Electronic structure of transition metal-hydrides

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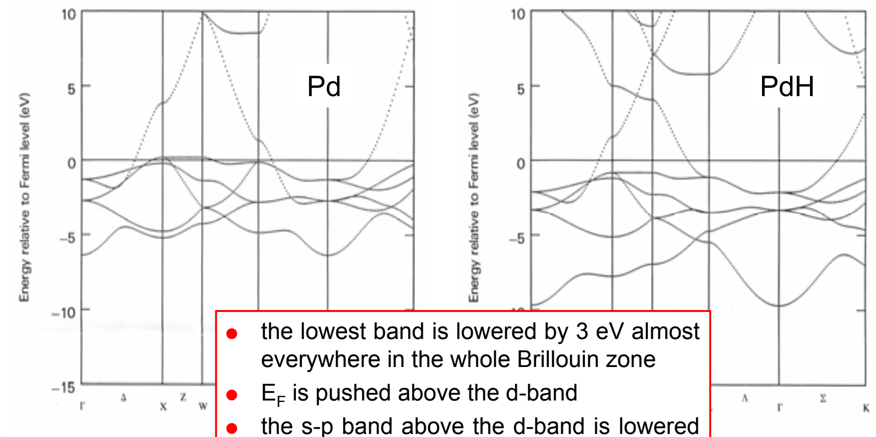
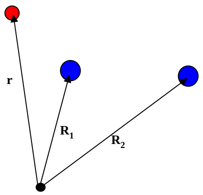
Purpose of this lecture



- the lowest band is lowered by 3 eV almost everywhere in the whole Brillouin zone
- E_F is pushed above the d-band
- the s-p band above the d-band is lowered somewhat. The shift is significantly smaller than that of the lowest band.
- the width of the d-band is reduced with respect to that of pure Pd.

1st reminder: the H_2^+ molecule ion



Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\Delta+V(\mathbf{R}_1-\mathbf{r})+V(\mathbf{R}_2-\mathbf{r})+V(\mathbf{R}_2-\mathbf{R}_1)\right]\psi(\mathbf{r})=\varepsilon\psi(\mathbf{r})$$

Solution as linear combination of atomic wave functions

$$\psi(\mathbf{r}) = a\,\phi_{1s}(\mathbf{R}_1-\mathbf{r})+b\,\phi_{1s}(\mathbf{R}_2-\mathbf{r})$$

$$a(\varepsilon_{1s}-V)-bt=\varepsilon a$$
$$-at+b(\varepsilon_{1s}-V)=\varepsilon b$$

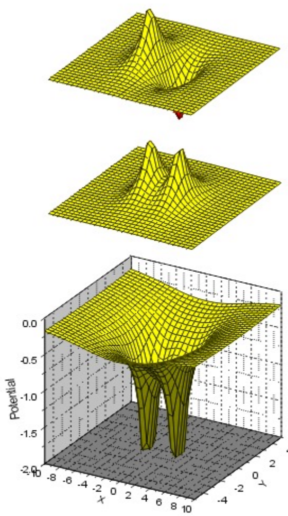
$$t \equiv -\left\langle \phi(\mathbf{r}-\mathbf{R}_1)\middle| V(\mathbf{r}-\mathbf{R}_2)\middle|\phi(\mathbf{r}-\mathbf{R}_2)\right\rangle$$

$$V \equiv -\left\langle \phi(\mathbf{r}-\mathbf{R}_1)\middle| V(\mathbf{r}-\mathbf{R}_2)\middle|\phi(\mathbf{r}-\mathbf{R}_1)\right\rangle$$

$$\begin{vmatrix} \varepsilon_{1s}-V-\varepsilon & -t \\ -t & \varepsilon_{1s}-V-\varepsilon \end{vmatrix} = 0$$

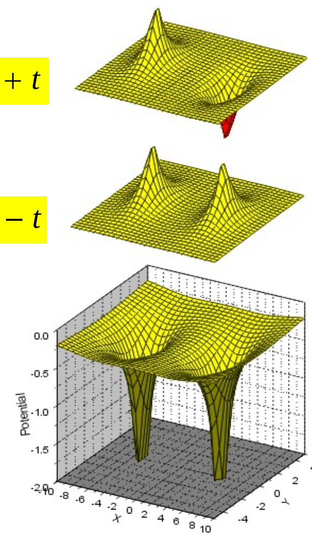
$$\varepsilon = \varepsilon_{1s} - V \pm t$$

Bonding and antibonding states



$\varepsilon = \varepsilon_{1s} - V + t$

$\varepsilon = \varepsilon_{1s} - V - t$



2nd reminder: a linear chain of atoms

Solution of the Schrödinger equation for one electron in a crystal

$$\psi_{\mathbf{k}}(x) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{kR}} \, \phi(\mathbf{r}-\mathbf{R})$$

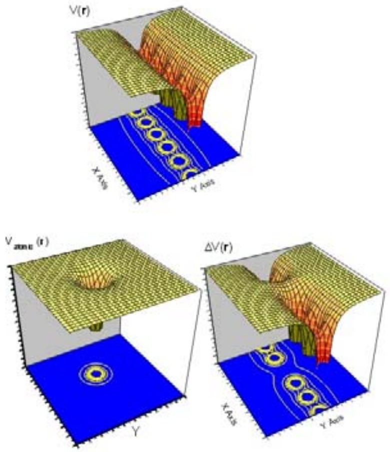
leads to the energy

$$\varepsilon_{\mathbf{k}} = E_{atomic} - \Delta V - t \sum_{\mathbf{R}_{nn}} e^{i\mathbf{k}\cdot\mathbf{R}}$$

with

$$t \equiv -\left\langle \phi(\mathbf{r}) \middle| \Delta V(\mathbf{r}) \middle| \phi(\mathbf{r}-\mathbf{R}) \right\rangle$$

$$\Delta V \equiv -\left\langle \phi(\mathbf{r}) \middle| \Delta V(\mathbf{r}) \middle| \phi(\mathbf{r}) \right\rangle$$



3rd reminder: only *s* –states, but in 3D

Solution of the Schrödinger equation for one electron in a crystal

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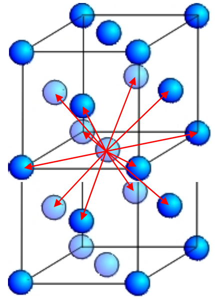


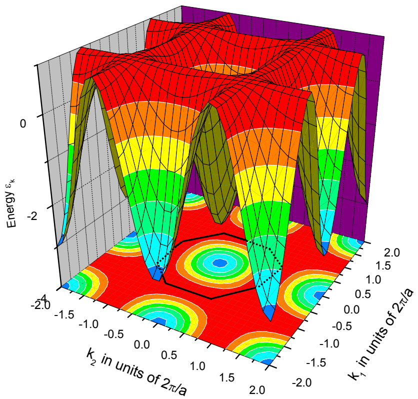
$$\mathbf{a}_1 = \frac{a}{2}(\pm\hat{\mathbf{x}} \pm \hat{\mathbf{y}})$$

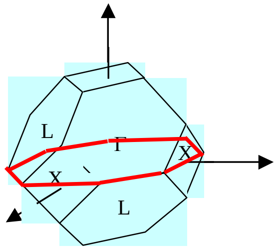
$$\mathbf{a}_2 = \frac{a}{2}(\pm\hat{\mathbf{y}} \pm \hat{\mathbf{z}})$$

$$\mathbf{a}_3 = \frac{a}{2}(\pm\hat{\mathbf{x}} \pm \hat{\mathbf{z}})$$

s – energy band

$$\varepsilon_{\mathbf{k}} = E_{atomic} - \Delta V - 2t\left[\cos\left(\frac{k_1 a}{2}\right)\cos\left(\frac{k_2 a}{2}\right) + \cos\left(\frac{k_1 a}{2}\right)\cos\left(\frac{k_3 a}{2}\right) + \cos\left(\frac{k_2 a}{2}\right)\cos\left(\frac{k_3 a}{2}\right)\right]$$





