

V CHAPTER : APPENDIX

V.1 BAND STRUCTURE OF A FCC TRANSITION METAL

In the FCC structure each atom has 12 nearest-neighbours and six second nearest-neighbours as can be seen in Fig.A. V.1. The overlap integrals B_{ij} can be evaluated from the Slater-Koster table by noting that two of the direction cosines are equal to $1/\sqrt{2}$ and the third one is zero. We have then

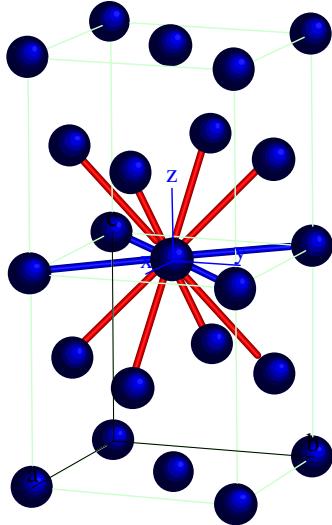


Fig.A. V.1: The 12 nearest neighbours in the FCC structure

Table A.V.1: Overlap integrals after Slater and Koster for the nearest-neighbours in the FCC lattice. The fundamental overlap integrals $dd\sigma$, $dd\pi$ and $dd\delta$ are defined in Table.VI.1. The $dd\delta$ overlap integral are set equal to zero

$B_{xy, xy}$	$3/4 dd\sigma$	for [110]
$B_{xy, xy}$	$1/2 dd\pi$	for [101] and [011]
$B_{xy, yz}$	0	for [011]
$B_{xy, yz}$	0	for [101] and [011]
$B_{xy, xz}$	0	for [011]
$B_{xy, xz}$	0	for [101] and [011]
B_{xy, x^2-y^2}	0	
B_{yz, x^2-y^2}	0	
B_{xz, x^2-y^2}	0	
$B_{xy, 3z^2-r^2}$	0	
$B_{yz, 3z^2-r^2}$	0	
$B_{xz, 3z^2-r^2}$	0	
$B_{x^2-y^2, x^2-y^2}$	$dd\pi$	for [110]
$B_{x^2-y^2, 3z^2-r^2}$	$3/16 dd\sigma + 1/4 dd\pi$	for [101] and [011]
$B_{3z^2-r^2, 3z^2-r^2}$	$1/4 dd\sigma$	for [110]
$B_{3z^2-r^2, 3z^2-r^2}$	$1/16 dd\sigma + 3/4 dd\pi$	for [101] and [011]

As the corresponding matrix $\mathbf{k} = (0, 0, k_z)$ is diagonal we can immediately evaluate

$$\begin{aligned}
E_k &= E_d + \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} B_{jj}(\mathbf{R}) \\
&= E_d + 2 \sum^* \cos(\mathbf{k} \cdot \mathbf{R}) B_{jj}(\mathbf{R})
\end{aligned} \tag{A. V.1}$$

for the five d-bands as

$$\begin{aligned}
E_{xy,xy} &= E_d + 4dd\pi \cos\left(\frac{k_z a}{2}\right) + 3dd\sigma \\
E_{yz,yz} &= E_d + 3dd\sigma \cos\left(\frac{k_z a}{2}\right) + 2dd\pi \left(1 + \cos\left(\frac{k_z a}{2}\right)\right) \\
E_{xz,xz} &= E_d + 3dd\sigma \cos\left(\frac{k_z a}{2}\right) + 2dd\pi \left(1 + \cos\left(\frac{k_z a}{2}\right)\right) \\
E_{x^2-y^2,x^2-y^2} &= E_d + 4dd\pi + \left(\frac{3}{2}dd\sigma + 2dd\pi\right) \cos\left(\frac{k_z a}{2}\right) + \\
E_{3z^2-r^2,3z^2-r^2} &= E_d + \left(\frac{1}{2}dd\sigma + 6dd\pi\right) \cos\left(\frac{k_z a}{2}\right) + dd\sigma
\end{aligned} \tag{A. V.2}$$

