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WORKING PARTY ON "FRACTURE PHYSICS"
(29 May - 16 June 1989)

THE APPLICATION OF SEMI-EMPIRICAL TIGHT-BINDING MODELS TO THE CALCULATION OF DEFECT STRUCTURES IN METALS

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Finnis, Paxton, Pettifor, Sutton and Ohta
'Interatomic Forces in Transition Metals'
Philosophical Magazine A 58, 143, (1988)

FORCE LAWS

TYPE	BIGGEST PROBLEM (N ATOMS)	CPU SCALING	NOTES
PAIRWISE	0.25×10^6	N	FOR METALS, INFO IS VERY QUALITATIVE. NO SURFACES!
EMPIRICAL μ_2 (TB) FINNIS-SINCLAIR EAM	10^6	N	QUALITATIVE WITH SURFACES. NO ANGULAR FORCES.
TBB	4×10^2	N	SEMI-QUANTITATIVE NOT ALWAYS RIGHT STRUCTURE SURFACE RECONST.
SC-DFT (LDA)	10^1-10^2	N^2	s-p BONDED METALS

THEORETICAL METALLURGY

PROPERTIES PROCESSES	N ATOMS	TECHNIQUES
MACROSCOPIC CREEP, FRACTURE ADHESION	10^{26}	MECHANICS, EFFECTIVE MEDIUM MODELS OF MICROSTRUCTURE
MICROSTRUCTURE	10^{7}	
	ATOMISTIC	
CRACKS, INTERFACES		
RADIATION DAMAGE CASCADES	10^{6}	MD MC, MS
DISLOCATION INTER. POINT DEFECT INTER.	10^{4}	← EFFECTIVE INTERATOMIC FORCES
SINGLE DEFECTS	10^{3}	
INTERFACE, DISLOCATION POINT DEFECT, FCS	10^{2}	← TB ← SELF CONSISTENT $\Psi(r,\theta)$.

INTERATOMIC FORCES

1. **PAIR POTENTIALS:**

$$U_i = \tfrac{1}{2}\sum_j V_{ij} \quad \left(+F(\text{volume})\right)$$

2. **'BOND ANGLE' FORCES, BOND CHARGES**

$$U_i = \sum_{jk} f(\underline{R}_{ij}\cdot\underline{R}_{ik})$$

3. **EFFECTIVE MEDIUM MODELS** QT

$$U_i = f(\rho_i) + \tfrac{1}{2}\sum_j V_{ij}$$

4. **TIGHT-BINDING MODELS**

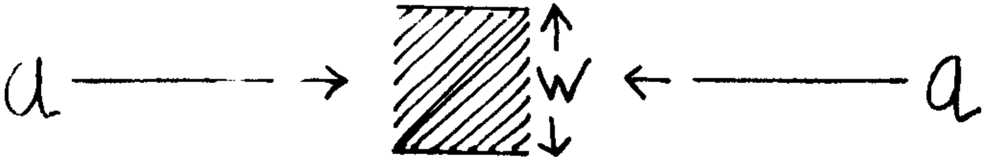
$$U_i = \sum_n \epsilon_n w_{ni} + \tfrac{1}{2}\sum_j V_{ij} \equiv$$

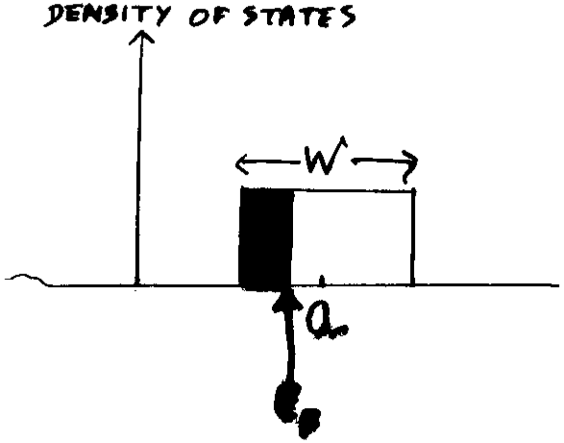
TB

$$U_i = \sum_{ji} \rho_{ij} H_{ij} + \tfrac{1}{2}\sum_j V_{ij}$$

5. **DENSITY FUNCTIONAL**

$$\sum_i U_i = \int^{E_F} E\,n(E)\,dE - \int n(r)\left(\tfrac{1}{2}\phi(r) + \mu_{xc}(r)\right) + E_{xc}[n(r)] + E_{ii}$$





$$\text{Band energy} = \int^{E_f} n(E)\,.\,E\,dE$$

$$= \int^{E_f} \frac{N}{W}\,E\,dE$$

$$= -\tfrac{1}{2} W n_e \left(1 - \frac{n_e}{N_{at}}\right) + n_e a$$

$$= \text{Bond energy} + n_e a$$

$$\mathbb{H}\Psi = E\Psi$$

$$H_{ij} = \int d\underline{r}\, \phi_i(\underline{r}) \left(-\tfrac{1}{2}\nabla^2\right) \phi_j(r) + \int d\underline{r}\, \phi_i(\underline{r})\, V_{eff}(\underline{r})\, \phi_j(r)$$

$$\Psi_n = \sum c_{ni} \phi_i$$

$$\sum_j H_{ij} c_{nj} = \sum_j \varepsilon_n S_{ij} c_{nj}$$

$$S_{ij} = \int d\underset{\sim}{r}\, \phi_i(r)\, \phi_j(r)$$

Approximations:
- incomplete basis
- 2-centre integrals only
- $S_{ij} = \delta_{ij}$

$n(E) = \sum_k \delta(E-E_k) \qquad H\psi_k = E_k\psi_k$

$$\tilde{\mu}_2 = \int_{-\infty}^{\infty} (E-a)^2 n(E)\, dE$$

$$= \mu_2 - a^2$$

$$\mu_2^{(i)} = \sum_j H_{ij}^2$$

$$\tilde{\mu}_2^{(i)} = \sum_{j \neq i} H_{ij}^2 \propto \text{[illegible]}$$

$$W \propto \sqrt{\tilde{\mu}_2}$$

For rectangular DOS

$$\tilde{\mu}_2 = \frac{NW^2}{12}$$

Second moment models

Effective: $H_{ij}^2 = dd\sigma^2(ij) + 2dd\pi^2(ij) + 2dd\delta^2(ij$

Vacancy studied by G. Allan and M. Lannoo
J. Phys. Chem. Solids **37**
699 (1976).