The tight-binding approximation

Schrödinger equation for one electron in a crystal

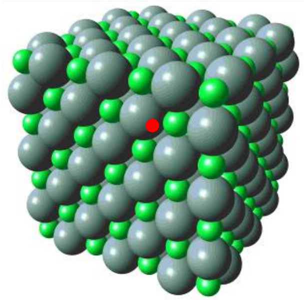
$$H\Psi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}}\Psi_{\mathbf{k}}$$

Solution of the form

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \underset{\substack{\text{sum over} \\ \text{all atomic sites}}}{\sum_{\mathbf{R}}} e^{i\mathbf{k}\cdot\mathbf{R}} \sum_j c_j \varphi_j(\mathbf{r}-\mathbf{R})$$

where $\varphi_j(\mathbf{r}-\mathbf{R})$ is an atomic wave function located at **R** which satisfies the atomic Schrödinger equation

$$H_{atomic}\varphi_j = E_j \varphi_j$$



The tight-binding approximation

Schrödinger equation for one electron in a crystal

$$H\Psi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}}\Psi_{\mathbf{k}}$$

Solution of the form

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \underbrace{\sum_{\mathbf{R}}}_{\text{sum over all atomic sites}} e^{i\mathbf{k}\cdot\mathbf{R}} \sum_j c_j \varphi_j(\mathbf{r}-\mathbf{R})$$

where $\varphi_j(\mathbf{r-R})$ is an atomic wave function located at **R** which satisfies the atomic Schrödinger equation

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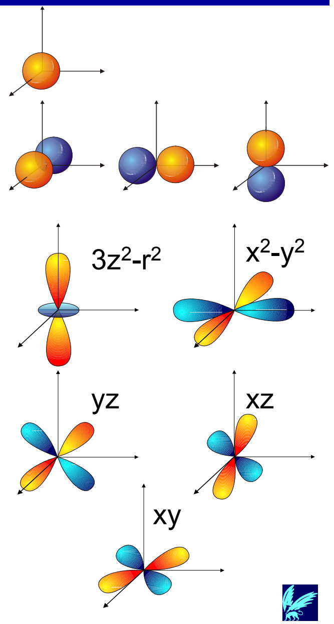


Schrödinger equation in a matrix form

Schrödinger equation in a matrix form. Multiply by an atomic function $\varphi_m(\mathrm{r})$

$$\varphi_m(\mathbf{r})H\Psi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}}\varphi_m(\mathbf{r})\Psi_{\mathbf{k}}(\mathbf{r})$$

and integrate over real space

$$\langle\varphi_m(\mathbf{r})|H|\Psi_{\mathbf{k}}(\mathbf{r})\rangle = E_{\mathbf{k}}\langle\varphi_m(\mathbf{r})|\Psi_{\mathbf{k}}(\mathbf{r})\rangle$$

Make use of the orthogonality of the $\varphi_j(\mathrm{r})$ located at the *same* atomic site,

$$\langle\varphi_m(\mathbf{r})|\varphi_j(\mathbf{r})\rangle = \delta_{mj}$$

and quasi-orthogonality $\langle\varphi_j(\mathbf{r})|\varphi_m(\mathbf{r}+\mathbf{R})\rangle \cong \delta_{R=0}\delta_{jm}$

Schrödinger equation in matrix form

Then

$$\begin{aligned}\langle\varphi_m(\mathbf{r})|H|\Psi_k(\mathbf{r})\rangle &= \sum_R e^{i\mathbf{k}\cdot\mathbf{R}} \sum_{j=1}^{L} c_j \langle\varphi_m(\mathbf{r})|H|\varphi_j(\mathbf{r}-\mathbf{R})\rangle \\ &= \sum_{j=1}^{L} c_j \left[\sum_R e^{i\mathbf{k}\cdot\mathbf{R}} \langle\varphi_m(\mathbf{r})|H|\varphi_j(\mathbf{r}-\mathbf{R})\rangle\right] \\ &= E_k \sum_j c_j \left[\sum_R e^{i\mathbf{k}\cdot\mathbf{R}} \langle\varphi_m(\mathbf{r})|\varphi_j(\mathbf{r}-\mathbf{R})\rangle\right] \\ &\cong E_k c_m\end{aligned}$$

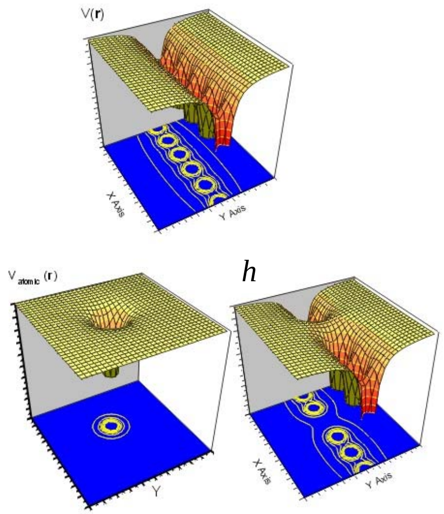
In matrix notation

$$\begin{bmatrix} \sum_R e^{i\mathbf{k}\cdot\mathbf{R}}\langle\varphi_1(\mathbf{r})|H|\varphi_1(\mathbf{r}-\mathbf{R})\rangle & \cdots & \sum_R e^{i\mathbf{k}\cdot\mathbf{R}}\langle\varphi_L(\mathbf{r})|H|\varphi_1(\mathbf{r}-\mathbf{R})\rangle \\ \vdots & \ddots & \vdots \\ \sum_R e^{i\mathbf{k}\cdot\mathbf{R}}\langle\varphi_1(\mathbf{r})|H|\varphi_L(\mathbf{r}-\mathbf{R})\rangle & \cdots & \sum_R e^{i\mathbf{k}\cdot\mathbf{R}}\langle\varphi_L(\mathbf{r})|H|\varphi_L(\mathbf{r}-\mathbf{R})\rangle \end{bmatrix} \begin{bmatrix} c_1 \\ \vdots \\ c_L \end{bmatrix} \cong E_k \begin{bmatrix} c_1 \\ \vdots \\ c_L \end{bmatrix}$$

The potential

Close to a given atom the crystal potential resembles strongly the atomic potential

$$H = H_{atomic} + h$$



Vanishing determinant

With the overlap integral $B_{mj}(\mathbf{R}) = \langle \varphi_m(\mathbf{r}) | h | \varphi_j(\mathbf{r}-\mathbf{R}) \rangle$

The matrix is

$$\begin{bmatrix} E_m + \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} B_{11}(\mathbf{R}) & \cdots & \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} B_{1L}(\mathbf{R}) \\ \vdots & \ddots & \vdots \\ \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} B_{L1}(\mathbf{R}) & \cdots & E_j + \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} B_{LL}(\mathbf{R}) \end{bmatrix} \begin{bmatrix} c_1 \\ \vdots \\ c_L \end{bmatrix} \cong E_k \begin{bmatrix} c_1 \\ \vdots \\ c_L \end{bmatrix}$$

A non-trivial solution exists if the determinant vanishes

$$\begin{vmatrix} E_1 + \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} B_{11}(\mathbf{R}) - E_k & \cdots & \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} B_{1L}(\mathbf{R}) \\ \vdots & \ddots & \vdots \\ \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} B_{L1}(\mathbf{R}) & \cdots & E_j + \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} B_{LL}(\mathbf{R}) - E_k \end{vmatrix} = 0$$

Vanishing determinant

With the overlap integral $B_{mj}(\mathbf{R}) = \langle \varphi_m(\mathbf{r}) | h | \varphi_j(\mathbf{r}-\mathbf{R}) \rangle$

