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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

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# PAIR POTENTIALS IN AMORPHOUS METALLIC ALLOYS: ORDER, STABILITY AND DYNAMICS

## Lecture II

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Summary of 1st lecture:

$\tilde{H}_{i-i} = H_{i-i} + E_{el}(\{\vec{R}_e\})$ effective ion-ion Hamilt.

$E_{el} = E_0 + E_1 + E_2 + \ldots$ electr. ground-state energ.

$E_0 = Z E_{eg}$

$E_1 = \beta Z / \Omega_0$

$E_2 = \sum_{q \neq 0} |S(\vec{q})|^2 F(q)$, $\quad F(q) = -\frac{1}{2} \Omega_0 \frac{\chi(q)}{\epsilon(q)} |w(\vec{q})|^2$

$\vdots$

$\tilde{H}_{i-i} = T_i + E_\Omega + \frac{1}{N} \sum_{i<j} V^{(2)}(|\vec{R}_i - \vec{R}_j|) + \ldots\ldots$

$E_\Omega = Z E_{eg} + \beta Z / \Omega_0 + \frac{1}{N} \sum_q F(q) + \lim_{q \to 0} \left( \frac{4\pi Z^2 e^2}{\Omega_0 q^2} + F(q) \right)$

$V_2^{(2)}(R) = \frac{Z^2 e^2}{R} + \frac{2!}{N} \sum_q e^{i\vec{q}\vec{R}} F(q)$

$V^{(2)}(R) = \sum_{k \geq 2} V_k^{(2)}(R)$

effective ion-ion interaction

- density-dependent
- higher-order contrib. important at small q

Asymptotic behaviour

$V^{(2)}(R) \Longrightarrow \frac{\cos(2k_F R + \delta)}{k_F^3 R^3}$

large R

## NON-LOCALITY

$E^{(1)} = \sum_{|\vec{k}| \leq k_F} \langle \vec{k} | W | \vec{k} \rangle n_{\vec{k}}$


$T_1(q)$


$T_2(q)$

(local PP: $T_1 = w T_2 = w^2 \chi$)

$E^{(2)} = \frac{1}{2} \Omega_0 \sum'_{\vec{q} \neq 0} |S(\vec{q})|^2 \left\{ T_1(\vec{q}) - \frac{4\pi e^2}{q^2 \epsilon(q)} |T_2(\vec{q})|^2 \right\}$

$T_1(\vec{q}) = \int \frac{d^3k}{(2\pi)^3} \frac{n_{\vec{k}} - n_{\vec{k}+\vec{q}}}{E_{\vec{k}} - E_{\vec{k}+\vec{q}}} |\langle \vec{k} | w | \vec{k}+\vec{q} \rangle|^2$

$T_2(\vec{q}) = \int \frac{d^3k}{(2\pi)^3} \frac{n_{\vec{k}} - n_{\vec{k}+\vec{q}}}{E_{\vec{k}} - E_{\vec{k}+\vec{q}}} \langle \vec{k} | w | \vec{k}+\vec{q} \rangle$

to be calculated numerically

## CHOICE OF A PSEUDOPOTENTIAL

### a) SCATTERING APPROACH

Construct an analytical pseudopotential or pseudo-wavefunction of imposed smoothness and determine the open parameters by the requirement that the scattering properties of the true potential are correctly reproduced.

### b) OPERATOR APPROACH

Construct pseudo-orbitals as a linear combination of true valence-orbitals and core orbitals such that they are nodeless and close to the true orbitals. Then construct a new pseudo-Hamiltonian whose eigenfunctions are the pseudo-orbitals and whose eigenvalues are identical to the true exact valence energies.