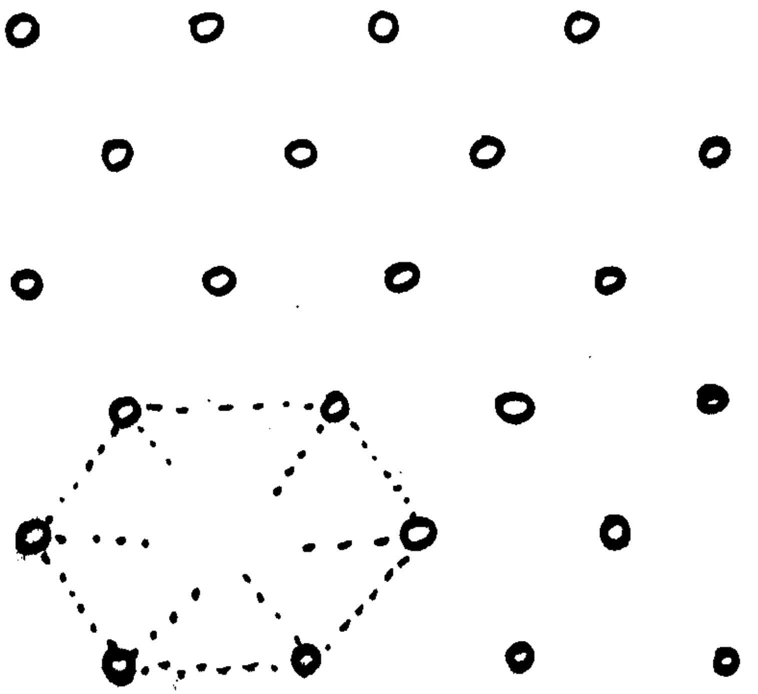
$$\mu_{2i} = \sum_j H_{ij}^2$$

$$n_i(\varepsilon) = \frac{1}{\sqrt{(2\pi\mu_{2i})}} \exp\left(\frac{-\varepsilon^2}{2\mu_{2i}}\right)$$

$$\beta(R) = \beta_0 \exp(-qR)$$

$$V(R) = V_0 \exp(-pR)$$

$$q/p = \frac{1}{5} \text{ to } \frac{1}{3} \rightarrow E_v^f$$



$$-E_{coh} = (z\phi)^{1/2} = u$$

$$E_v^f = -(z u' - z u)$$

$$= -z\left[((z-1)\phi)^{1/2} - (z\phi)^{1/2}\right]$$

$$\approx -z\left[z^{1/2}\left(1 - \frac{1}{2z}\right)\phi^{1/2} - z^{1/2}\phi^{1/2}\right]$$

$$= \frac{1}{2}(z\phi)^{1/2}$$

$$\underline{E_v^f = \frac{1}{2} E_{coh}}$$

VIBES!

Moruzzi, Janak, Williams 1978

"Calculated Electronic Properties of Metals" (Pergamon)

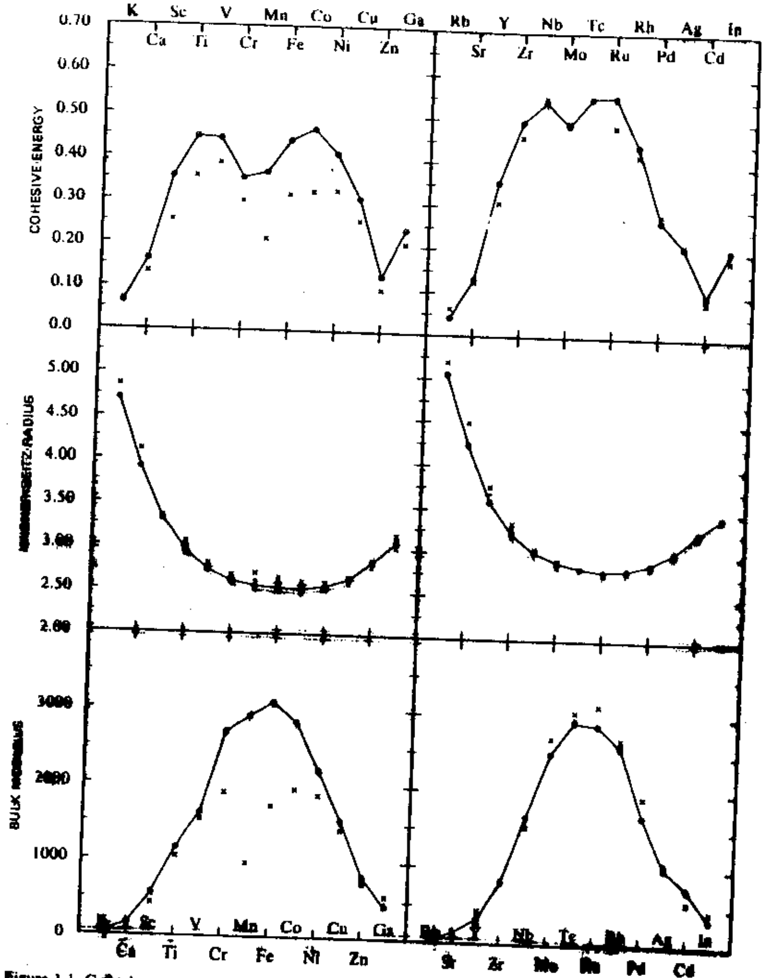


Figure 1.1 Cohesive properties. Top row- cohesive energy (Ry/atom). Middle row- Wigner-Seitz radius (a.u.). Bottom row- bulk modulus (Kbar). Measured values are indicated by crosses.

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D.O.S. for canonical d band
by summation to ten shells
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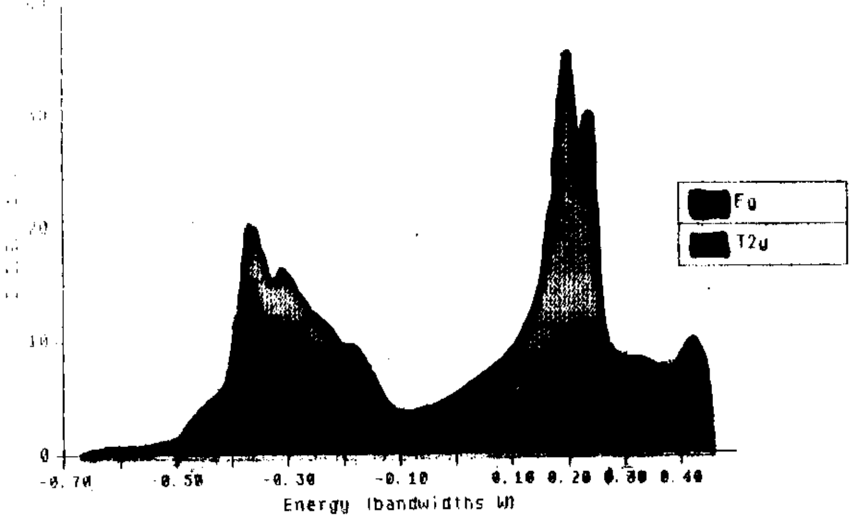


TOTAL ENERGY

DENSITY FUNCTIONAL THEORY
LOCAL DENSITY APPROX.