A non-trivial solution exists if the determinant vanishes

$$\begin{vmatrix} E_1 + \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} B_{11}(\mathbf{R}) - E_k & \cdots & \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} B_{1L}(\mathbf{R}) \\ \vdots & \ddots & \vdots \\ \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} B_{L1}(\mathbf{R}) & \cdots & E_j + \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} B_{LL}(\mathbf{R}) - E_k \end{vmatrix} = 0$$

$$\begin{vmatrix} \varepsilon_{1s} + G - \varepsilon & -t \\ -t & \varepsilon_{1s} + G - \varepsilon \end{vmatrix} = 0 \qquad t \equiv -\langle \phi(\mathbf{r}-\mathbf{R}_1) | V(\mathbf{r}-\mathbf{R}_2) | \phi(\mathbf{r}-\mathbf{R}_2) \rangle$$

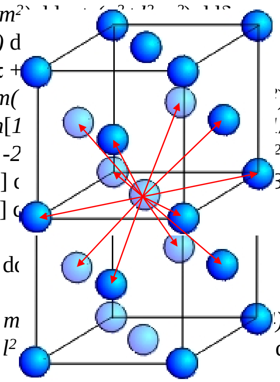
Overlap integrals after Slater and Koster (1954)

(l, m, n) are the direction cosines of the lattice vector **R.** The fundamental overlap integrals are ddσ, ddπ and ddδ

$B_{xy,\,xy}$	$3 l^2m^2$ ddσ $+(l^2+m^2-4 l^2 m^2)$ ddπ $+ (n^2+l^2 m^2)$ ddδ
$B_{xy,\,yz}$	$3 l^2 m^2n$ ddσ $+ln(1-4 m^2)$ ddπ $+ ln(m^2-1)$ ddδ
$B_{xy,\,xz}$	$3 l^2mn$ ddσ $+(1-4 l^2)$ ddπ $+ mn(l^2-1)$ ddδ
$B_{xy,\,x^2-y^2}$	$(3/2)lm (l^2- m^2)$ ddσ $+2lm(m^2- l^2)$ ddπ $+ (1/2)lm(l^2- m^2)$ ddδ
$B_{yz,\,x^2-y^2}$	$(3/2)mn (l^2- m^2)$ ddσ $-mn[1+2(l^2- m^2)]$ddπ $+ mn[1+(1/2)(l^2- m^2)]$ ddδ
$B_{xz,\,x^2-y^2}$	$(3/2)nl (l^2- m^2)$ ddσ $-nl[1-2(l^2- m^2)]$ddπ $- nl[1-(1/2)(l^2- m^2)]$ ddδ
$B_{xy,\,3z^2-r^2}$	$\sqrt{3}\, lm[n^2-(1/2) (l^2+ m^2)]$ ddσ $-2\sqrt{3}\, lmn^2$ ddπ $+ (1/2)\sqrt{3}\, (1+n^2)$ ddδ
$B_{yz,\,3z^2-r^2}$	$\sqrt{3}mn[n^2-(1/2) (l^2+ m^2)]$ ddσ $+\sqrt{3}\, mn(l^2+m^2-n^2)$ ddπ $- (1/2)\sqrt{3}mn (l^2+m^2)$ ddδ
$B_{xz,\,3z^2-r^2}$	$\sqrt{3}ln[n^2-(1/2) (l^2+ m^2)]$ ddσ $+\sqrt{3}\, ln(l^2+m^2-n^2)$ ddπ $- (1/2)\sqrt{3}ln (l^2+m^2)$ ddδ
$B_{x^2-y^2,\,x^2-y^2}$	$(3/4)(l^2- m^2)^2$ ddσ $+[l^2+ m^2 -(l^2- m^2)^2]dd\pi$ $+[n^2+ (1/4)(l^2- m^2)^2]$ ddδ
$B_{x^2-y^2,\,3z^2-r^2}$	$(\sqrt{3}/2)(l^2- m^2) [n^2- (1/2)(l^2+ m^2)]$ ddσ $+\sqrt{3}n^2 (m^2- l^2)]dd\pi$ $+[(1+n^2) (l^2- m^2)]$ ddδ
$B_{3z^2-r^2,\,3z^2-r^2}$	$[n^2- (1/2)(l^2+ m^2)]^2$ ddσ $+3n^2 (l^2+ m^2)$ ddπ $+ (3/4)(l^2+ m^2)^2$ ddδ

Overlap integrals after Slater and Koster (1954)

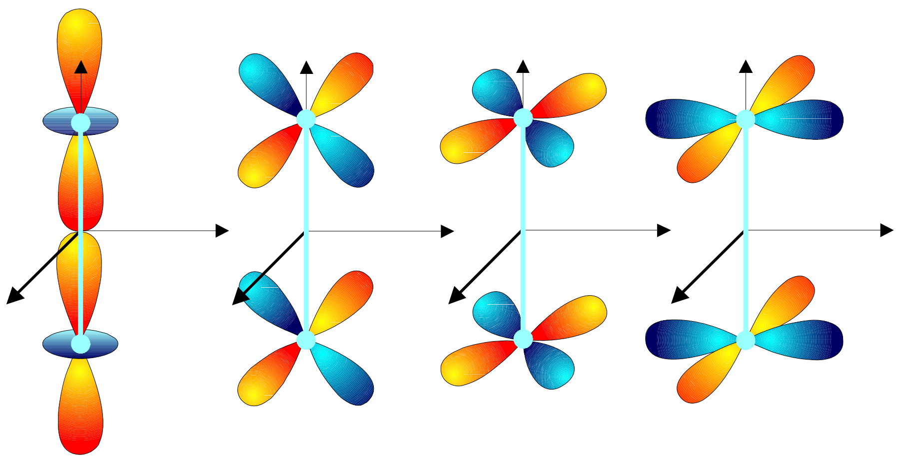
(l, m, n) are the direction cosines of the lattice vector **R.** The fundamental overlap integrals are ddσ, ddπ and ddδ



$B_{xy,\,xy}$	$3 l^2m^2$ ddσ $+(l^2+m^2-4 l^2 m^2$ …
$B_{xy,\,yz}$	$3 l^2 m^2n$ ddσ $+ln(1-4 m^2)$ d …
$B_{xy,\,xz}$	$3 l^2mn$ ddσ $+(1-4 l^2)$ ddπ + …
$B_{xy,\,x^2-y^2}$	$(3/2)lm (l^2- m^2)$ ddσ $+2lm($ …) ddδ
$B_{yz,\,x^2-y^2}$	$(3/2)mn (l^2- m^2)$ ddσ $-mn[1$ … $/2)(l^2- m^2)]$ ddδ
$B_{xz,\,x^2-y^2}$	$(3/2)nl (l^2- m^2)$ ddσ $-nl[1-2$ … $- m^2)]$ ddδ
$B_{xy,\,3z^2-r^2}$	$\sqrt{3}\, lm[n^2-(1/2) (l^2+ m^2)]$ … $3 (1+n^2)$ ddδ
$B_{yz,\,3z^2-r^2}$	$\sqrt{3}mn[n^2-(1/2) (l^2+ m^2)]$ … $- (1/2)\sqrt{3}mn (l^2+m^2)$ ddδ
$B_{xz,\,3z^2-r^2}$	$\sqrt{3}ln[n^2-(1/2) (l^2+ m^2)]$ … $- (1/2)\sqrt{3}ln (l^2+m^2)$ ddδ
$B_{x^2-y^2,\,x^2-y^2}$	$(3/4)(l^2- m^2)^2$ ddσ $+[l^2+ m$ … $)(l^2- m^2)^2]$ ddδ
$B_{x^2-y^2,\,3z^2-r^2}$	$(\sqrt{3}/2)(l^2- m^2) [n^2- (1/2)(l^2$ … ddπ $+[(1+n^2) (l^2- m^2)]$ ddδ
$B_{3z^2-r^2,\,3z^2-r^2}$	$[n^2- (1/2)(l^2+ m^2)]^2$ ddσ $+3n^2 (l^2+ m^2)$ ddπ $+ (3/4)(l^2+ m^2)^2$ ddδ

