Condensed Matter Physics

Molecular dynamics II.

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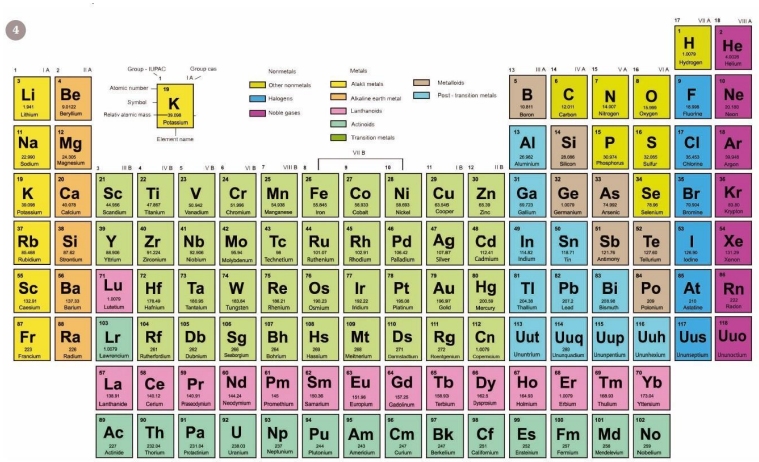
Transition metal



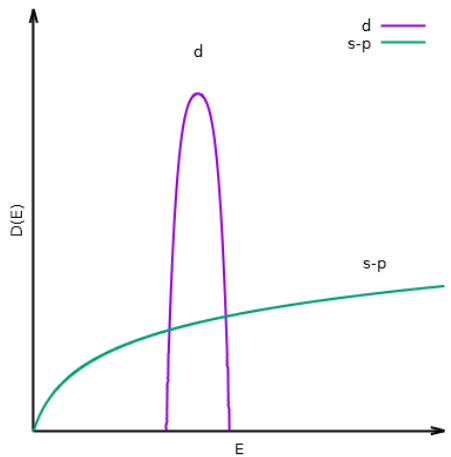


Figure: Density of states

Friedel-model

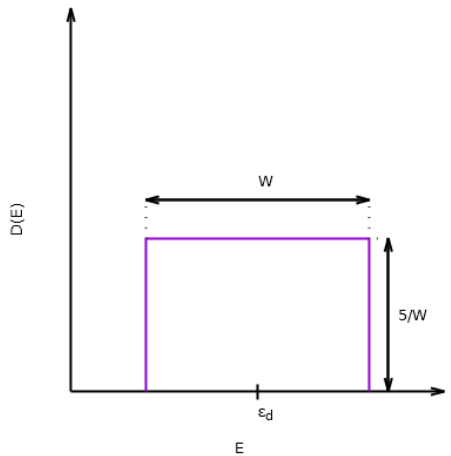


Figure: Density of states in the Friedel-model

There are 2*5 d elektron states

$$E_{bond} = 2\int^{E_f}(E-\alpha)D(E)dE$$

For our case

$$E_{bond} = 2\int_{\varepsilon_d-\frac{W}{2}}^{E_f}(E-\varepsilon_d)\frac{5}{W}dE =$$

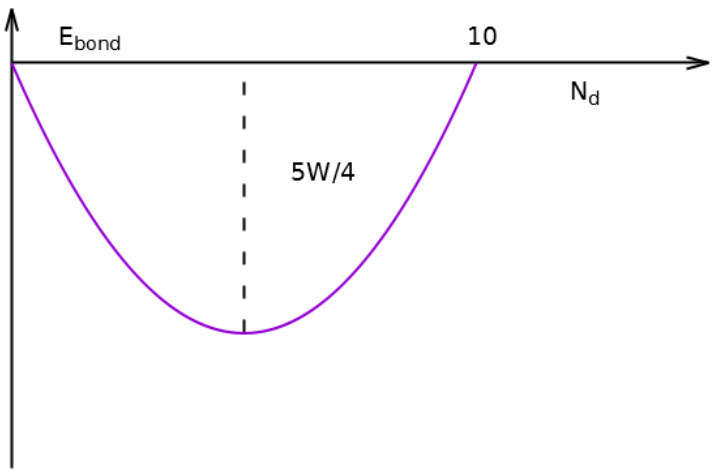
Friedel-model

The Fermi energy is determined by the number of electrons

$$N_d = 2 \int_{\varepsilon_d - \frac{W}{2}}^{E_f} \frac{5}{W} dE = \frac{10}{W} \left(E_f - \varepsilon_d + \frac{W}{2} \right)$$