1) Superimpose atomic charges ρ_i

$\rightarrow \rho^{+}$

Kohn-Sham effective potential

$$V_{eff} = v(r) + v_H^{+}(r) + \mu_{xc}^{+}(r)$$

2) Solve single-particle Hamiltonian

$$\hat{H} = -\tfrac{1}{2}\nabla^2 + V_{eff} \quad , \quad \hat{H}|n\rangle = \epsilon_n|n\rangle$$

3) Construct output charge density

ρ^{out}

4) Iterate until $\rho \rightarrow \rho^{sc}$

$$E_{TOTAL}^{sc} = \sum_n a_n \epsilon_n^{sc} - \int \rho^{sc}\left(\tfrac{1}{2}v_H^{sc} + \mu_{xc}^{sc}\right)$$
$$+ E_{xc}[\rho^{sc}] + E_{ii}$$

FOULKES AND HARRIS
[illegible] APPROXIMATION (J. Harris, PRB 31 1770 (1985))

$$E^{\text{Harris}}_{\text{TOTAL}} = \sum_n a_n \varepsilon_n - \int \rho^f \left(\tfrac{1}{2} V_H^f + \mu_{xc}^f \right) + E_{xc}[\rho^f] + E_{ii} + O[\rho^{sc} - \rho^f]^2$$

N.B.:

$$E^{\text{Harris}}_{\text{TOTAL}} \neq E[\rho^f]$$

so we cannot say $E^{\text{Harris}}_{\text{TOTAL}} > E^{sc}_{\text{TOTAL}}$

$$\int \rho^{4/3} dr$$

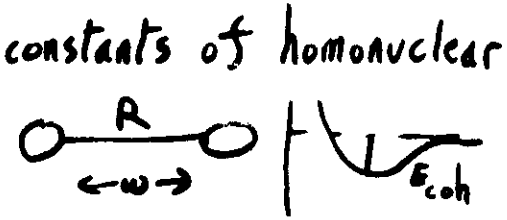
$$= \int \left(\sum_k \rho_k \right)^{\frac{4}{3}}$$

$$= \sum_i \rho_i \left(\sum_k \rho_k \right)^{\frac{1}{3}}$$

$$= \sum_i \rho_i^{\frac{4}{3}} \left(1 + \sum_{k \neq i} \frac{\rho_k}{\rho_i} \right)^{\frac{1}{3}}$$

$$\approx \sum_i \rho_i^{4/3} + \frac{1}{3} \sum_{i, k \neq i} \rho_i^{\frac{1}{3}} \rho_k$$

Spectroscopic constants of homonuclear dimers

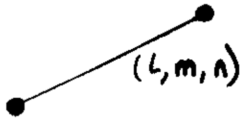


J. Harris PRB 31 1770 (1985)

		Harris	Painter & Averill	Expt.
Be_2	E_{coh}	0.49	0.50	~0.1
	R	4.50	4.63	4.66
	ω	45	45	28
C_2	E_{coh}	8.7	7.19	6.2
	R	2.30	2.36	2.35
	ω	246	232	230
N_2	E_{coh}	10.7	11.34	9.91
	R	2.03	2.08	2.07
	ω	346	290	292
F_2	E_{coh}	3.3	3.32	1.68
	R	2.71	2.62	2.68
	ω	120	133	111
Cu_2	E_{coh}	2.9	2.65	2.03
	R	4.10	4.10	4.20
	ω	35	41	33

J. C. SLATER and G. F. KOSTER
Phys. Rev. 94, 1498, (1954)

TABLE I. Energy integrals for crystal in terms of two-center integrals.

