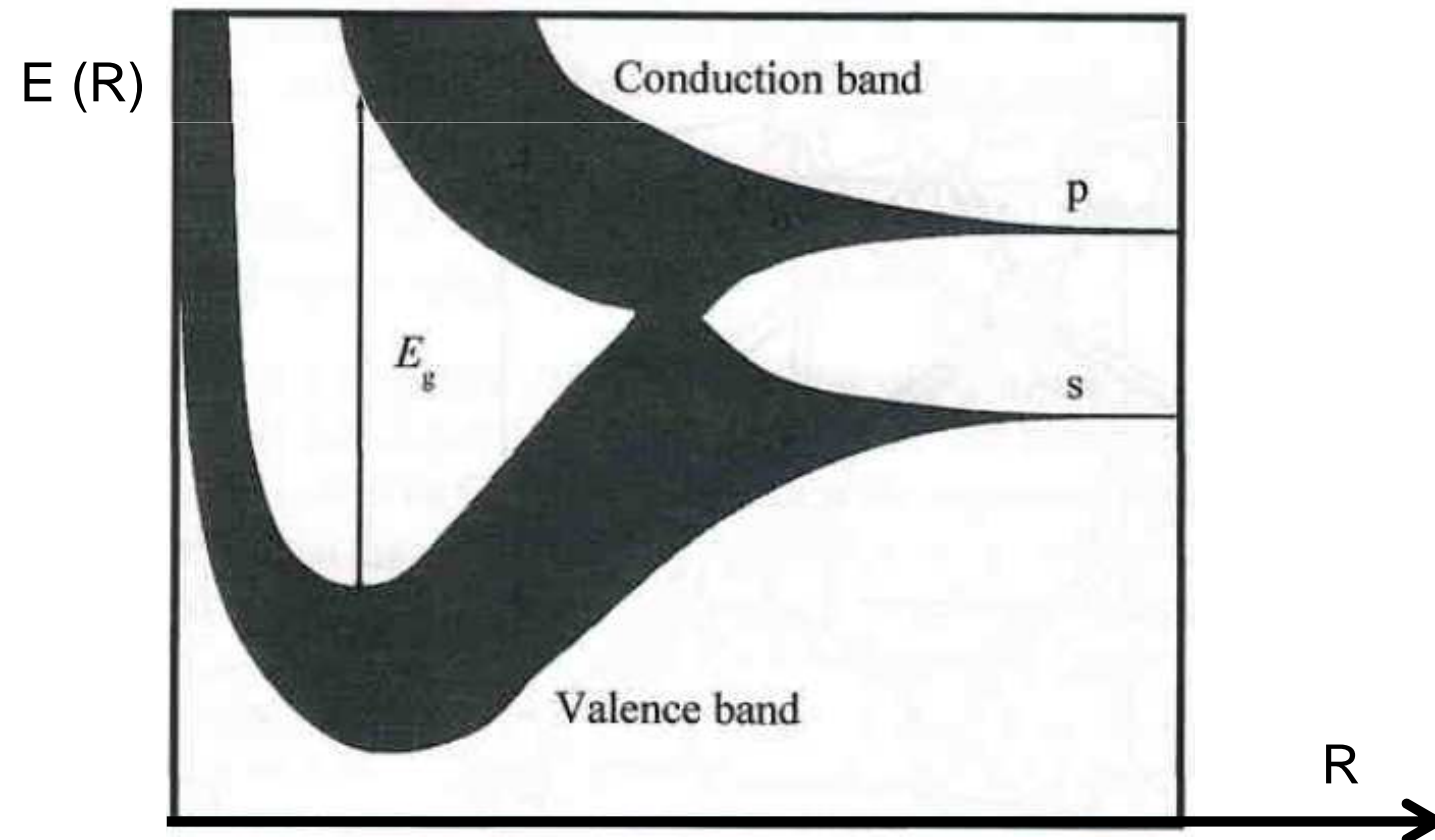


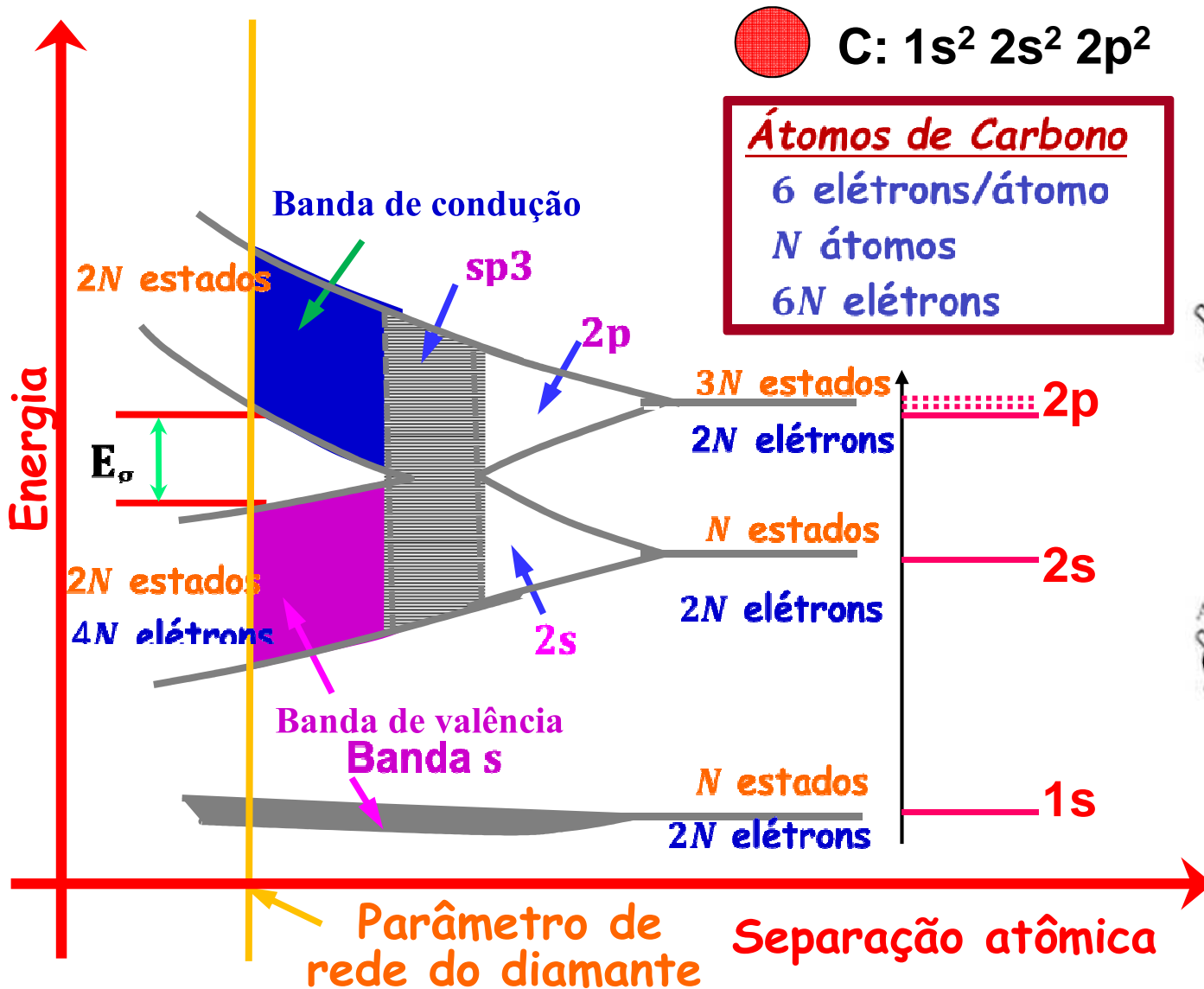
Fig. 4.5 Schematic of the formation of sp^3 hybrid bonding states in carbon (diamond).

Table 4.1 Energy gaps and lattice parameters a for the Group IV elements; a is the edge of the conventional cubic cell shown in Fig. 4.4. (The band-gaps shown are the direct gaps; see Chapter 6.)

Element	E_g	a
C	5 eV	0.356 nm
Si	1.1 eV	0.543 nm
Ge	1.0 eV	0.566 nm
Sn	metallic	0.646 nm