Elementary overlap integrals

ddσ ddπ ddδ ddδ



d-d overlap integrals for FCC

Overlap integrals after Slater and Koster for the nearest-neighbours in the FCC lattice. The fundamental overlap integrals ddσ, ddπ and ddδ are defined in Table.VI.1. The ddδ overlap integral are set equal to zero

$B_{xy,\,xy}$	3/4 ddσ	for [110]
$B_{xy,\,xy}$	1/2 ddπ	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	
$B_{x^2-y^2,\,x^2-y^2}$	ddπ	for [110]
$B_{x^2-y^2,\,3z^2-r^2}$	3/16ddσ +1/4ddπ	for [101] and [01
$B_{3z^2-r^2,\,3z^2-r^2}$	1/4 ddσ	for [110]
$B_{3z^2-r^2,\,3z^2-r^2}$	1/16 ddσ +3/4 ddπ	for [101] and [011]

For a FCC metal

$$E_k = E_d + \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} B_{jj}(\mathbf{R})$$

$$= E_d + 2\sum{}^{*} \cos(\mathbf{k}\cdot\mathbf{R}) B_{jj}(\mathbf{R})$$

$$E_{xy,xy} = E_d + 4dd\pi\cos(\frac{k_z a}{2}) + 3dd\sigma$$

$$E_{yz,yz} = E_d + 3dd\sigma\cos(\frac{k_z a}{2}) + 2dd\pi\left(1+\cos(\frac{k_z a}{2})\right)$$

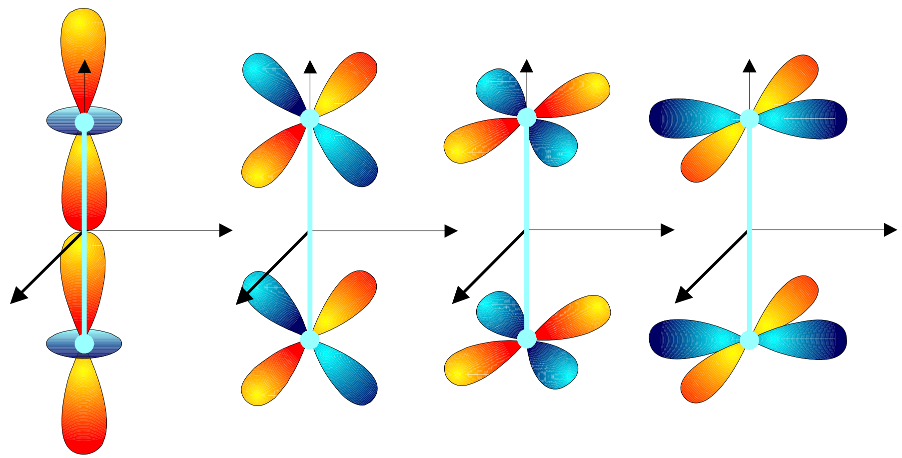
$$E_{xz,xz} = E_d + 3dd\sigma\cos(\frac{k_z a}{2}) + 2dd\pi\left(1+\cos(\frac{k_z a}{2})\right)$$

$$E_{x^2-y^2,x^2-y^2} = E_d + 4dd\pi + \left(\frac{3}{2}dd\sigma + 2dd\pi\right)\cos(\frac{k_z a}{2}) +$$

$$E_{3z^2-r^2,3z^2-r^2} = E_d + \left(\frac{1}{2}dd\sigma + 6dd\pi\right)\cos(\frac{k_z a}{2}) + dd\sigma$$

Approximation $dd\sigma = -2dd\pi$

ddσ ddπ ddδ ddδ



Approximation

$$dd\sigma = -2dd\pi$$

$$E_{xy,xy} = E_d + 4dd\pi\left(\cos(\frac{k_z a}{2}) - \frac{3}{2}\right)$$

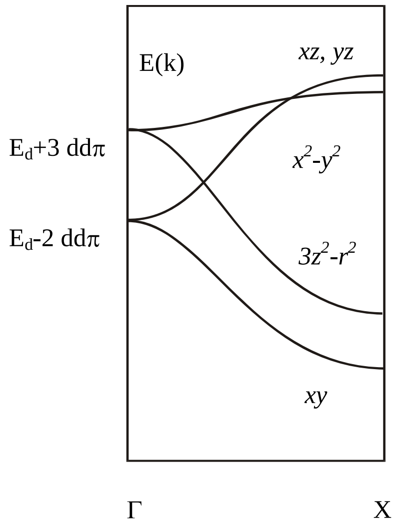
$$E_{yz,yz} = E_d + 2dd\pi\left(1 - 2\cos(\frac{k_z a}{2})\right)$$

$$E_{xz,xz} = E_d + 2dd\pi\left(1 - 2\cos(\frac{k_z a}{2})\right)$$

$$E_{x^2-y^2,x^2-y^2} = E_d + dd\pi\left(4 - \cos(\frac{k_z a}{2})\right)$$

$$E_{3z^2-r^2,3z^2-r^2} = E_d + 5dd\pi\left(\cos(\frac{k_z a}{2}) - \frac{2}{5}\right)$$

Bands along ΓX



$$E_{xy,xy} = E_d + 4dd\pi\left(\cos(\frac{k_z a}{2}) - \frac{3}{2}\right)$$

$$E_{yz,yz} = E_d + 2dd\pi\left(1 - 2\cos(\frac{k_z a}{2})\right)$$

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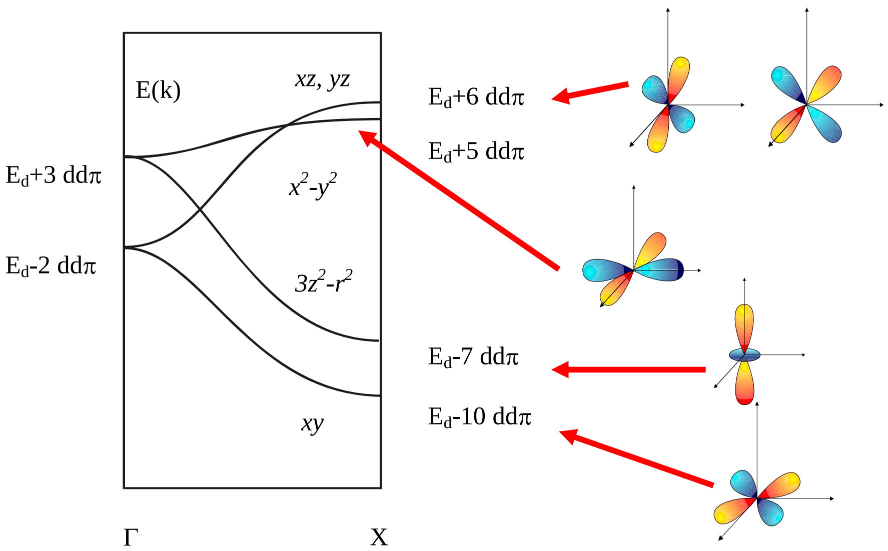
$$E_{3z^2-r^2,3z^2-r^2} = E_d + 5dd\pi\left(\cos(\frac{k_z a}{2}) - \frac{2}{5}\right)$$

Bands along ΓX

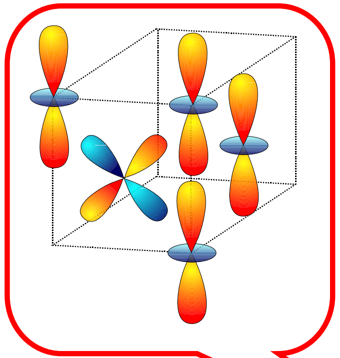


d-states only

Determinant for **k** parallel to the z-axis if one considers only 1s- and 5d- states.