As $dd\sigma \approx -2dd\pi$ we can further simplify these expressions to

$$\begin{aligned}
E_{xy,xy} &= E_d + 4dd\pi \cos\left(\frac{k_z a}{2}\right) - 6dd\pi \\
E_{yz,yz} &= E_d + 2dd\pi \left(1 - 2 \cos\left(\frac{k_z a}{2}\right)\right) \\
E_{xz,xz} &= E_d + 2dd\pi \left(1 - 2 \cos\left(\frac{k_z a}{2}\right)\right) \\
E_{x^2-y^2,x^2-y^2} &= E_d + 4dd\pi - dd\pi \cos\left(\frac{k_z a}{2}\right) \\
E_{3z^2-r^2,3z^2-r^2} &= E_d + 5dd\pi \cos\left(\frac{k_z a}{2}\right) - 2dd\pi
\end{aligned} \tag{A. V.3}$$

These five d-bands are shown in

Fig.A.V.2. The xz - and yz -bands are degenerate. The shape of the d-bands corresponds nicely with those obtained for example by Moruzzi for Pd (see Fig.V.1).

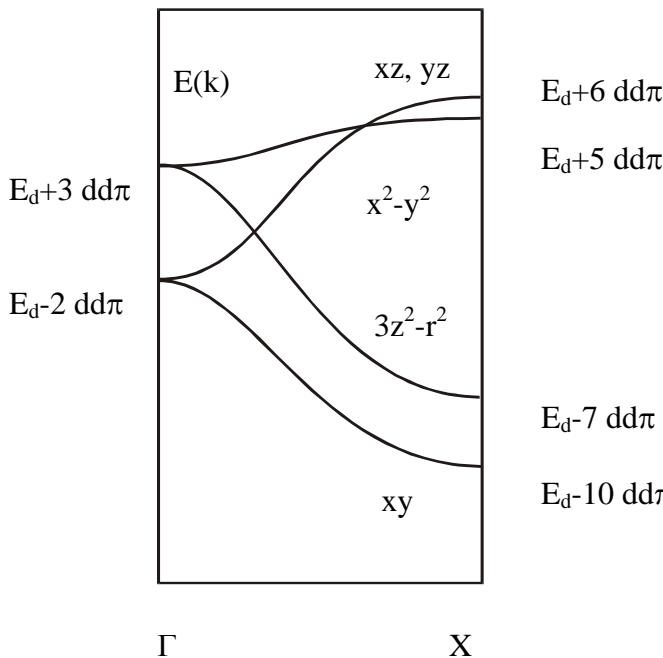


Fig.A.V.2: d-band structure along the k_z direction of a metal with a FCC lattice when only nearest neighbour overlaps are taken into account (i.e. calculated from Eq.A.V.3)

V.2 BAND STRUCTURE OF A BCC TRANSITION METAL

In the BCC structure each atom has 8 nearest-neighbours and six second nearest-neighbours as can be seen in Fig.A. V.3. The overlap integrals B_{ij} can be evaluated from the Slater-Koster table by noting that all the direction cosines are equal to $\pm 1/\sqrt{3}$. We have then

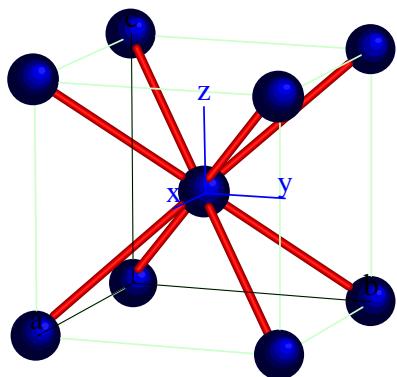


Fig.A. V.3: The 8 nearest neighbours in the BCC structure.

Table A. V.2: Overlap integrals after Slater and Koster for the nearest-neighbours in the BCC lattice. The fundamental overlap integrals $dd\sigma$, $dd\pi$ and $dd\delta$ are defined in Table.VI.1. The $dd\delta$ overlap integral is set equal to zero and we indicate within parentheses the corresponding expressions result for the case $dd\sigma \equiv -2dd\pi$