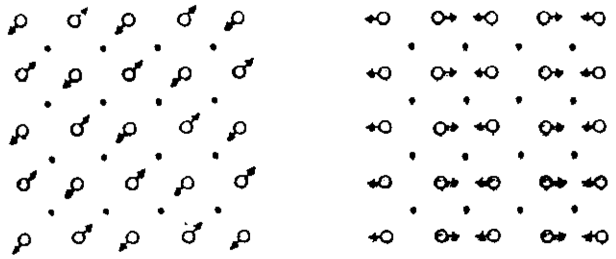


$E_{s,s}$	$(ss\sigma)$
$E_{s,x}$	$l(sp\sigma)$
$E_{x,x}$	$l^2(pp\sigma)+(1-l^2)(pp\pi)$
$E_{x,y}$	$lm(pp\sigma)-lm(pp\pi)$
$E_{x,z}$	$ln(pp\sigma)-ln(pp\pi)$
$E_{s,xy}$	$\sqrt{3}lm(sd\sigma)$
E_{s,x^2-y^2}	$\frac{1}{2}\sqrt{3}(l^2-m^2)(sd\sigma)$
$E_{s,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)](sd\sigma)$
$E_{x,xy}$	$\sqrt{3}l^2m(pd\sigma)+m(1-2l^2)(pd\pi)$
$E_{x,yz}$	$\sqrt{3}lmn(pd\sigma)-2lmn(pd\pi)$
$E_{x,zx}$	$\sqrt{3}l^2n(pd\sigma)+n(1-2l^2)(pd\pi)$
E_{x,x^2-y^2}	$\frac{1}{2}\sqrt{3}l(l^2-m^2)(pd\sigma)+l(1-l^2+m^2)(pd\pi)$
E_{y,x^2-y^2}	$\frac{1}{2}\sqrt{3}m(l^2-m^2)(pd\sigma)-m(1+l^2-m^2)(pd\pi)$
E_{z,x^2-y^2}	$\frac{1}{2}\sqrt{3}n(l^2-m^2)(pd\sigma)-n(l^2-m^2)(pd\pi)$
$E_{x,3z^2-r^2}$	$l[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}ln^2(pd\pi)$
$E_{y,3z^2-r^2}$	$m[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}mn^2(pd\pi)$
$E_{z,3z^2-r^2}$	$n[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)+\sqrt{3}n(l^2+m^2)(pd\pi)$
$E_{xy,xy}$	$3l^2m^2(dd\sigma)+(l^2+m^2-4l^2m^2)(dd\pi)+(n^2+l^2m^2)(dd\delta)$
$E_{xy,yz}$	$3lm^2n(dd\sigma)+ln(1-4m^2)(dd\pi)+ln(m^2-1)(dd\delta)$
$E_{xy,zx}$	$3l^2mn(dd\sigma)+mn(1-4l^2)(dd\pi)+mn(l^2-1)(dd\delta)$
E_{xy,x^2-y^2}	$\frac{3}{2}lm(l^2-m^2)(dd\sigma)+2lm(m^2-l^2)(dd\pi)+\frac{1}{2}lm(l^2-m^2)(dd\delta)$
E_{yz,x^2-y^2}	$\frac{3}{2}mn(l^2-m^2)(dd\sigma)-mn[1+2(l^2-m^2)](dd\pi)+mn[1+\frac{1}{2}(l^2-m^2)](dd\delta)$
E_{zx,x^2-y^2}	$\frac{3}{2}nl(l^2-m^2)(dd\sigma)+nl[1-2(l^2-m^2)](dd\pi)-nl[1-\frac{1}{2}(l^2-m^2)](dd\delta)$
$E_{xy,3z^2-r^2}$	$\sqrt{3}lm[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)-2\sqrt{3}lmn^2(dd\pi)+\frac{1}{2}\sqrt{3}lm(1+n^2)(dd\delta)$
$E_{yz,3z^2-r^2}$	$\sqrt{3}mn[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}mn(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}mn(l^2+m^2)(dd\delta)$
$E_{zx,3z^2-r^2}$	$\sqrt{3}ln[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}ln(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}ln(l^2+m^2)(dd\delta)$
$E_{x^2-y^2,x^2-y^2}$	$\frac{3}{4}(l^2-m^2)^2(dd\sigma)+[l^2+m^2-(l^2-m^2)^2](dd\pi)+[n^2+\frac{1}{4}(l^2-m^2)^2](dd\delta)$
$E_{x^2-y^2,3z^2-r^2}$	$\frac{1}{2}\sqrt{3}(l^2-m^2)[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}n^2(m^2-l^2)(dd\pi)+\frac{1}{4}\sqrt{3}(1+n^2)(l^2-m^2)(dd\delta)$
$E_{3z^2-r^2,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)]^2(dd\sigma)+3n^2(l^2+m^2)(dd\pi)+\frac{3}{4}(l^2+m^2)^2(dd\delta)$

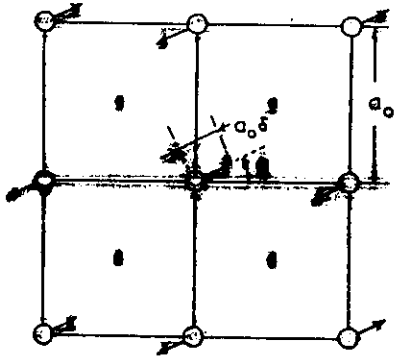
*

$$E_{xy,xy} = 3l^2m^2(dd\sigma) + (l^2+m^2-4l^2m^2)(dd\pi) + (n^2+l^2m^2)(dd\delta)$$

Terakura et al Surf. Sci. <u>111</u> 479 (1981)



(a) (b)



	Mo	W
$dd\sigma$	-0.08594	-0.08959
$dd\pi$	0.06444	0.07662
$dd\delta$	-0.02402	-0.03663
	$\propto R^{-3.57}$	$\propto R^{-3.255}$

Fit
LCAO bands

$V = A \exp(-p R)$

Lattice const.
Bulk modulus

Numerical procedure of previous TB approaches
for μ_n, $n > 4$

$$\Delta E = \int \varepsilon n_i^{(1)} d\varepsilon - \int \varepsilon n_i^{(2)} d\varepsilon$$

For force on atom i,
$n_j(\varepsilon)$ must be evaluated for
all j to obtain $\sum \Delta n_j$.

e.g. Legrand evaluated Δn_i
to μ_6, other Δn_j to μ_2.

<u>Direct</u> calculation of force? → TBB
Tight Binding Bond
model.

The TBB model

TIGHT BINDING BOND

Finnis, et al
Phil. Mag. A 58
143 (1988).

Band picture:

$$U = \int^{\varepsilon_F} \varepsilon\, n(\varepsilon)\, d\varepsilon \quad + \quad U_{rep}$$

↙ Pairwise

U_{rep}

$$= -\int d\underset{\sim}{r}\; n(\underset{\sim}{r})\left(\tfrac{1}{2}\phi(\underset{\sim}{r}) + \mu_{xc}(\underset{\sim}{r})\right)$$
$$+ E_{xc}[n(\underset{\sim}{r})] + E_{ii}$$

Kohn - Sham 1965
Harris 1985, [illegible], 1990
(Validates pairwise description of U_{rep})

$$U_{band} = \int^{\varepsilon_F} \varepsilon\, n(\varepsilon)\, d\varepsilon$$
$$= -\tfrac{1}{\pi}\int^{\varepsilon_F} \varepsilon\, \mathrm{Im}\,\mathrm{Tr}\, G$$

Definition of G:

$$(\varepsilon - H)G = 1$$

U_{band}

$$= -\frac{1}{\pi}\int^{\varepsilon_F} \varepsilon\, \mathrm{Im}\,\mathrm{Tr}\, G\, d\varepsilon$$

$$= -\frac{1}{\pi}\int^{\varepsilon_F} \mathrm{Im}\,\mathrm{Tr}\, HG\, d\varepsilon$$

$$= -\frac{1}{\pi}\int^{\varepsilon_F} \sum_{ij} \mathrm{Im}\, G_{ij} H_{ji}\, d\varepsilon$$