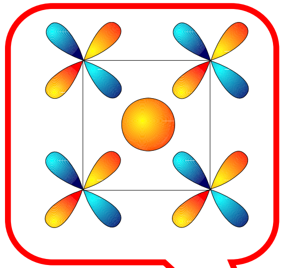
$$\begin{vmatrix} E_s + \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} B_{ss} - E_k & 0 & 0 & \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} B_{s,3z^2-r^2} & 0 & 0 \\ 0 & \ddots & 0 & \vdots & 0 & 0 \\ 0 & 0 & \ddots & \vdots & 0 & 0 \\ \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} B_{s,3z^2-r^2} & 0 & 0 & E_d + \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} B_{3z^2-r^2,3z^2-r^2}(\mathbf{R}) - E_k & 0 & 0 \\ 0 & 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & \ddots \end{vmatrix} = 0$$

No overlap



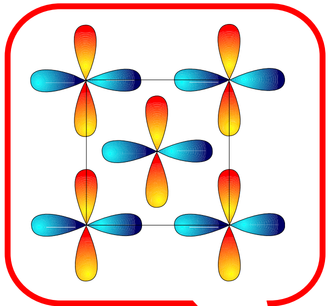
$$\begin{vmatrix} E_s+\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{ss}-E_k & 0 & 0 & \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{s,3z^2-r^2} & 0 & 0 \\ 0 & \ddots & 0 & \vdots & 0 & 0 \\ 0 & 0 & \ddots & 0 & 0 & 0 \\ \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{s,3z^2-r^2} & 0 & 0 & E_d+\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{3z^2-r^2,3z^2-r^2}(\mathbf{R})-E_k & 0 & 0 \\ 0 & 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & \ddots \end{vmatrix}=0$$

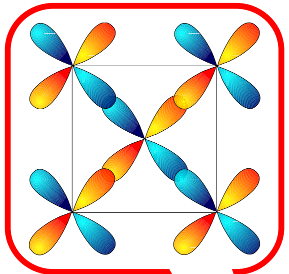
No hybridisation



$$\begin{vmatrix} E_s+\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{ss}-E_k & 0 & 0 & \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{s,3z^2-r^2} & 0 & 0 \\ 0 & \ddots & 0 & \vdots & 0 & 0 \\ 0 & 0 & \ddots & \vdots & 0 & 0 \\ \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{s,3z^2-r^2} & 0 & 0 & E_d+\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{3z^2-r^2,3z^2-r^2}(\mathbf{R})-E_k & 0 & 0 \\ 0 & 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & \ddots \end{vmatrix}=0$$

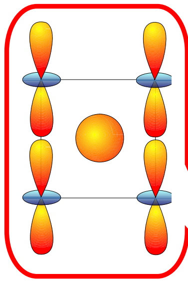
Diagonal *d* - elements

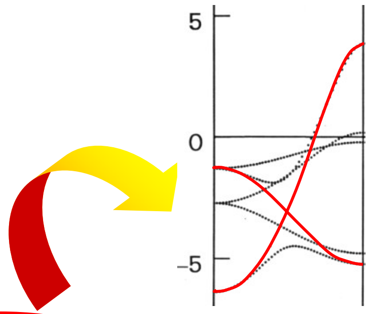




$$\begin{vmatrix} E_s+\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{ss}-E_k & 0 & 0 & \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{s,3z^2-r^2} & 0 & 0 \\ 0 & \ddots & 0 & \vdots & 0 & 0 \\ 0 & 0 & \ddots & \vdots & 0 & 0 \\ \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{s,3z^2-r^2} & 0 & 0 & E_d+\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{3z^2-r^2,3z^2-r^2}(\mathbf{R})-E_k & 0 & 0 \\ 0 & 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & \ddots \end{vmatrix}=0$$

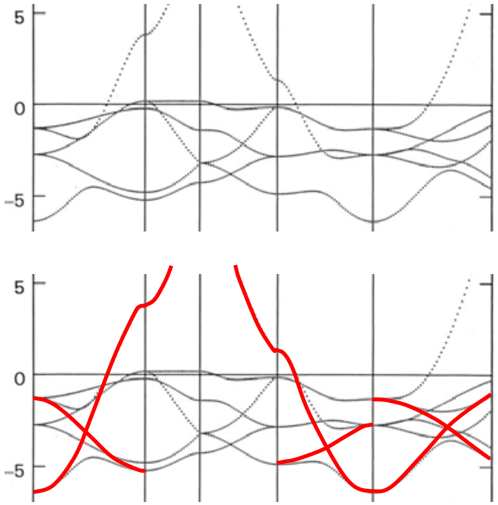
s-*d*-hybridisation



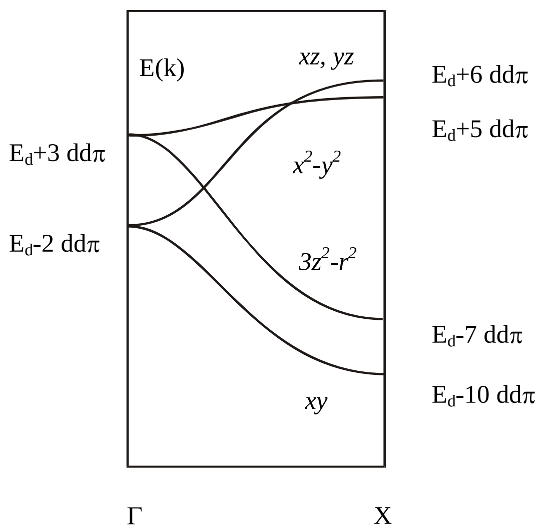


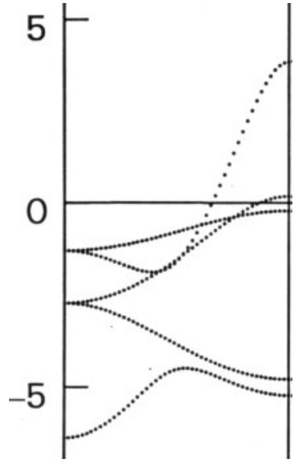
$$\begin{vmatrix} E_s+\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{ss}-E_k & 0 & 0 & \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{s,3z^2-r^2} & 0 & 0 \\ 0 & \ddots & 0 & \vdots & 0 & 0 \\ 0 & 0 & \ddots & \vdots & 0 & 0 \\ \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{s,3z^2-r^2} & 0 & 0 & E_d+\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}B_{3z^2-r^2,3z^2-r^2}(\mathbf{R})-E_k & 0 & 0 \\ 0 & 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & \ddots \end{vmatrix}=0$$