$B_{xy, xy}$	$1/3 dd\sigma + 2/9 dd\pi$	$(-4/9 dd\pi)$
$B_{xy, yz}$	$1/3 dd\sigma - 1/9 dd\pi$	$(-7/9 dd\pi)$
$B_{xy, xz}$	$1/3 dd\sigma + 2/9 dd\pi$	$(-7/9 dd\pi)$
$B_{xy, x^2 - y^2}$	0	
$B_{yz, x^2 - y^2}$	$-1/3 dd\pi$	
$B_{xz, x^2 - y^2}$	$1/3 dd\pi$	
$B_{xy, 3z^2 - r^2}$	$-(2\sqrt{3})/9 dd\pi$	
$B_{yz, 3z^2 - r^2}$	$1/(3\sqrt{3}) dd\pi$	
$B_{xz, 3z^2 - r^2}$	$1/(3\sqrt{3}) dd\pi$	
$B_{x^2 - y^2, x^2 - y^2}$	$2/3 dd\pi$	
$B_{3z^2 - r^2, 3z^2 - r^2}$	$2/3 dd\pi$	

As the corresponding matrix for $\mathbf{k} = (0, 0, k_z)$ is diagonal we can immediately evaluate

$$\begin{aligned} E_k &= E_d + \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} B_{jj}(\mathbf{R}) \\ &= E_d + 2 \sum^* \cos(\mathbf{k} \cdot \mathbf{R}) B_{jj}(\mathbf{R}) \end{aligned} \quad (\text{A. V.4})$$

for the five d-bands with again $dd\sigma \equiv -2dd\pi$, we obtain

$$\begin{aligned} E_{xy, xy} &= E_d - 32/9 dd\pi \cos\left(\frac{k_z a}{2}\right) \\ E_{yz, yz} &= E_d - 32/9 dd\pi \cos\left(\frac{k_z a}{2}\right) \\ E_{xz, xz} &= E_d - 32/9 dd\pi \cos\left(\frac{k_z a}{2}\right) \\ E_{x^2 - y^2, x^2 - y^2} &= E_d + 16/3 dd\pi \cos\left(\frac{k_z a}{2}\right) \\ E_{3z^2 - r^2, 3z^2 - r^2} &= E_d + 16/3 dd\pi \cos\left(\frac{k_z a}{2}\right) \end{aligned} \quad (\text{A. V.5})$$

These five d-bands are shown in Fig.A. V.4. The xz-, yz- and yz –bands are degenerate as well as the x^2-y^2 and the $3z^2-r^2$ bands. This degeneracy is partially lifted when second nearest neighbours are taken into account. The xz- and yz- bands remain, however, degenerate for $\mathbf{k}=(0,0, k_z)$.

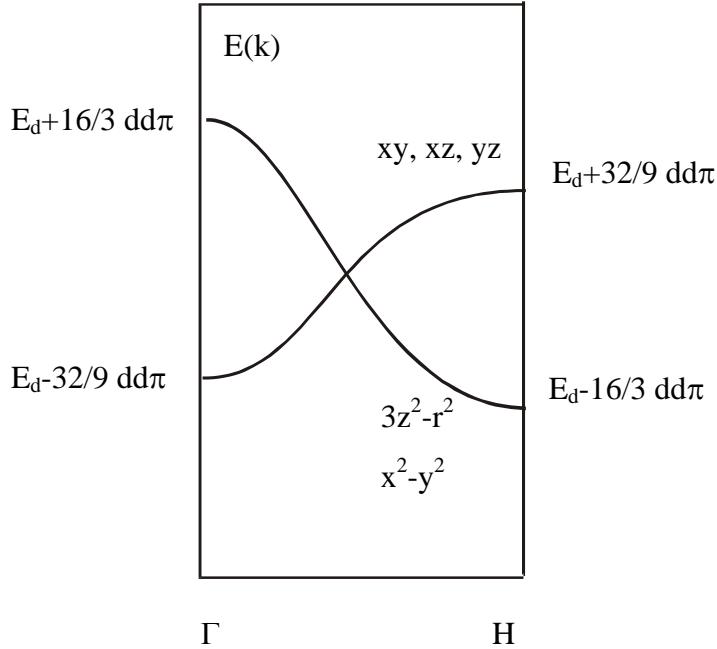


Fig.A. V.4: d-band structure of a metal with a BCC lattice when only nearest neighbour overlaps are taken into account (i.e. calculated from Eq.A.V.3). The overall shape is similar to that obtained for typical BCC metals such as Cr, Fe, and Mo.