$$= \underline{\sum_{ij} \rho_{ji} H_{ij}}$$

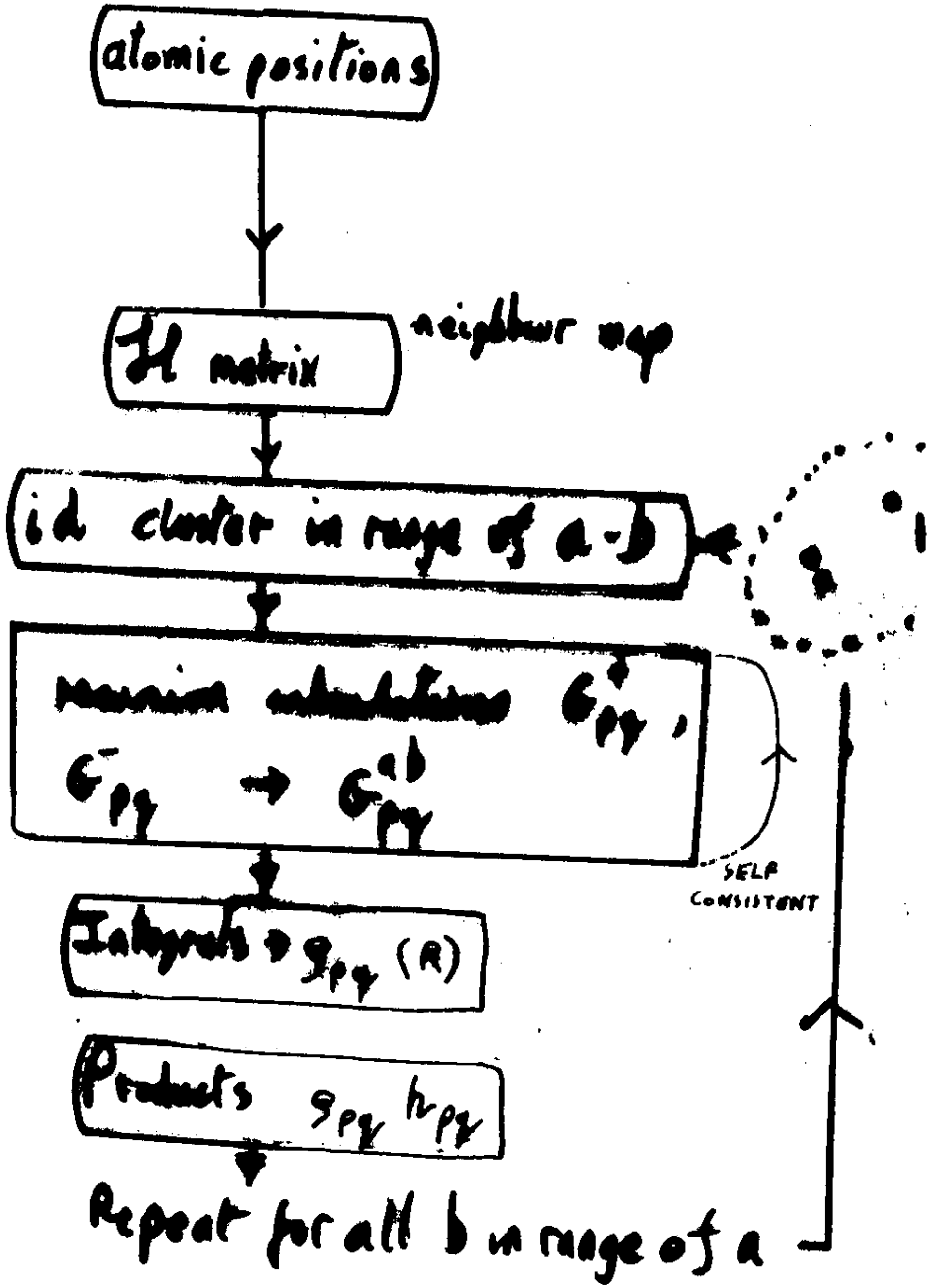
'charge' × 'potential'

$$U_{coh} = \sum_i \sum_{j\neq i} \rho_{ji} H_{ij} \quad + \quad U_{rep}$$

Forces:

$$\delta U = \sum_i \sum_{j\neq i} \rho_{ji}\, \delta H_{ij} \quad + \quad \delta U_{rep}$$

To calculate the force on an atom a



CANONICAL d-BAND PARAMETERS

$$H_{11} = H_{44} = dd\delta(R) = -2\left(\frac{s}{R}\right)^5$$

$$H_{22} = H_{33} = dd\pi(R) = 8\left(\frac{s}{R}\right)^5$$

$$H_{55} = dd\sigma(R) = -12\left(\frac{s}{R}\right)^5$$

Energy of bond

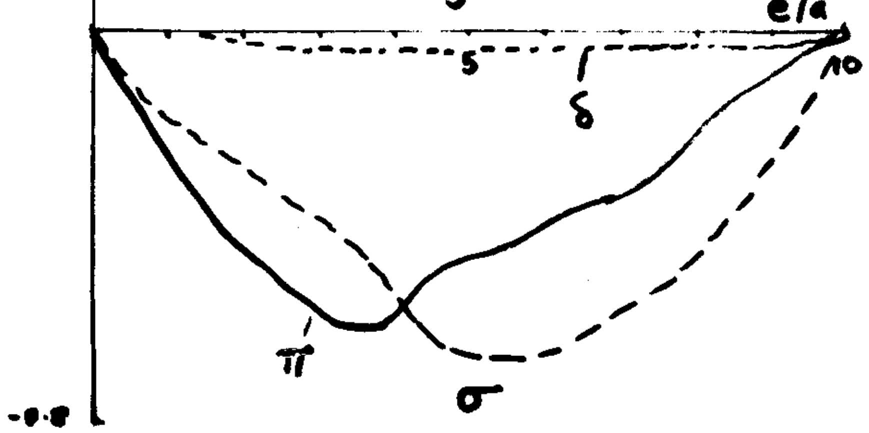
$$U^{ij}_{bond} = dd\sigma \times g_{55} + dd\pi \times (g_{22} + g_{33}) + dd\delta \times (g_{11} + g_{44})$$