## OPERATOR-APPROACH

$\psi$... exact valence orbital

$\varphi$.. pseudo-valence orbital

$$\langle \vec{r}|\varphi\rangle = \langle \vec{r}|\psi\rangle + \sum_c a_c \langle \vec{r}|\psi_c\rangle$$

Schrödinger-equation

$$(T+V)|\psi\rangle = E|\psi\rangle$$

↝ pseudo-Schrödinger equation

$$T|\varphi\rangle + \underbrace{V|\varphi\rangle + \sum_c (E-E_c)\, a_c|\psi_c\rangle}_{W|\varphi\rangle} = E|\varphi\rangle$$

pseudopotential

Require maximum similarity of $\varphi$ and $\psi$ outside the core-region ↝ $a_c = \langle\psi_c|\varphi\rangle$

↝ $$T|\varphi\rangle + V|\varphi\rangle + \sum_c (E-E_c)\langle\psi_c|\varphi\rangle|\psi_c\rangle = E|\varphi\rangle$$

Phillips-Kleinman equation

$$|\psi\rangle = (1-P)|\varphi\rangle = 1 - \sum_c \langle\psi_c|\varphi\rangle|\psi_c\rangle$$

exact orbital = projection of the pseudo-orbital onto the subspace orthogonal to the core states

## NON-UNIQUENESS OF $\varphi$ AND W

$$|\psi\rangle = (1-P)|\varphi\rangle = (1-P)|\tilde{\varphi}\rangle$$

$$|\tilde{\varphi}\rangle = |\varphi\rangle + \sum_c b_c |\psi_c\rangle$$

$b_c$ arbitrary

$$W|\varphi\rangle = V|\varphi\rangle + \sum_c \langle F_c|\varphi\rangle |\psi_c\rangle$$

Austin, Heine, Sham

$F_c$ .. arbitrary functions

## OPTIMIZATION OF THE PSEUDOPOTENTIAL

Smoothest possible pseudo-wave function

$$\frac{\langle\nabla\varphi|\nabla\varphi\rangle}{\langle\varphi|\varphi\rangle} = -\frac{\langle\varphi|\Delta\varphi\rangle}{\langle\varphi|\varphi\rangle} \sim \text{Min.}$$

Cohen, Heine

$$\rightsquigarrow \quad \frac{\langle\varphi|T|\varphi\rangle}{\langle\varphi|\varphi\rangle} \sim \text{Min}$$

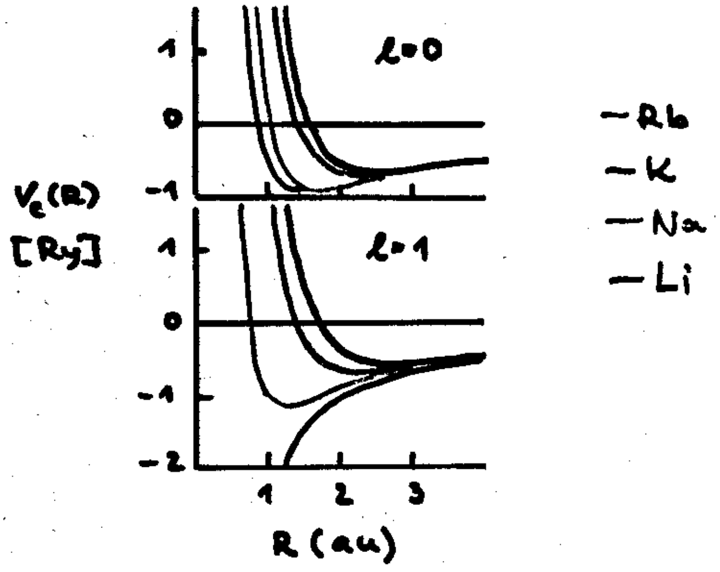
$$\frac{\langle\varphi|W|\varphi\rangle}{\langle\varphi|\varphi\rangle} \sim \text{Max}$$

$\rightsquigarrow$ Maximum cancellation between the attractive crystal potential V and the repulsive pseudopotential

$$W|\vec{k}\rangle = V|\vec{k}\rangle + \sum_c \left(\frac{\hbar^2 k^2}{2m} + \langle\vec{k}|W|\vec{k}\rangle - E_c\right)\langle\psi_c|\vec{k}\rangle|\psi_c\rangle$$