Influence of *s*-*d*-hybridisation

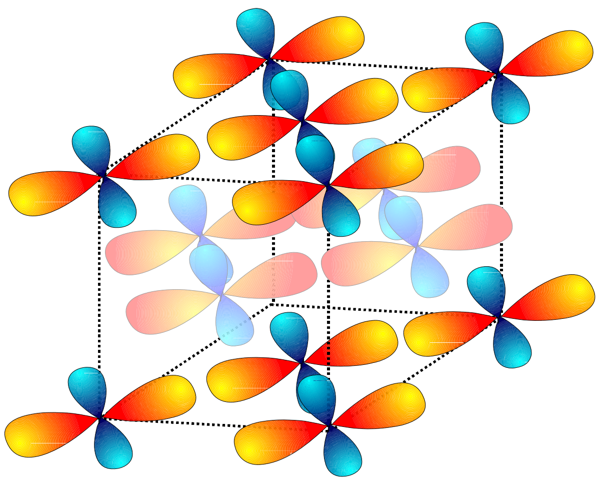


Comparison

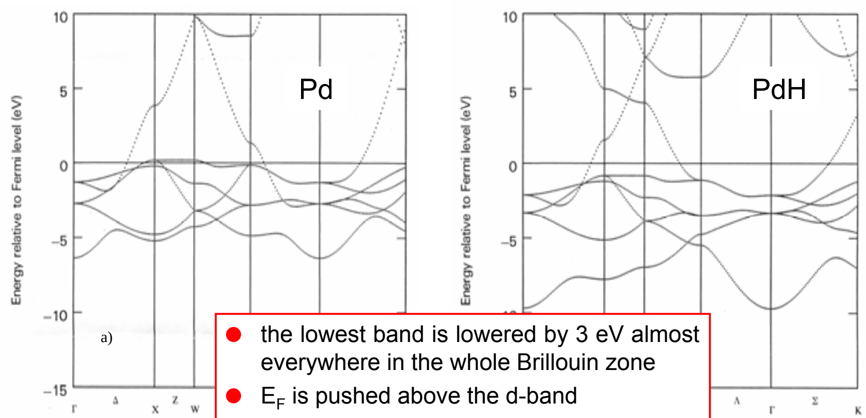




For FCC metals d_{xy} has the lowest energy

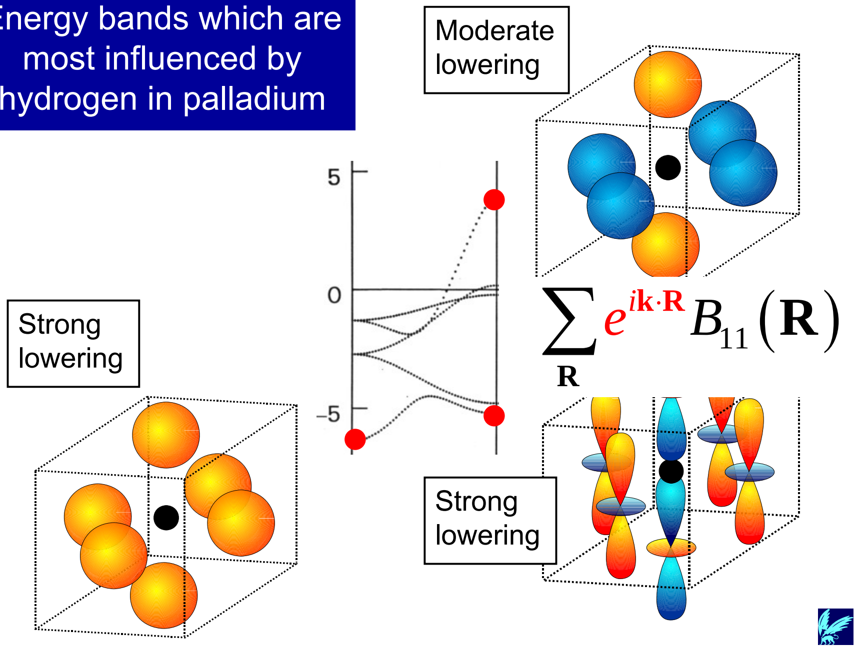


You are now ready to understand this !

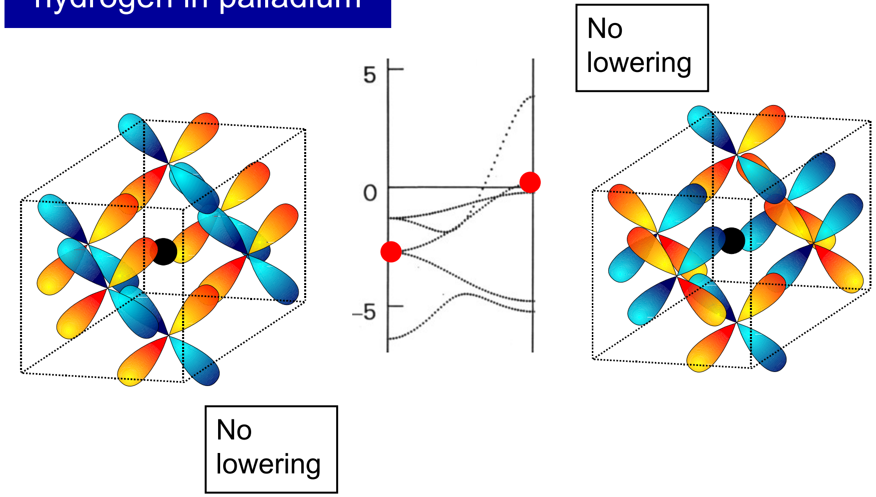


- the lowest band is lowered by 3 eV almost everywhere in the whole Brillouin zone
- E_F is pushed above the d-band
- the s-p band above the d-band is lowered somewhat. The shift is significantly smaller than that of the lowest band.
- the width of the d-band is reduced with respect to that of pure Pd.

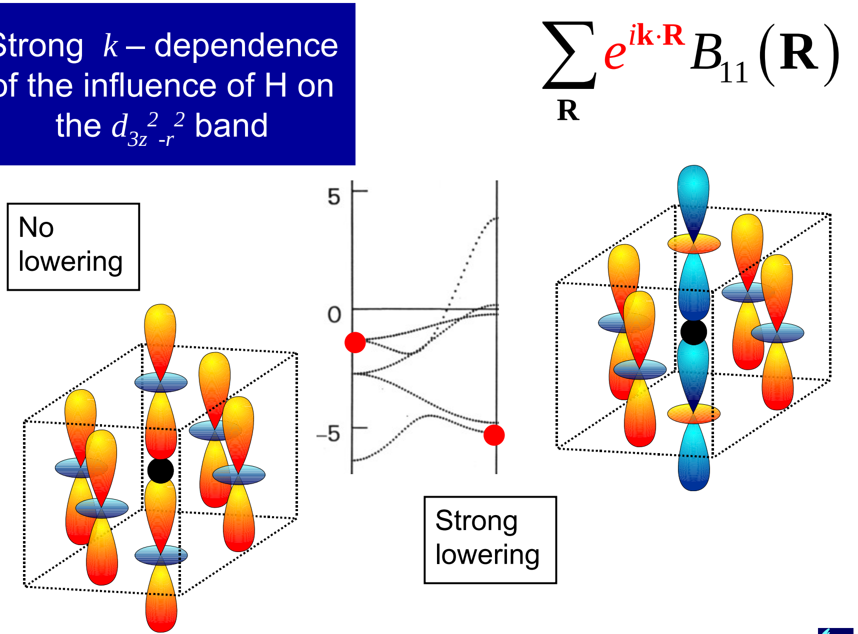
Energy bands which are most influenced by hydrogen in palladium



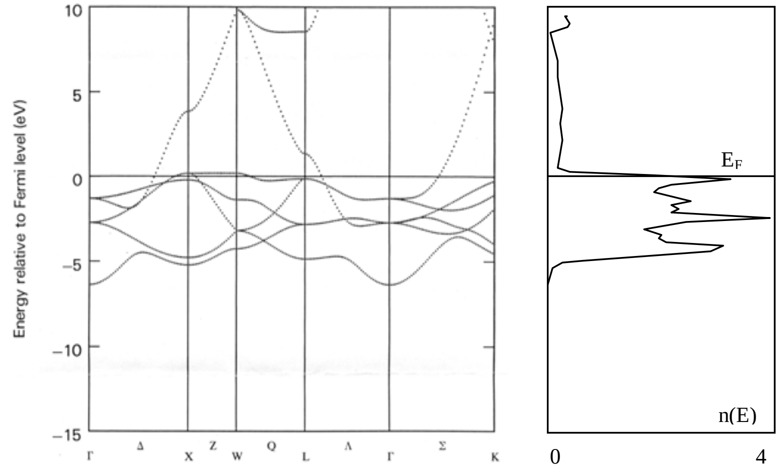
Energy bands which are not influenced by hydrogen in palladium



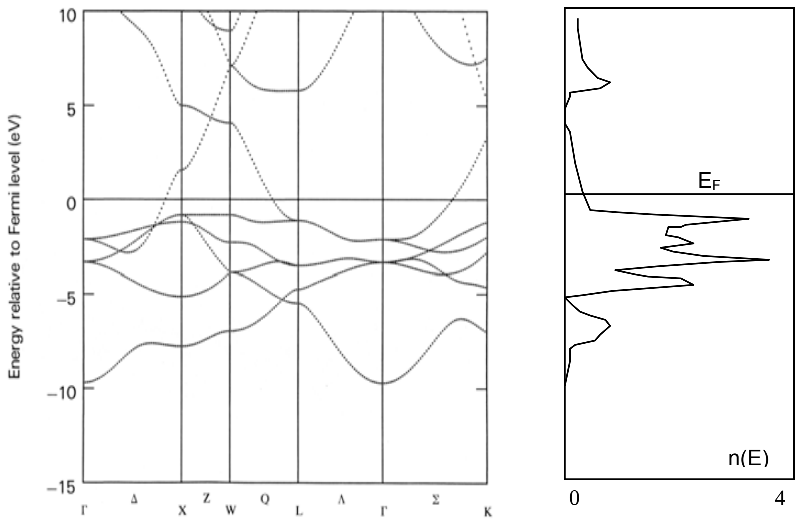
Strong k – dependence of the influence of H on the $d_{3z^2-r^2}$ band