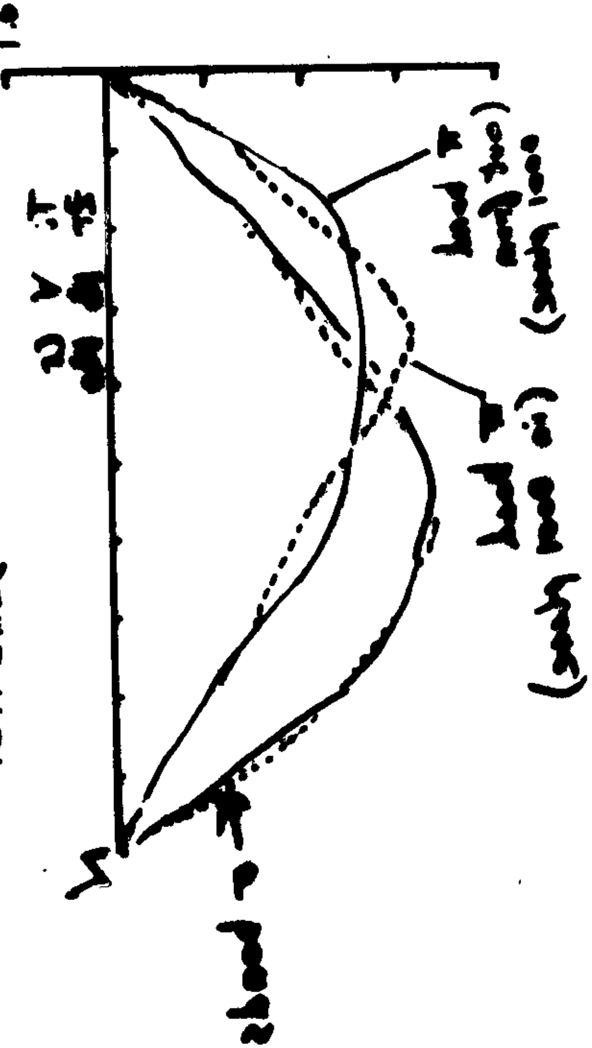
Radial force

$$F^{ij}_{bond} = -\frac{5}{R} \times U^{ij}_{bond}$$

But generally also transverse $\underline{F}$.

BOND ENERGY IN FCC
versus filling of d-band





BOND ENERGY IN IDEAL HCP

c/a → < 1.6 in Zr, Ti

Moments of local DOS on atom i

$$\mu_N = \int_{-\infty}^{\infty} E^N n_i(E)\, dE$$

$$= \int E^N \sum_k \delta(E - \varepsilon_k) \langle i|k\rangle\langle k|i\rangle$$

$$= \sum_k \langle i|k\rangle E_k^N \langle k|i\rangle$$

$$= \sum_k \langle i|k\rangle\langle k|H^N|k\rangle\langle k|i\rangle$$

$$= \sum_{k,k'} \langle i|k\rangle\langle k|H^N|k'\rangle\langle k'|i\rangle$$

$$= \langle i|H^N|i\rangle$$

$$= \sum_{k,k',k''\ldots} \langle i|H|k\rangle\langle k|H|k'\rangle\langle k'|H|k''\rangle \cdots |H|i\rangle$$

Shell		Moments
0		μ_0, μ_1
1		μ_0, μ_1 μ_2 μ_3
2		μ_0 μ_1 μ_2 μ_3 μ_4 μ_5

$$\mu_1 = H_{00} = a = \varepsilon_d$$

$$\mu_2 = a^2 + \underset{\substack{\uparrow \\ \text{sum of pairwise terms}}}{\sum_j H_{0j}^2}$$

26-02-86

Finnis and Sinclair : bcc transition metals

$$E_i = -\sqrt{\rho_i} + \tfrac{1}{2}\sum_j V(R_{ij})$$

$$\rho_i = \sum_j \phi(R_{ij})$$

$$\phi(R_{ij}) = A^2 (R_{ij} - d)^2 \qquad R_{ij} < d$$

$$V(R_{ij}) = (R_{ij} - c)^2 (c_0 + c_1 r + c_2 r^2) \qquad R_{ij} < c$$

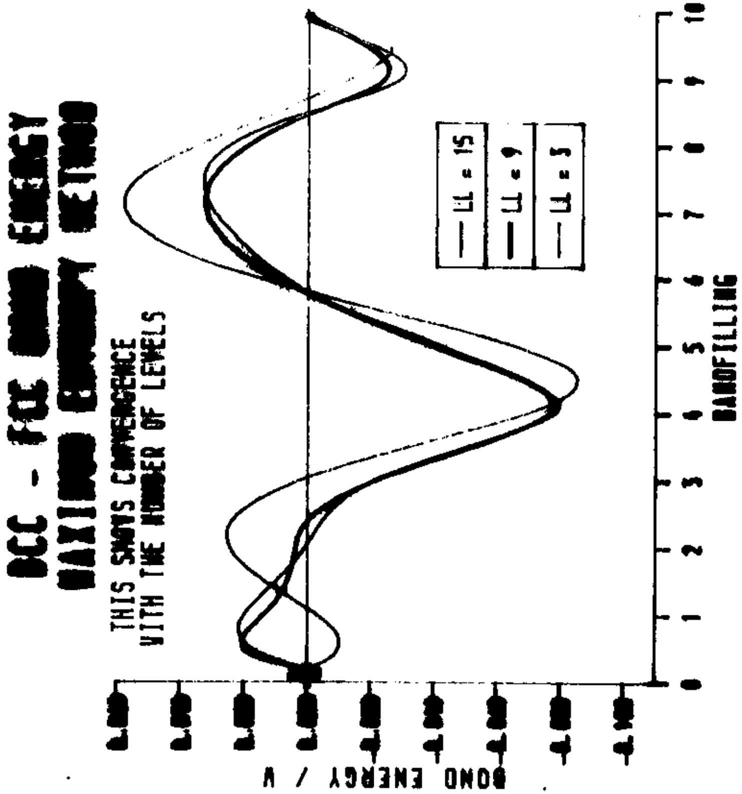
cutoffs c and d between 2nd and 3rd neighbours.

PARAMETERS

c_0, c_1, c_2, A are determined by fitting to E_{coh}, ρ, B, $c_{11}-c_{12}$.

Various cutoffs then to fit C_{44} (non-linear) and $\sim E_v^f$.

c and d.