V.3 EFFECT OF H ON A LINEAR CHAIN OF M ATOMS

We consider a linear chain of metal (M) atoms. The influence of interstitial hydrogen atoms (H) on the electronic structure is treated within the tight-binding approximation. The position of the building blocks is measured from the block without index in Fig.A. V.5.

The one-electron Schrödinger equation for the linear chain considered here is

$$\mathbf{H}\Psi_{\mathbf{k}}(\mathbf{r}) = (T + V_M + V_H + h)\Psi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}}\Psi_{\mathbf{k}}(\mathbf{r}) \quad (\text{A. V.6})$$

where T is the kinetic energy operator and V_i are the atomic potential of atom i in the building block with $R=0$ and h is the remaining potential. We seek a solution as a combination of atomic wave functions $\phi_j(\mathbf{r}-\mathbf{R}_j)$ (in the following to be indicated by $|M_j\rangle$) for an atomic wave function of a metal atom in building block j and by $|H_j\rangle$ for an atomic wave function of a hydrogen atom in the same building block j) located at the position of the atoms and satisfying the atomic Schrödinger equation

$$(T + V_M)|M\rangle = E_M|M\rangle \quad \text{and} \quad (T + V_H)|H\rangle = E_H|H\rangle \quad (\text{A. V.7})$$