Harrison

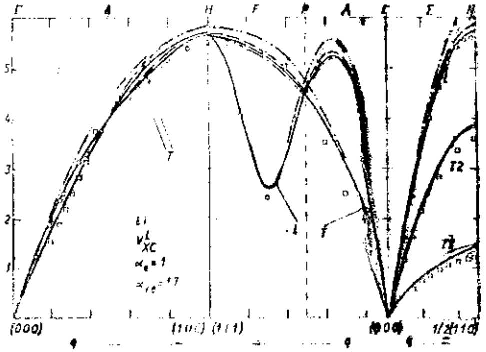
$$\langle\vec{r}|\vec{k}\rangle = \Omega^{-1/2}\exp(i\vec{k}\vec{r})$$



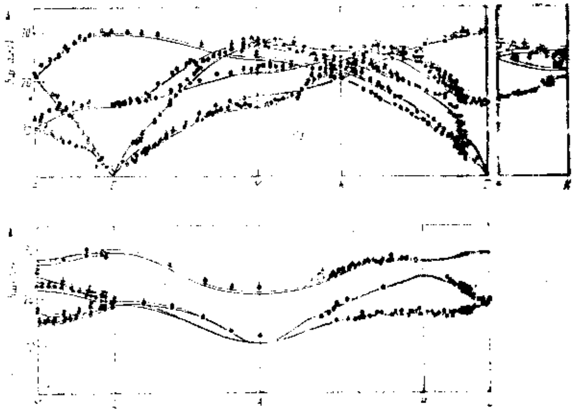
A. Zunger and M.H. Cohen:
Alkali core pseudopotentials
(PK-type)

- hard repulsive core
- Li potential strong and nonlocal

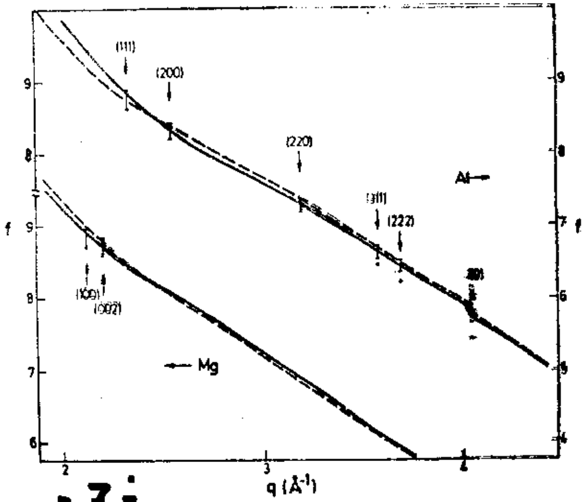
PHONONEN IN Li
(HAFNER 1975)



PHONONEN IN MG
(HAFNER u.
ESCHRIG 1975)



RÖNTGENSTREU-
FORMFAKTOR
IN Al u. Mg
(HAFNER 1970)



## SCATTERING APPROACH

**Heine-Abarenkov-Animalu**

$$w^{HAA}(r) = \begin{cases} -A_\ell(E)P_\ell & r \le R_M \\ -\frac{Ze}{r} & r > R_M \end{cases}$$

$A_\ell(E)$ determined by fitting the eigen-energies of a single electron in the field of the ion

**Shaw:** Optimization ~ "optimized model potential"

$$w^{OMP}(r) = \begin{cases} -A_\ell(E)P_\ell & r \le R_\ell \\ -\frac{Ze}{r}P_\ell & r > R_\ell \end{cases}$$

$$R_\ell = \frac{Ze}{A_\ell(E_F)}$$

~ continuous in r-space

**Dagens-Rasolt-Taylor (DRT)**

$A_\ell(E)$ determined by fitting the pseudo-chargedensity to the charge density induced by a single ion immersed in an electron gas of appropriate density, as calculated by a self-consistent nonlinear technique (Dagens)