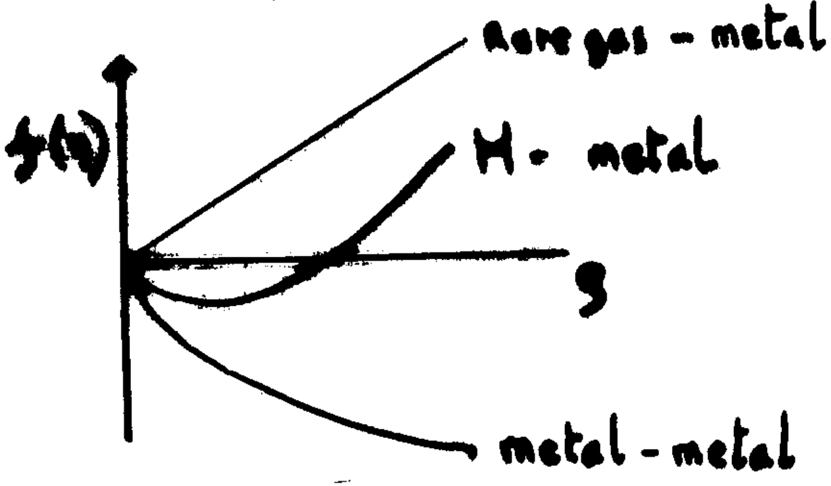
Empirical N-body potentials - EAM

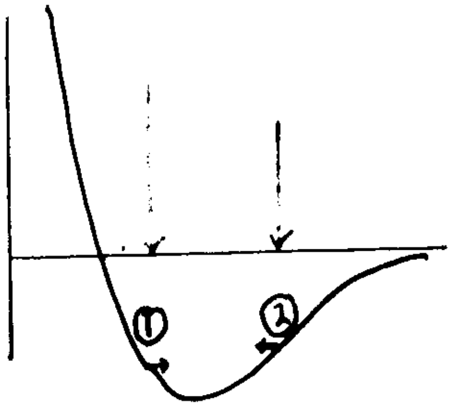
Stott & Zaremba
Norskov
Daw & Baskes

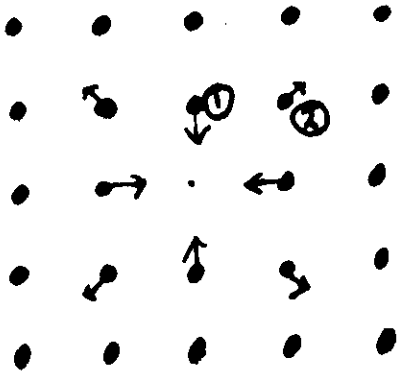
Finnis & Sinclair
Ackland et al
Bacon et al
Ercolessi et al

$$E_i = f(\rho_i) + \tfrac{1}{2}\sum_j V(R_{ij})$$

$$\rho_i = \sum_j \phi(R_{ij})$$







VACANCY IN BCC TRANSITION METALS

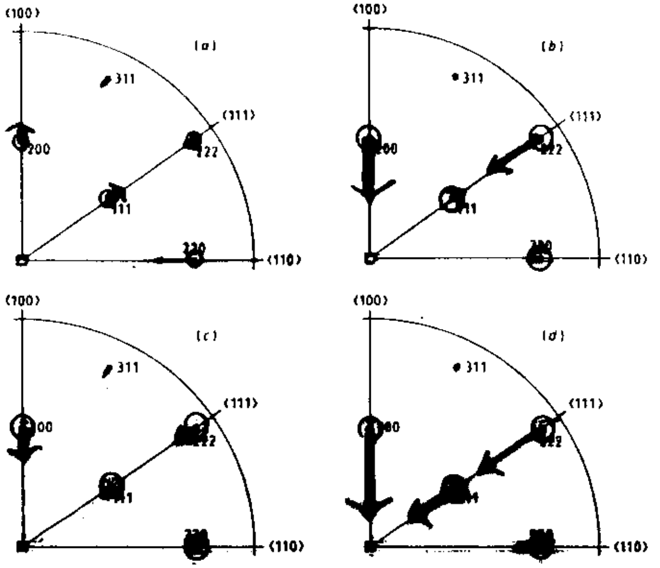


Figure 1. The force fields around the unrelaxed vacancy in (a) Zr, (b) Nb, (c) Mo and (d) Fe. Arrows indicate the direction and relative magnitude of the forces acting on the neighbours of the vacancy [illegible] 1.16 eV/a.

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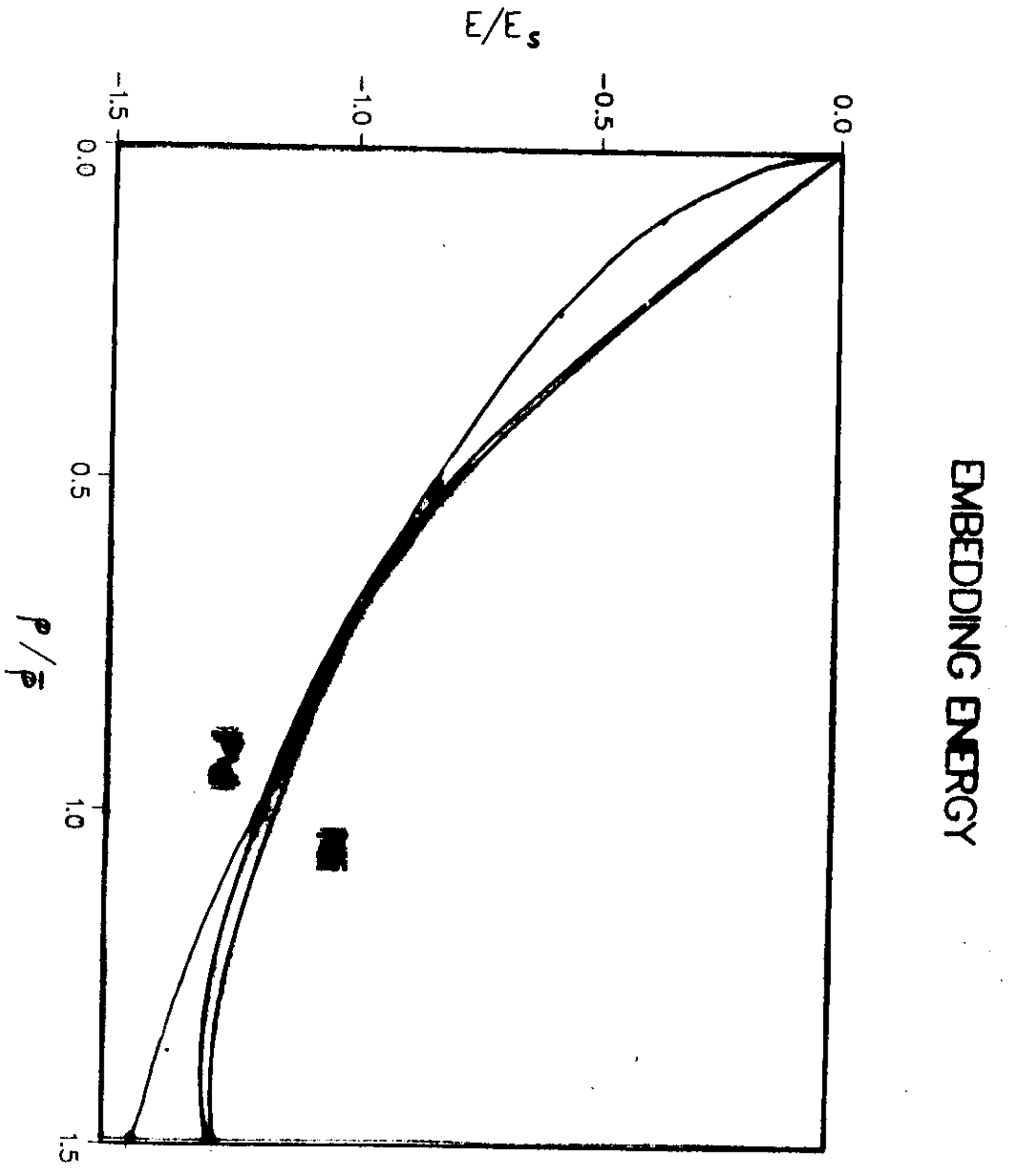
Mo the values are 0.126 eV, 0.044 eV and 0.006 eV for the first, second and third neighbours, respectively, and less than 0.002 eV for more distant neighbours, so that they hardly affect the patterns of the force fields. A similar result has been noticed in the surface relaxation calculation (Terakura *et al* 1981) for Mo. In Zr and Fe the force fields are very different from those in Nb and Mo reflecting the difference in the structural stability of the lattice.