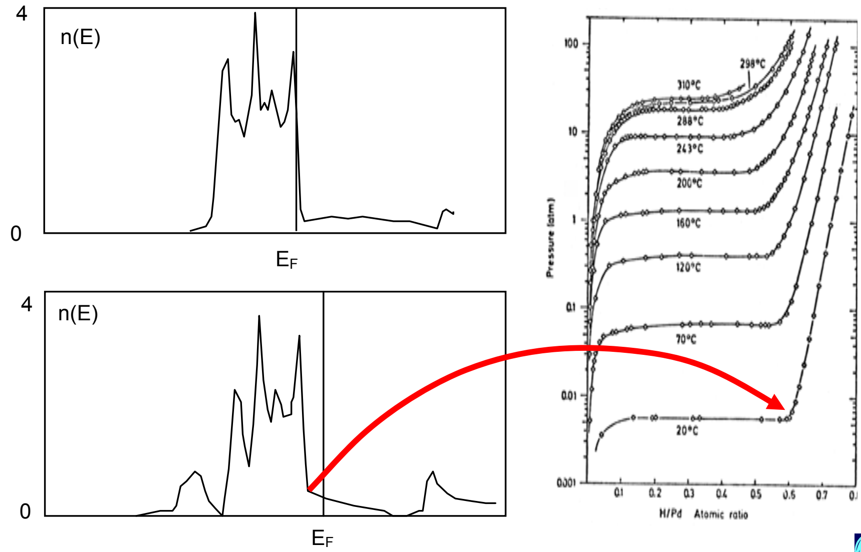
Density of states of Pd



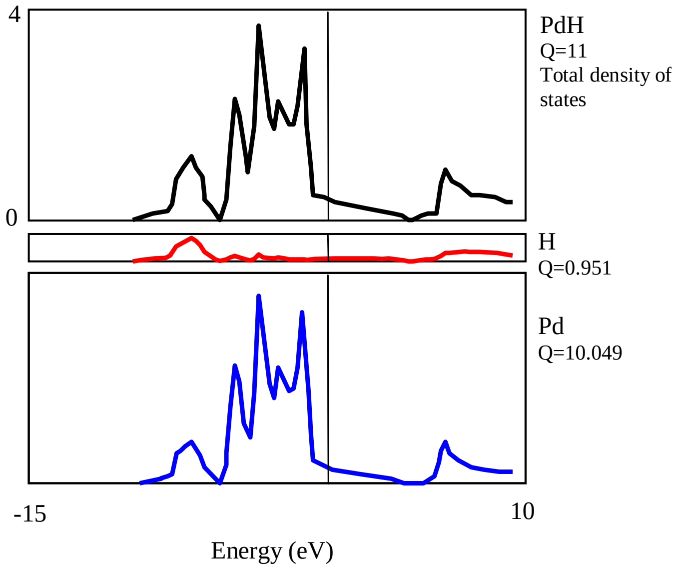
Density of states of PdH



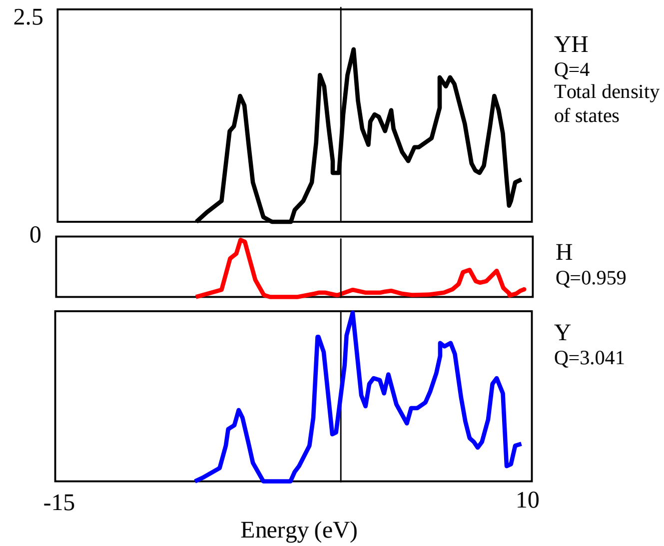
Influence of H on the density of states



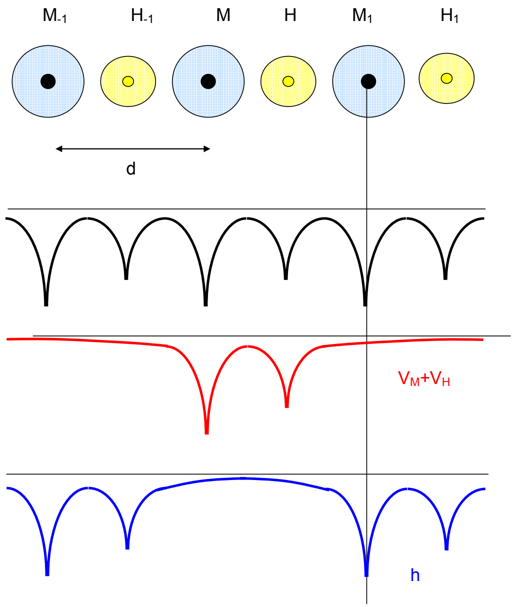
Site projected density of states in PdH

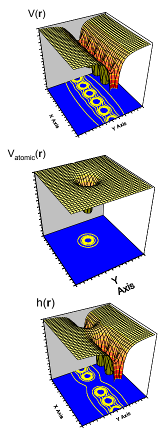


Site projected density of states in YH

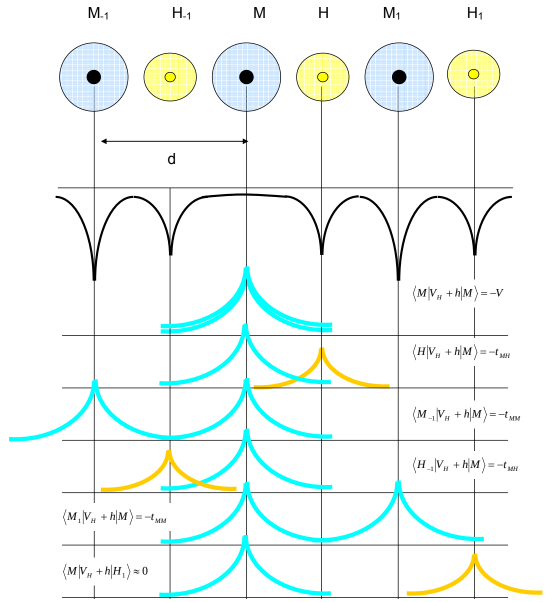


Simple linear chain model for MH

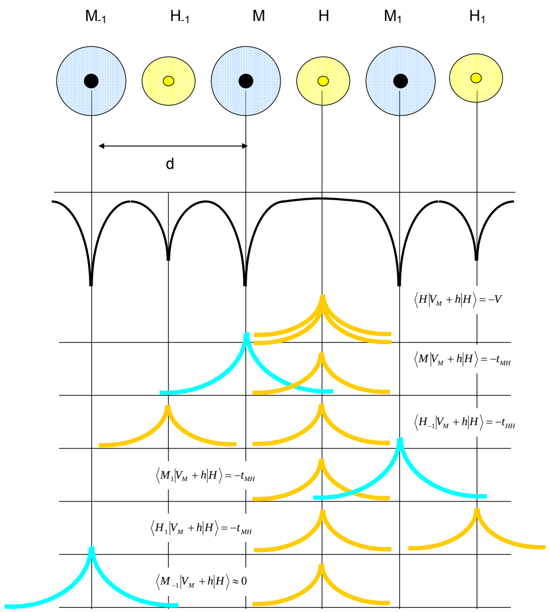




Overlap integrals of the form $\langle X | V_H + h | H \rangle$



Overlap integrals of the form $\langle X | V_M + h | H \rangle$



Band structure MH

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R_j}} \left(\alpha \left| M_j \right\rangle + \beta \left| H_j \right\rangle \right)$$