## Hamann-Schlüter-Chiang

## Kerker

Simple analytic form of ψ, parameters determined by conditions

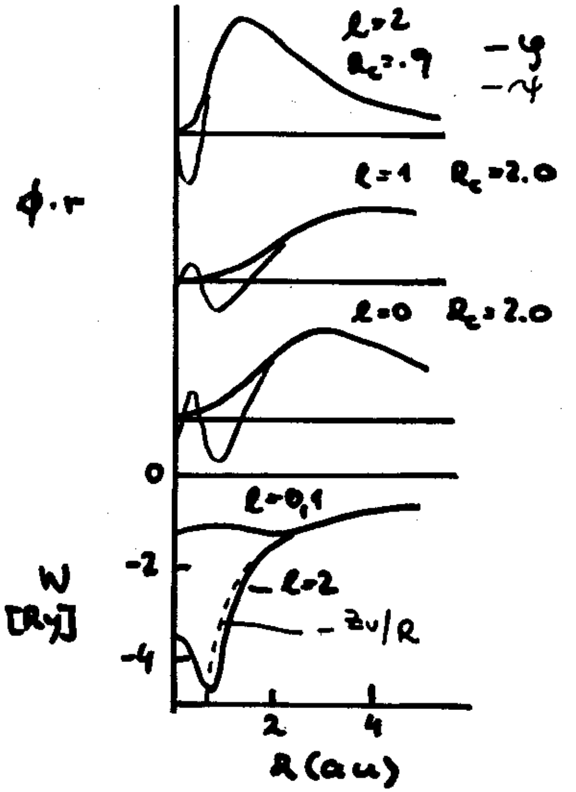
(1) eigenvalues agree for chosen configuration

(2) ψ and φ agree beyond a radius $r_c$

(3) the norm is conserved

(4) logarithmic derivatives of φ and ψ and their energy derivatives agree for $r > r_c$

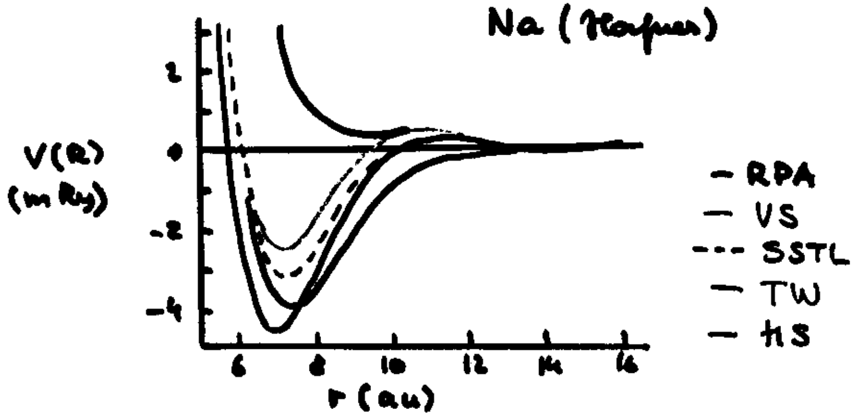
W determined by inversion of the radial Schrödinger equation

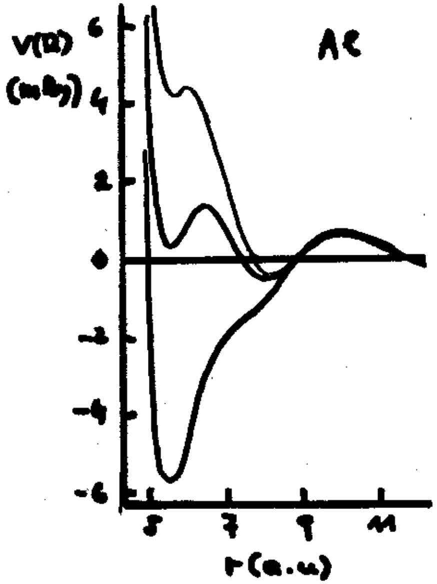


Mo (atomic PP)