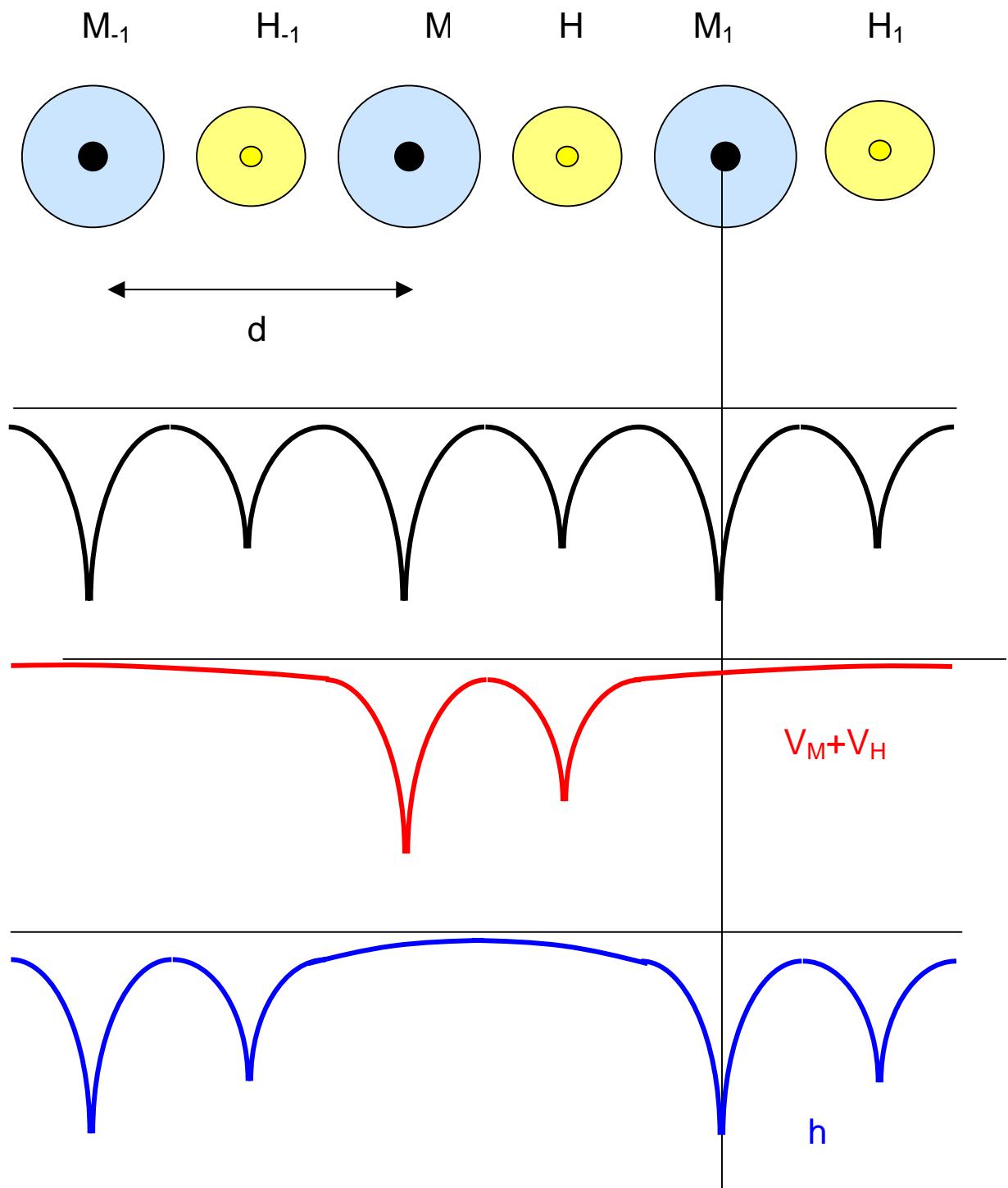


Fig.A. V.5: A linear chain of equidistant M atoms with H atoms added at each interstitial site. The distance between two M atoms is d . The periodic potential (black) is decomposed into a local potential V_M+V_H (red) and the remaining potential h (blue)