$$\langle \Psi_{\mathbf{k}}(\mathbf{r}) | \mathbf{H} | M \rangle = \langle \Psi_{\mathbf{k}}(\mathbf{r}) | T + V_M + V_H + h | M \rangle =$$
$$= \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R_j}} \left(\alpha \langle M_j | + \beta \langle H_j | \right) \left| T + V_M + V_H + h \right| M \rangle = E_{\mathbf{k}} \alpha$$

$$\langle \Psi_{\mathbf{k}}(\mathbf{r}) | \mathbf{H} | H \rangle = \langle \Psi_{\mathbf{k}}(\mathbf{r}) | T + V_M + V_H + h | H \rangle =$$
$$= \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R_j}} \left(\alpha \langle M_j | + \beta \langle H_j | \right) \left| T + V_M + V_H + h \right| H \rangle = E_{\mathbf{k}} \beta$$

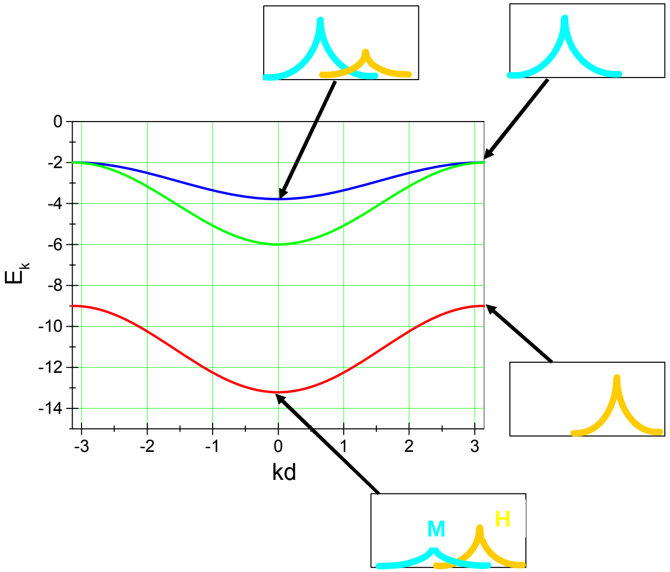
$$+\alpha \left(E_M - V_M - 2t_{MM} \cos kd \right) - \beta\, t_{MH} \left[1 + e^{+ikd} \right] = E_k \alpha$$
$$-\alpha\, t_{MH} \left[1 + e^{-ikd} \right] + \beta \left(E_H - V_H - 2t_{HH} \cos kd \right) = E_k \beta$$

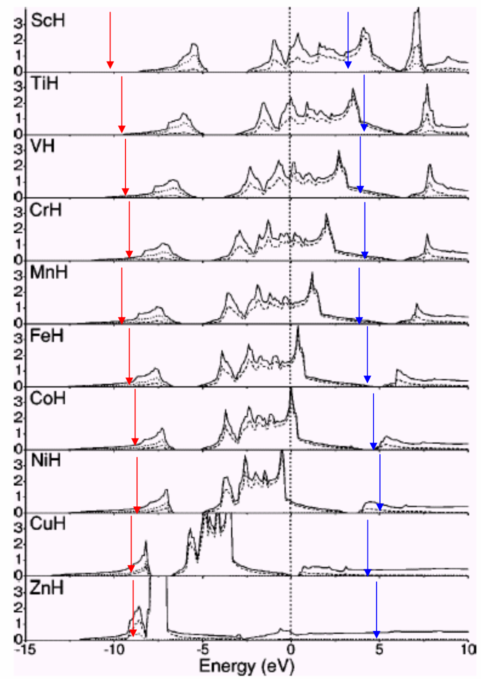
$$\left(E_M - V_M - 2t_{MM} \cos kd - E_k \right)\left(E_H - V_H - 2t_{HH} \cos kd - E_k \right) - t_{MH}^2 \left[1 + e^{ikd} \right]\left[1 + e^{-ikd} \right] = 0$$

$$\left(E_M - V_M - 2t_{MM} \cos kd - E_k \right)\left(E_H - V_H - 2t_{HH} \cos kd - E_k \right) - 2t_{MH}^2 \left[1 + \cos kd \right] = 0$$

Band structure of MH

$E_M = -4$,
$E_H = -10$
$V_M = V_H = 0$
$t_{MM} = 1$
$t_{HH} = 0.5$
$t_{MH} = 2$

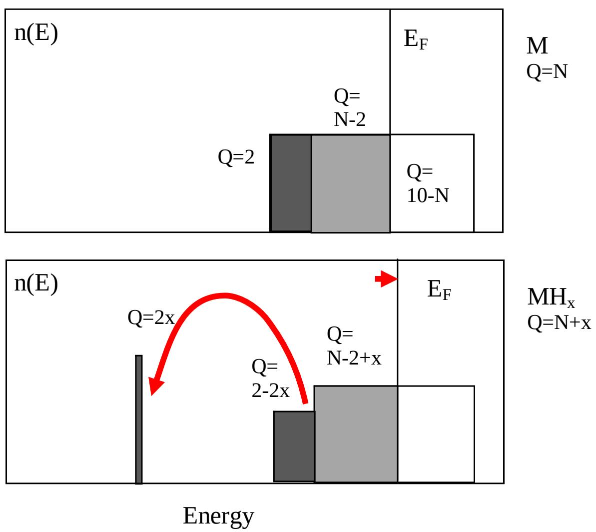


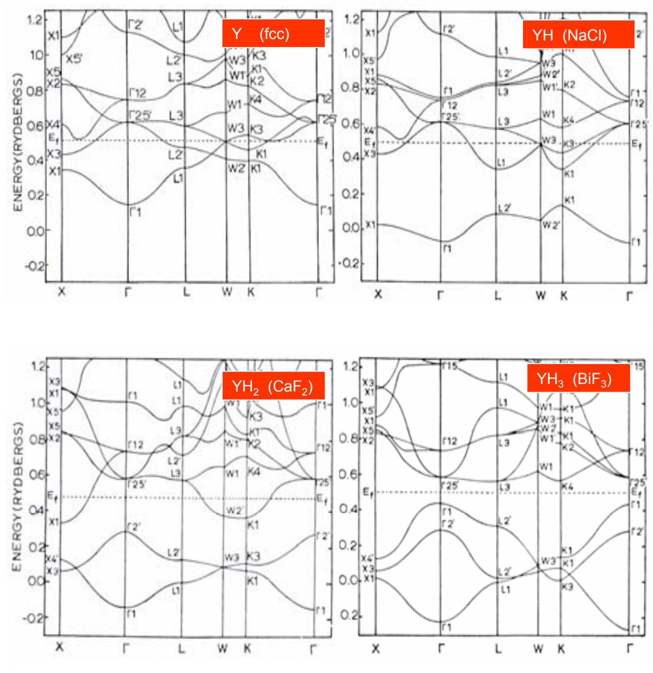


Density of states of transition metal-hydrides

Smithson, H., C.A. Marianetti, D. Morgan, A. van der Ven, A. Predith and G. Ceder, Phys. Rev. B66 (2002) 144107

Schematic influence of H on DOS of PdH_x





Low lying bands in YH_n

Why is YH_3 not a metal ?

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More than 24 theoretical papers !