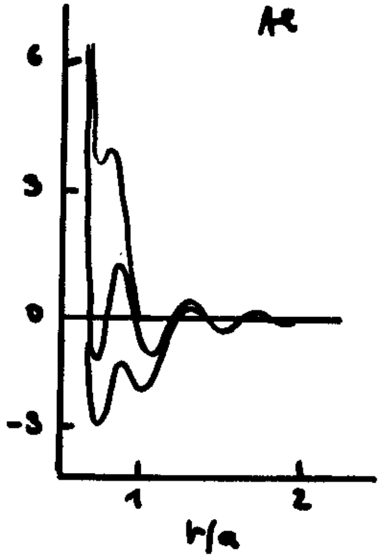
— [illegible] core

— nodeless ψ





Hafner

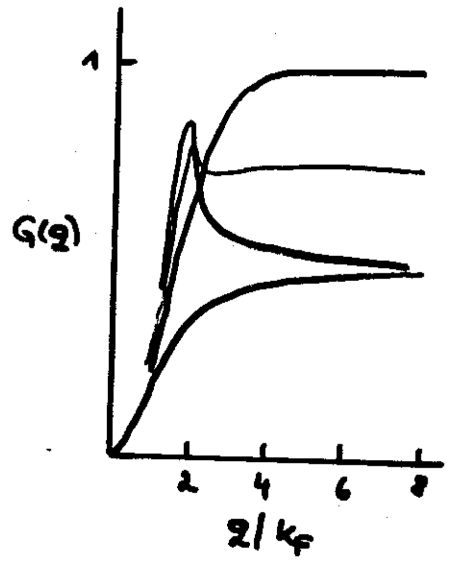


Dagens-Rasolt-Taylor

## EXCHANGE AND CORRELATION IN THE DIELECTRIC FUNCTION

$$\tilde{\varepsilon}(q) = 1 + \underbrace{\frac{4\pi e^2}{q^2}\left(1 - G(q)\right)}_{v_{eff}(e)} \chi(q)$$

effective el.-el. interaction



- Hubbard-Geldart-Vosko-Sham -HS
- Vashishta-Singwi
- Toigo-Woodruff
- Yasuhara-Watabe

Conditions to be satisfied by $G(q)$:

a) COMPRESSIBILITY SUM RULE

$$G(q) \rightarrow \gamma\, q^2/k_F^2 \qquad q \ll k_F$$

$$\gamma = \frac{1}{4} - \frac{\pi\alpha}{24} r_s^5 \frac{d}{dr_s}\left[r_s^{-2} \frac{d}{dr_s} E_{corr}(r_s)\right]$$

$$\alpha = \left(4/9\pi\right)^{1/3}$$

$$r_s = \left(\frac{3\Omega_0}{4\pi}\right)^{1/3} \frac{me^2}{\hbar^2}$$

$E_{corr}$ in Ry

b) POSITIVE ELECTRON-ELECTRON PAIR CORRELATION FUNCTION FOR $r \rightarrow 0$

$$\lim_{q \to \infty} G(q) = 1 - g(0)$$

$$g(0) > 0$$

# PSEUDOPOTENTIALS FOR BINARY ALLOYS

Formal theory:

## Factorization of pseudopotential matrix element

$$W(\vec{q}) = S_A(\vec{q})\, w_A(\vec{q}) + S_B(\vec{q})\, w_B(\vec{q})$$

$$= S(\vec{q})\, \bar{w}(\vec{q}) + D(\vec{q})\, \Delta w(\vec{q})$$

$$\bar{w} = c\, w_A + (1-c)\, w_B$$

$$\Delta w = w_A - w_B$$

### Total structure factor

$$S(\vec{q}) = N^{-1} \sum_j \exp(-i\vec{q}\vec{R}_j)$$

### "Difference" structure factor

$$D(\vec{q}) = N^{-1} \sum_j \left(\bar{g} + g(\vec{R}_j)\right) \exp(-i\vec{q}\vec{R}_j)$$