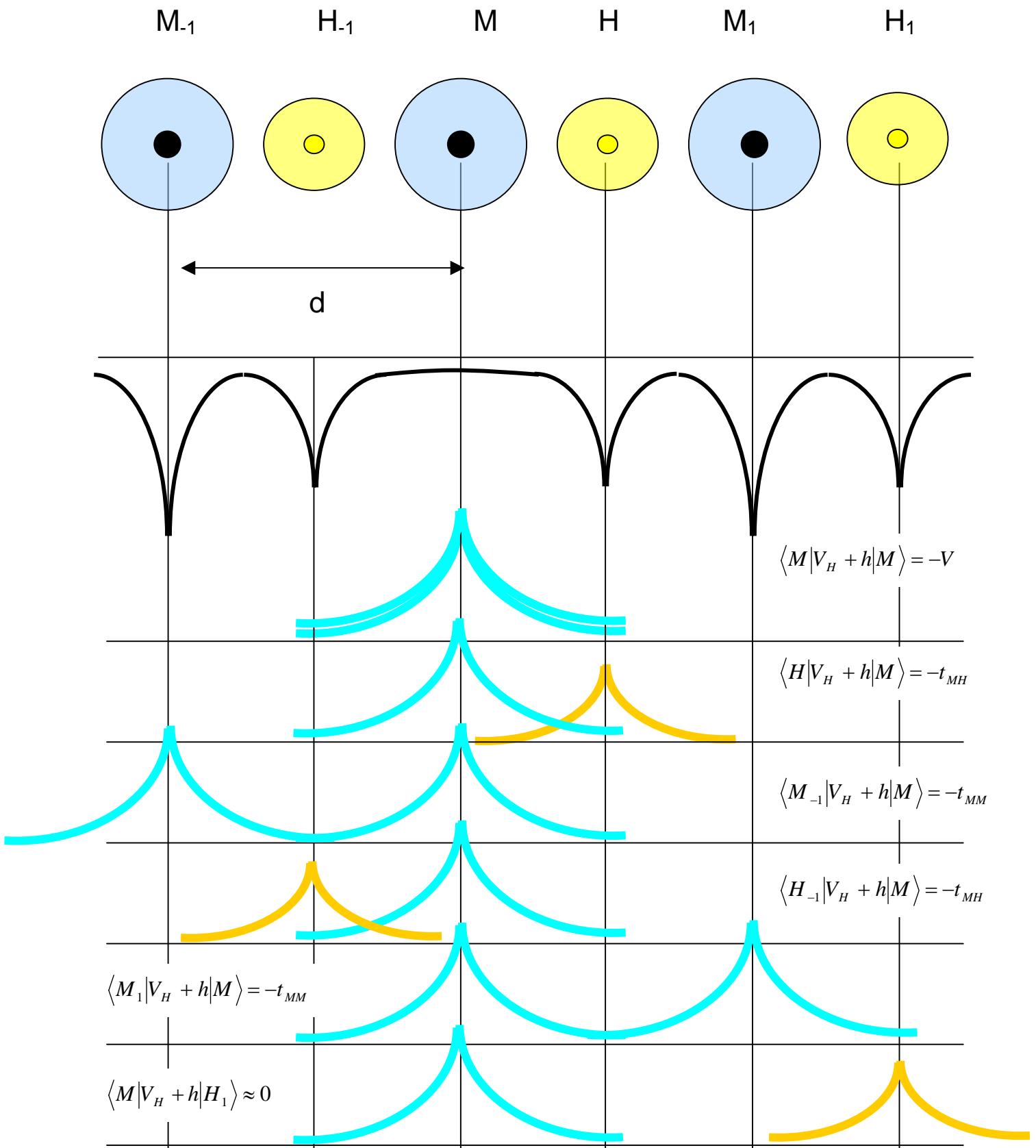


Fig.A. V.6: The various overlap integrals of the form $\langle X|V_H + h|M \rangle$ involved in the calculations of the linear M-H chain problem.