The bounding energy is

$$E_{bond} = -\frac{W}{20} N_d (10 - N_d)$$



Second moment of the density of states

Let us consider a base system given by $|i\rangle$
The density of states corresponding to the state $|i\rangle$ can be defined as

$$d_i(E) = \sum_{\text{all } E_k} \delta(E - E_k)\langle i|\psi_k\rangle\langle\psi_k|i\rangle$$

The second moment of $d_i(E)$ is

$$\mu_i^{(2)} = \int (E - H_{ii})^2 d_i(E) dE$$

That is

$$\mu_i^{(2)} = \int_{band} \sum_{E_k} (E - H_{ii})^2 \delta(E - E_k)\langle i|\psi_k\rangle\langle\psi_k|i\rangle dE$$

leading to

$$\mu_i^{(2)} = \sum_{E_k} (E_k - H_{ii})^2 \langle i|\psi_k\rangle\langle\psi_k|i\rangle$$

$$\mu_i^{(2)} = \langle i| \underbrace{\left(\sum_{E_k} |\psi_k\rangle (E_k - H_{ii})^2 \langle\psi_k| \right)}_{(\hat{H} - H_{ii})^2} |i\rangle$$

$$\mu_i^{(2)} = \sum_{i'} \langle i|(\hat{H} - H_{ii})|i'\rangle\langle i'|(\hat{H} - H_{ii})|i\rangle$$

Second moment of the density of states

Since

$$\langle i|\hat{H} - H_{ii}|i\rangle = 0 \qquad \langle i|\hat{H} - H_{ii}|i'\rangle = H_{ii'} \qquad i \neq i'$$

one gets

$$\mu_i^{(2)} = H_{ii'} H_{i'i}$$

That is

$$\mu_i^{(2)} = z\beta^2$$

with z is the number of core electrons, and β is the "hopping" probability.
In the Friedel model

$$\mu_i^{(2)} = \int_{\varepsilon_d - \frac{W}{2}}^{\varepsilon_d + \frac{W}{2}} (E - \varepsilon_d)^2 \frac{1}{W} dE = \frac{W^2}{12}$$

From this one gets W

$$W = (12z)^{\frac{1}{2}} |\beta| \qquad \beta(R) \approx N_d e^{-\kappa R}$$

β is an exponential function with characteristic length scale $1/\kappa$.

Interaction energy

Bounding energy

$$E_{bond} = -\frac{bN_d^2(12z)^{\frac{1}{2}}}{20} e^{-\kappa R} N_d(10 - N_d) \tag{1}$$

Repulsive energy

$$E_{rep} = aN_d^2 e^{-2\kappa R} \tag{2}$$

Total energy

$$E_{\omega h} = E_{rep} + E_{bond} \tag{3}$$

With these

$$E_{\omega h} = Ae^{-2\kappa R} - Be^{-\kappa R} \tag{4}$$

B is calculated, A and κ are empirical parameters.