### Partial structure factors

$$S_A(\vec{q}) = N^{-1} \sum_j \left(\tfrac{1}{2} + g(\vec{R}_j)\right) \exp(-i\vec{q}\vec{R}_j)\,, \quad S_A(0) = c$$

$$S_B(\vec{q}) = N^{-1} \sum_j \left(\tfrac{1}{2} - g(\vec{R}_j)\right) \exp(-i\vec{q}\vec{R}_j)\,, \quad S_B(0) = (1-c)$$

$$g(\vec{R}_j) = \begin{cases} +\frac{1}{2} & \text{if } \vec{R}_j \text{ occ. by A-ion} \\ -\frac{1}{2} & \text{------ " ------ B-ion} \end{cases}$$

$$\bar{g} = \sum_j g(\vec{R}_j) = \tfrac{1}{2} - c$$

## Partial energy wave-number characteristics

$$F_{ij}(q) = -\tfrac{1}{2}\Omega_0 \frac{\chi(q)}{\epsilon(q)}\, w_i(\vec{q})\, w_j(-\vec{q}) \qquad i,j = A,B$$

or

$$F_{NN}(\vec{q}) = -\tfrac{1}{2}\Omega_0 \frac{\chi(q)}{\epsilon(q)} \left|\bar{w}(\vec{q})\right|^2$$

$$F_{NC}(\vec{q}) = -\tfrac{1}{2}\Omega_0 \frac{\chi(q)}{\epsilon(q)}\, \bar{w}(\vec{q})\, \Delta w(-\vec{q})$$

$$F_{CC}(\vec{q}) = -\tfrac{1}{2}\Omega_0 \frac{\chi(q)}{\epsilon(q)} \left|\Delta w(\vec{q})\right|^2$$

## Second-order electronic energy

$$E_2 = \sum_{\vec{q}\neq 0} \Big\{ |S(\vec{q})|^2 F_{NN}(q) + \left(S(\vec{q}) D^*(\vec{q}) + S^*(\vec{q}) D(\vec{q})\right) F_{NC}(q) + |D(\vec{q})|^2 F_{CC}(q) \Big\}$$

$$= \sum_{i,j = A,B}\ \sum_{\vec{q}\neq 0} S_i^*(\vec{q})\, S_j(\vec{q})\, F_{ij}(q)$$

## Partial pair potentials

$$V_{ij}^{(2)}(R) = \frac{z_i z_j e^2}{R} + \frac{2}{N} \sum_{q} e^{i\vec{q}\vec{R}} F_{ij}(q)$$

### Average pair potential

$$\bar{V}^{(2)}(R) = c\, V_{AA}(R) + (1-c)\, V_{BB}(R) + 2\sqrt{c(1-c)}\; V_{AB}(R)$$

$$\Delta V(R) = V_{AA}(R) + V_{BB}(R) - 2 V_{AB}(R)$$

### "Alloying" pair potential

**All** pair potentials $V_{ij}(R) \sim \dfrac{\cos(2k_F R)}{R^3}$ $R \to \infty$

$\bar{V}, \Delta V$

## Are bare ionic pseudopotentials transferable?

a) Construction of an alloy-pseudopotential in the operator approach

$$|\psi\rangle = \Big(1 - \sum_{c\{A\}} |\psi_c^A\rangle\langle\psi_c^A| - \sum_{c\{B\}} |\psi_c^B\rangle\langle\psi_c^B|\Big)|\varphi\rangle$$

$$= (1 - P_A - P_B)|\varphi\rangle = (1-P)|\varphi\rangle$$

orthogonalize to two different sets of core orbitals

→ generalized Phillips-Kleinman equation (Hafner '76)

$$T|\varphi\rangle + V|\varphi\rangle + \Big\{\sum_{c\{A\}} (E - E_c^{A(AB)})\langle\psi_c^A|\varphi\rangle|\psi_c^A\rangle + \sum_{c\{B\}} (E - E_c^{B(AB)})\langle\psi_c^B|\varphi\rangle|\psi_c^B\rangle\Big\} = E|\varphi\rangle$$