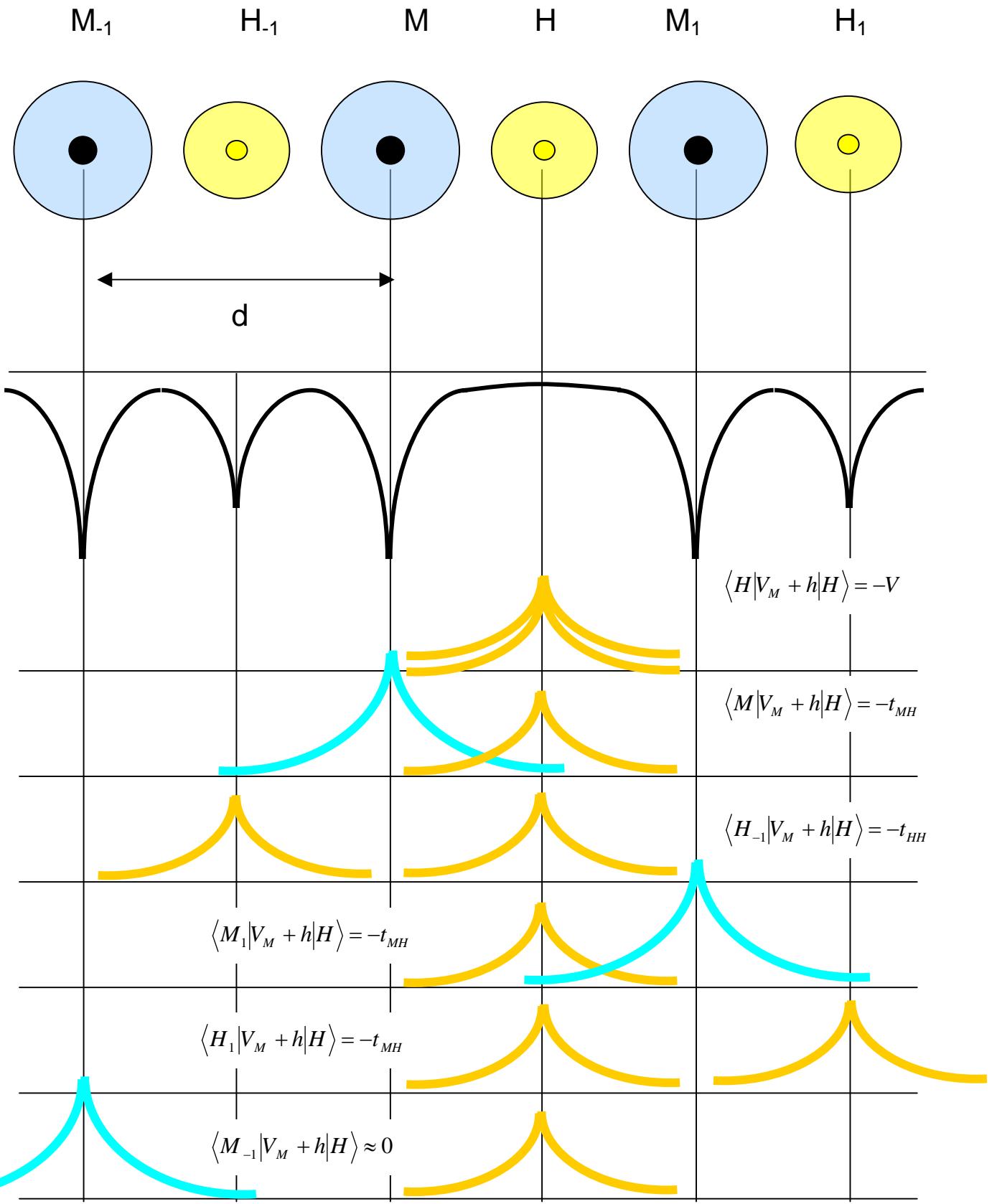


Fig.A. V.7: The various overlap integrals of the form $\langle X | V_M + h | H \rangle$ involved in the calculations of the linear M-H chain problem.

We seek a solution of Eq.A.V.7 in the form

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}_j} (\alpha |M_j\rangle + \beta |H_j\rangle) \quad (\text{A. V.8})$$

In the spirit of the tight-binding approximation we consider

$$\begin{aligned} \langle \Psi_{\mathbf{k}}(\mathbf{r}) | \mathbf{H} | M \rangle &= \langle \Psi_{\mathbf{k}}(\mathbf{r}) | T + V_M + V_H + h | M \rangle = \\ &= \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}_j} (\alpha \langle M_j | + \beta \langle H_j |) T + V_M + V_H + h | M \rangle = E_{\mathbf{k}} \alpha \end{aligned} \quad (\text{A. V.9})$$

and

$$\begin{aligned} \langle \Psi_{\mathbf{k}}(\mathbf{r}) | \mathbf{H} | H \rangle &= \langle \Psi_{\mathbf{k}}(\mathbf{r}) | T + V_M + V_H + h | H \rangle = \\ &= \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}_j} (\alpha \langle M_j | + \beta \langle H_j |) T + V_M + V_H + h | H \rangle = E_{\mathbf{k}} \beta \end{aligned} \quad (\text{A. V.10})$$

Keeping only nearest-neighbour terms these two equations lead to

$$\alpha(E_M - V_M - 2t_{MM} \cos kd) - \beta t_{MH} [1 + e^{ikd}] = E_k \alpha \quad (\text{A. V.11})$$

and

$$-\alpha t_{MH} [1 + e^{-ikd}] + \beta(E_H - V_H - 2t_{HH} \cos kd) = E_k \beta \quad (\text{A. V.12})$$

The various parameters t and V are defined in Fig.A. V.6 and Fig.A. V.7.
A non-trivial solution exists only when the following determinant vanishes,

$$\begin{aligned} (E_M - V_M - 2t_{MM} \cos kd - E_k)(E_H - V_H - 2t_{HH} \cos kd - E_k) \\ - t_{MH}^2 [1 + e^{ikd}] [1 + e^{-ikd}] = 0 \end{aligned} \quad (\text{A. V.13})$$

that can be simplified to

$$\begin{aligned} (E_M - V_M - 2t_{MM} \cos kd - E_k)(E_H - V_H - 2t_{HH} \cos kd - E_k) \\ - 2t_{MH}^2 [1 + \cos kd] = 0 \end{aligned} \quad (\text{A. V.14})$$

For each k-value there are two solutions. In Fig.A. V.8 we give a numerical example. The effect of hydrogen is to create a low-lying bonding state as observed in band structure calculations. In a

d-band metal there would be additional states corresponding to $3z^2-r^2$, x^2-y^2 , xy , xz , and yz . The green curve in Fig.A. V.8 can be associated with the $3z^2-r^2$ state since this is the only one that can couple to the hydrogen s-state. The other four d-states remain unchanged after insertion of hydrogen atoms.