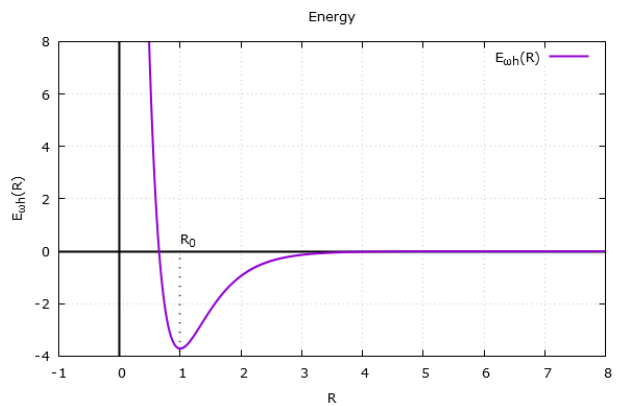


Figure: $E_{\omega h}(R)$

Interaction energy

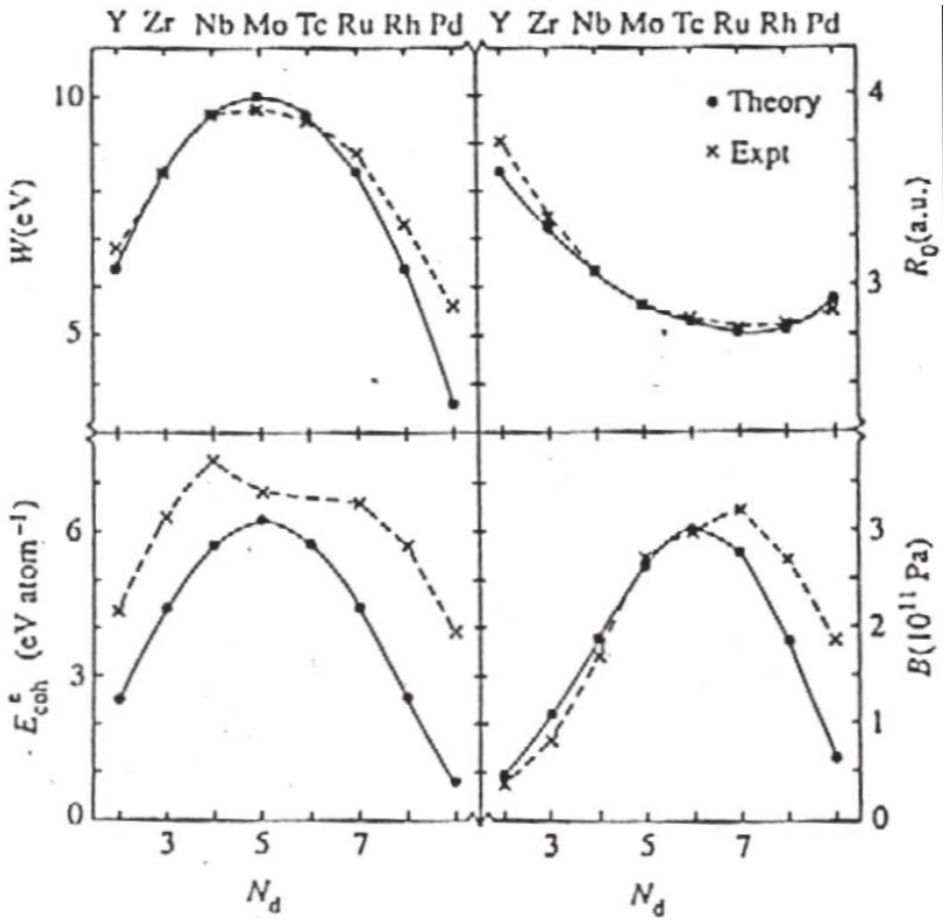


Figure: Predicted variations in properties across the 4d transient metal series based on the Friedel model in the second moment approximation compared with experiment (from Pettifor 1987). Top left: the bandwidth, W. Top right: the equilibrium bond ength, R_0 in Bohr. Bottom left: the cohersive energy, $E^e_{\rm coh}$. Bottom right: the bulk modulus B in 10^{11} Pa units.

Finnis-Sinclair potential

They assumed that the states are “localized” to the *i*th atom
The bounding energy is

$$E_{bond} = 2 \sum_i \int^{E_f} (E - \varepsilon_i) d_i(E) dE$$

For the density of state Finnis suggested a Gaussian function:

$$d_i(E) = \frac{5}{\sqrt{2\pi\mu_i^{(2)}}} \exp\left(-\frac{(E-\varepsilon_i)^2}{2\mu_i^{(2)}} \right)$$

So the energy of the electron “bounded to the *i*th atom is:

$$E_{bond}^{(i)} = 2 \int_{-\infty}^{E_f} d_i(E)(E-\varepsilon_i) dE = -\frac{10}{\sqrt{2\pi}} \sqrt{\mu_i^{(2)}} \exp\left(-\frac{(E_f-\varepsilon_i)^2}{2\mu_i^{(2)}} \right)$$

Assuming that the atoms are neutral

$$N_d = \int_{-\infty}^{E_f} d_i(E) dE$$

Finnis-Sinclair potential

Let us introduce L_i with:

$$N_d = \frac{10}{\sqrt{\pi}} \int_{-\infty}^{L_i} e^{-x^2} dx \qquad\qquad L_i = \frac{(E_f - \varepsilon_i)}{\sqrt{2\mu_i^{(2)}}}$$

Assuming that the number of electrons(N_d) are the same for all atoms one sees L_i is independent from i:

$$L_i := L$$

Az így kapott kötési energián azt látjuk, hogy nem párok összegeként áll elő:

$$E_{bond}^{(i)} = const.\sqrt{\mu_i^{(2)}}$$

Where

$$\mu_i^{(2)} = \sum_j H_{ij} H_{ji} = \sum_j \phi(r_{ij})$$

is a sum.

Embedded potential

Total energy

$$V(\vec{r}_1, \vec{r}_2, \ldots) = \sum_{i \neq j} \phi_1(\vec{r}_1 - \vec{r}_i) + \sum_i \sqrt{\sum_j \phi(r_{ij})}$$

Generalized form

$$V(\vec{r}_1, \vec{r}_2, \ldots) = \sum_{i \neq j} \phi_1(\vec{r}_1 - \vec{r}_i) + \sum_i F\left(\sum_j \phi(r_{ij})\right)$$

where F is some function.