$E_c^{A(A,B)}$ core-eigenvalues in the alloy

$\neq E_c^A$ — " — pure metal

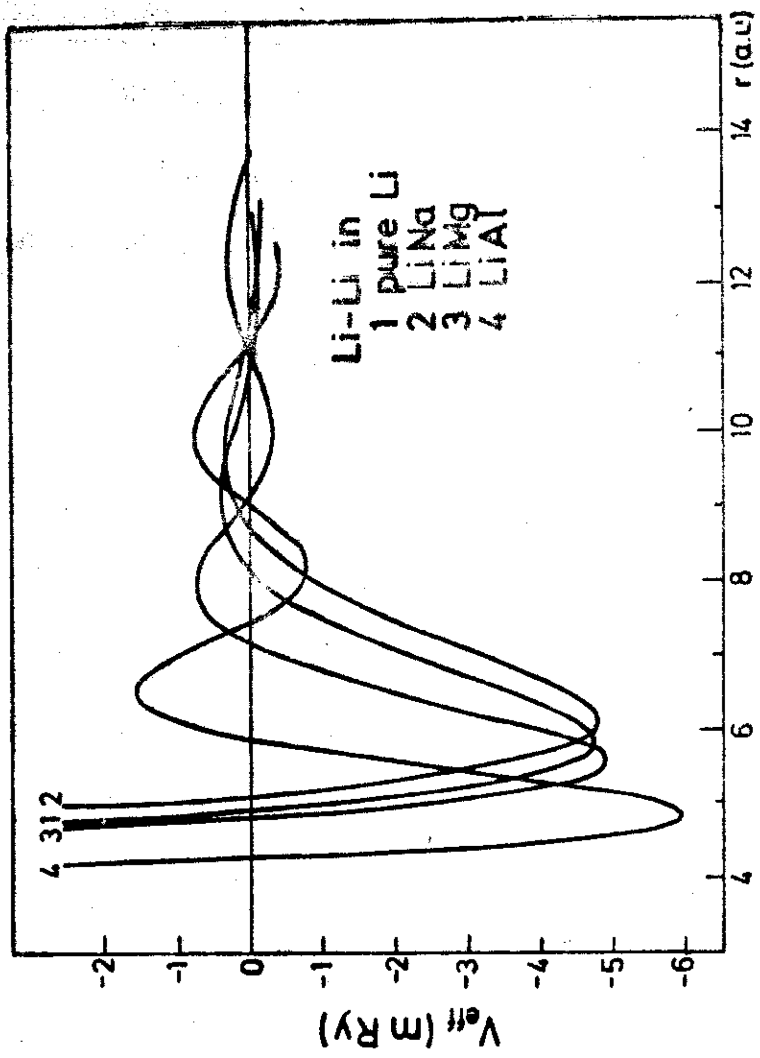
$\neq \varepsilon_c^A$ — " — free atom

"core shift"

Optimization →

$$W|\vec{k}\rangle = V|\vec{k}\rangle + \sum_{c\{A\}} \Big(\frac{\hbar^2k^2}{2m} + \langle\vec{k}|W|\vec{k}\rangle - E_c^{A(A,B)}\Big)\langle\psi_c^A|\vec{k}\rangle|\psi_c^A\rangle$$

$$+ \sum_{c\{B\}} \Big(\frac{\hbar^2k^2}{2m} + \langle\vec{k}|W|\vec{k}\rangle - E_c^{B(A,B)}\Big)\langle\psi_c^B|\vec{k}\rangle|\psi_c^B\rangle$$