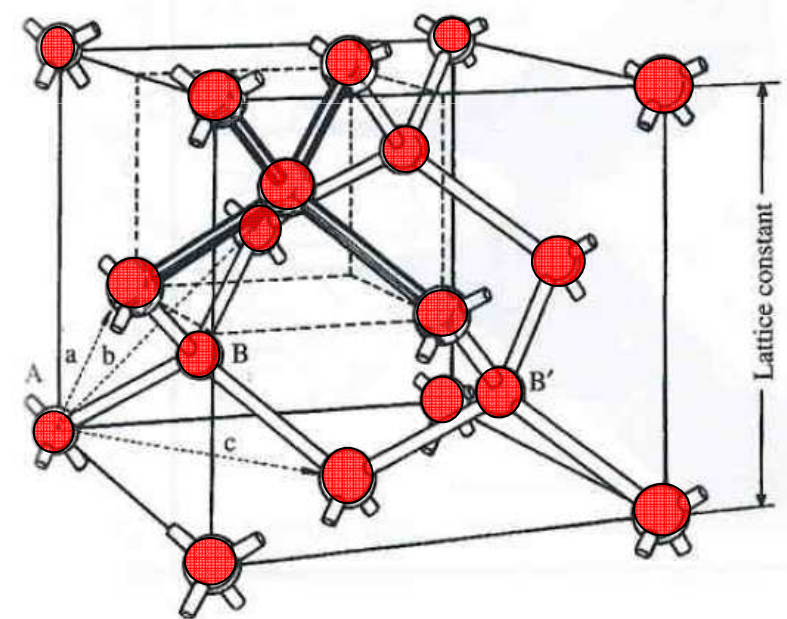


Exemplo: diamante (isolante).



● C: 1s² 2s² 2p²

Átomos de Carbono
 6 elétrons/átomo
 N átomos
 6N elétrons



E_g ≅ 7 eV → Isolante.

Tight-binding para sistemas π -conjugados = aproximação de Huckel.

- LCAO que considera apenas orbitais p do carbono em hibridização sp^2
- Aplicação para moléculas aromáticas cíclicas ou planares do tipo C_nH_{n+2}
- (vide notas de aula)
- **Tarefa 9 (hoje):** encontrar as energias dos estados ligantes e anti-ligantes do etileno em termos dos parâmetros de Huckel (α e β).

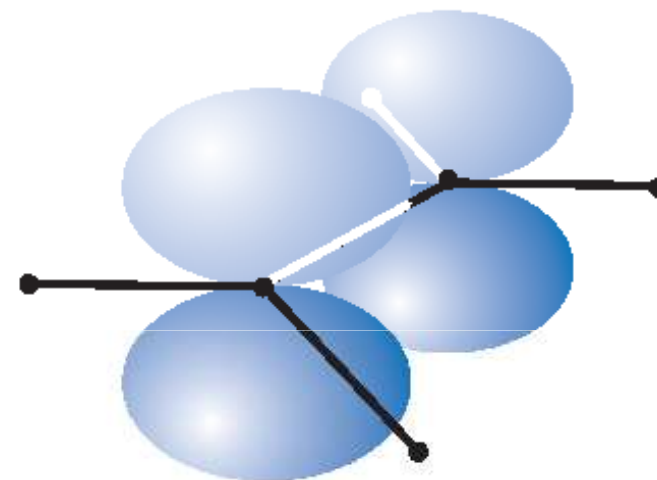
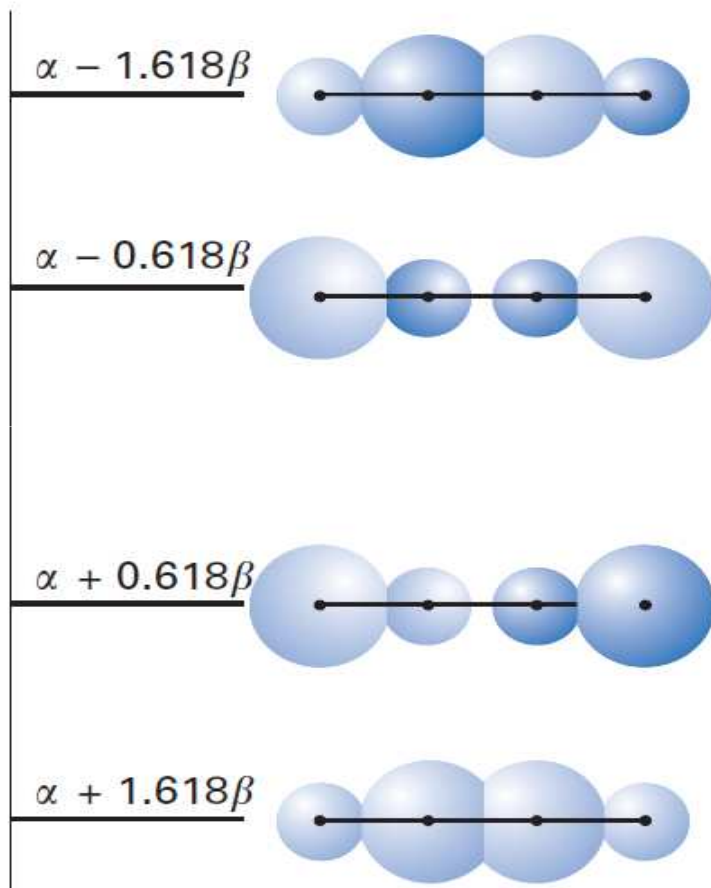
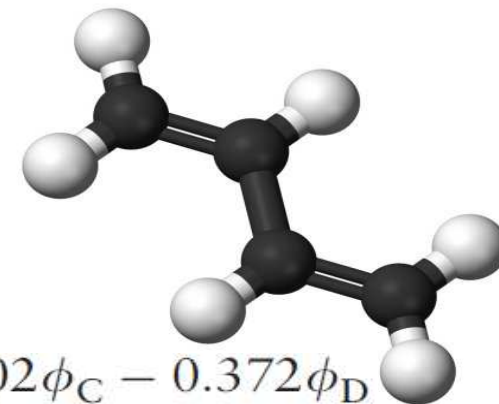