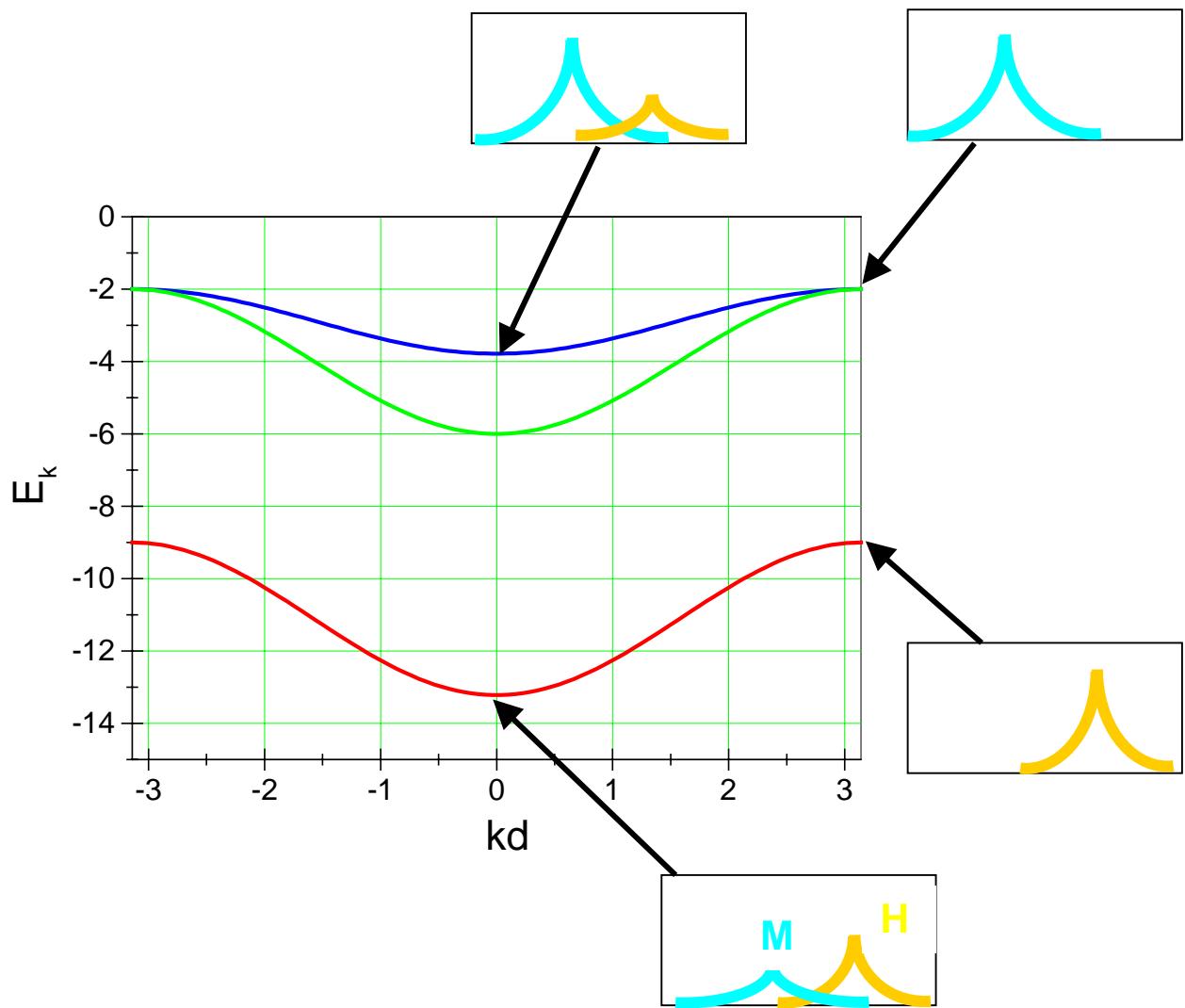


Fig.A. V.8: Electronic band structure of the linear M-H chain of atoms obtained from Eq.A.V.14 with $E_M = -4$, $E_H = -10$, $V_M = V_H = 0$, $t_{MM} = 1$, $t_{HH} = 0.5$ and $t_{MH} = 2$. In absence of hydrogen $t_{HH} = t_{MH} = 0$ and one obtains the green curve. The eigenvectors are schematically indicated for four characteristic points. At the boundary of the Brillouin zone the states are either purely “metal” or purely “hydrogen”. At the centre of the Brillouin zone the bonding state has 77% hydrogen character and the antibonding state 23% hydrogen character.