The bare ionic pseudopotential changes on alloying due to

a) Change in core-eigenvalues (core-shift)

b) Different norm of $\varphi$ (different orthogonalization charges)

c) Altered energy dependence

$$\left( E \sim \frac{\hbar^2 k^2}{2m} + \underbrace{\langle k | W | k \rangle}_{\text{total pseudopotentials}} \right)$$

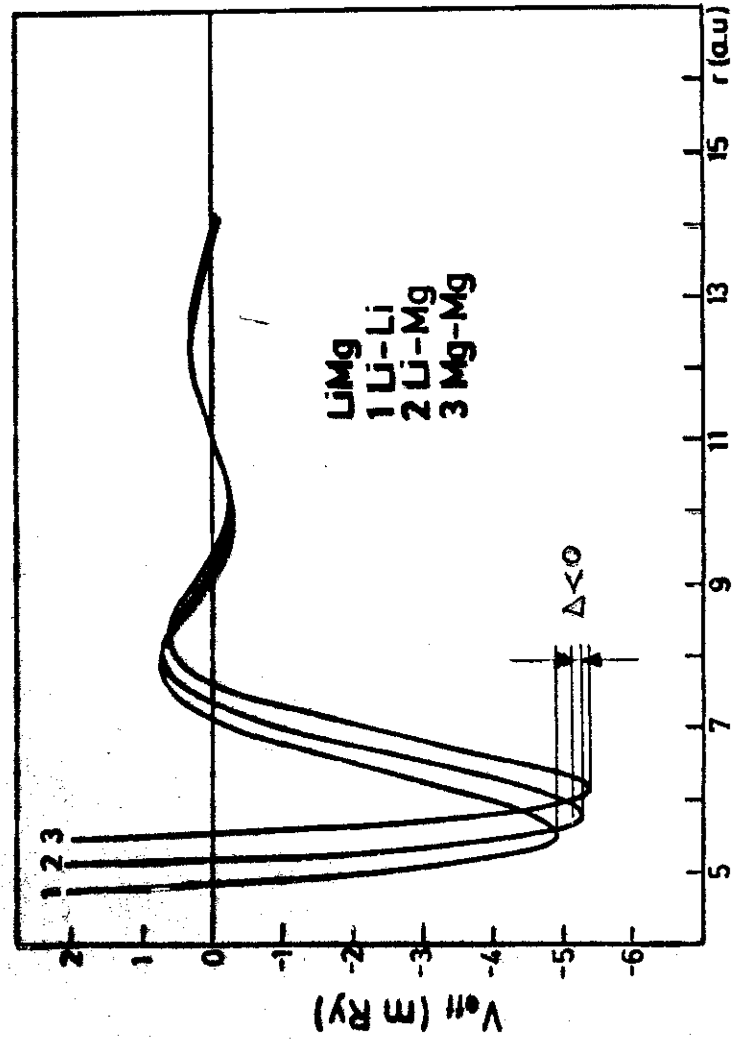
in addition, the screened pseudopotential changes due to the

d) shift of the Fermi-energy.

b) Other pseudopotentials:

HAA: adapted to free-ion configuration
↝ transferable, but relatively inaccurate

DRT: fitted to pure-metal like ion-in-jellium configuration
↝ not transferable



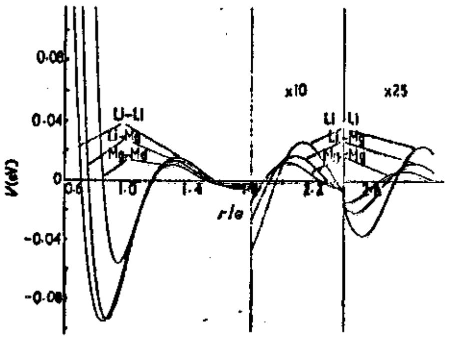


Figure 4 : Interionic potentials for Li-Li, Li-Mg and Mg-Mg corresponding to 15 at % Mg.

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Pseudopotentials for binary alloys

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