Fig. 8.27 The structure of the π -orbital in ethene.



Teoria de Hückel: Butadieno



$$\psi(4\pi) = 0.372\phi_A - 0.602\phi_B + 0.602\phi_C - 0.372\phi_D$$

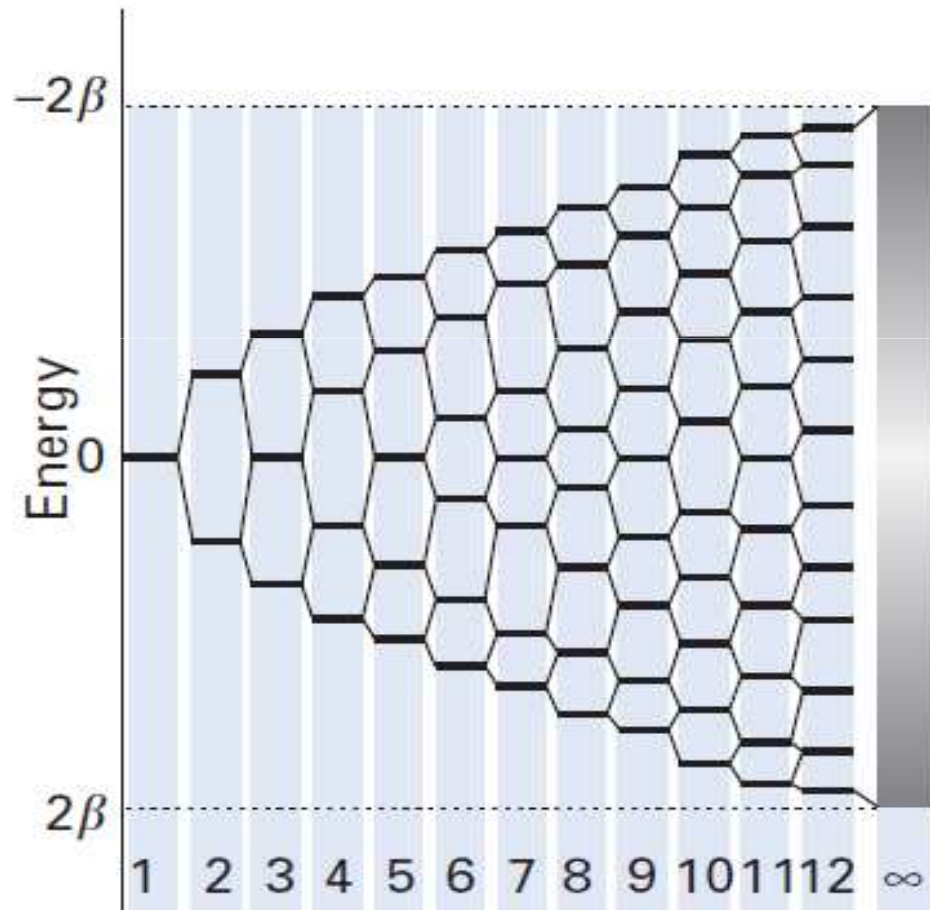
$$\psi(3\pi) = -0.602\phi_A + 0.372\phi_B + 0.372\phi_C - 0.602\phi_D$$

$$\psi(2\pi) = -0.602\phi_A - 0.372\phi_B + 0.372\phi_C + 0.602\phi_D$$

$$\psi(1\pi) = 0.372\phi_A + 0.602\phi_B + 0.602\phi_C + 0.372\phi_D$$

Cadeias lineares: limite N grande

$$E_k = \alpha + 2\beta \cos\left(\frac{k\pi}{N+1}\right) \quad k = 1, 2, \dots, N$$



$$\lim_{N \rightarrow \infty} E^{(N)}(k) = \alpha + 2\beta \cos(k.a)$$