The TBB model enables one to see how the interatomic bonds change and how these force fields appear when the vacancy is introduced. Figure 2 illustrates the vacancy-induced changes in the strength of the bonds in bcc transition metals obtained from the quantitative calculations of the bond energies in Nb and Mo. The major changes are (i) the marked strengthening of the bonds A–B connecting [111] to [222] (energy gain of 0.104 eV per bond), and (ii) a lesser strengthening of the bonds A–C connecting [111] to [$11\bar{1}$] and A–D connecting [111] to [200] (energy gains of 0.047 eV and 0.037 eV per bond, respectively). A characteristic capped cube with eight legs is formed around the vacancy (see figure 2). The second-moment tight-binding model can not predict such characteristic features, although it predicts the homogeneous strengthening of the bonds around the vacancy because the covalent bonding energy in this model is simply proportional to the inverse of the square root of the coordination number. These changes in the bond energy could be understood within the written first-order perturbation theory in



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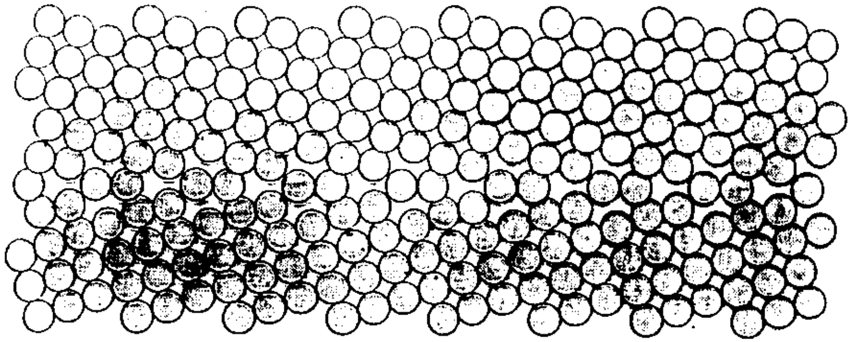

Figure 1 $\Sigma=5$ (310) [001] Grain Boundary in Copper

Figure 2 $\Sigma=5$ (310) [001] Grain Boundary in Cu_3Au

Figure 3 $\Sigma=5$ (310) [001] Grain Boundary in Ni_3Al

FS
- preloaded 0.75 K_a
- relaxed
- dynamic : loading rate 0.5 K_a/ps

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FEM '88 congress
14/15 Nov 1988
Baden-Baden

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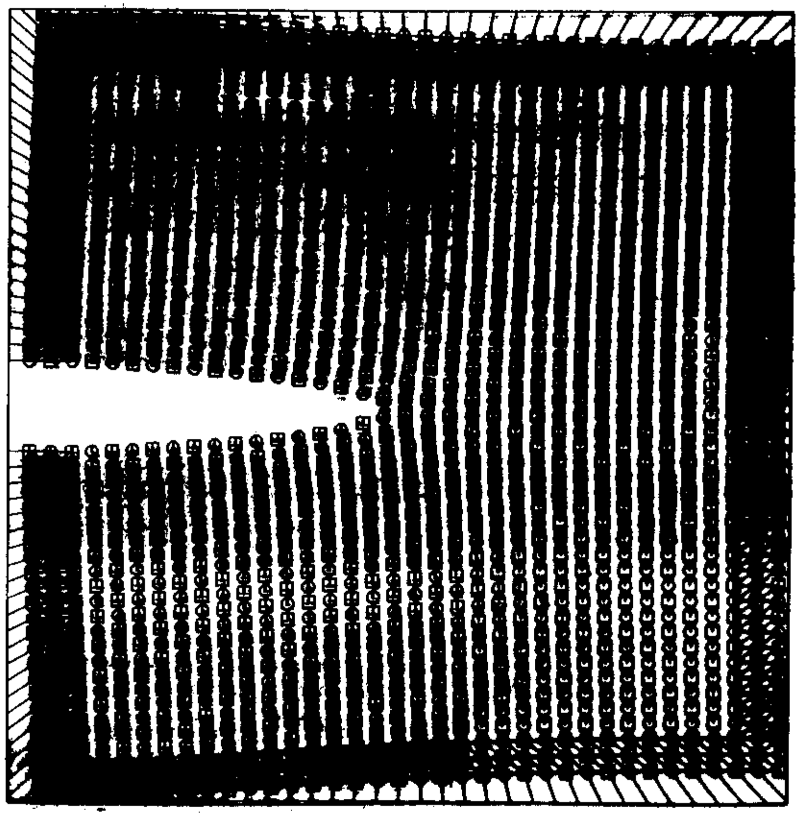

Time Step 700 = 3.500

TBB MODEL : DISCUSSION

ADVANTAGES (with recursion method)

1. Physical description of charge redistribution between bonds
2. Controlled introduction of local environment (μ_n) → μ_2
3. Simplest physical model of structural energy differences
4. CPU time ∝ N (c.f. N^3 for matrix inversion) so large problems should be suitable

[illegible]

1. Limited basis. Need to investigate transferability of H_{ij}. How good are the simplest assumptions, e.g. d orbitals, orthogonality?
2. Still costly ($10^2 - 10^3 \times$ cost of V_{ij}) for μ_5 ...

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Interatomic forces in transition metals

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ABSTRACT

This article reviews some recent progress in the derivation of physical models for calculating the behaviour of defects in transition metals by atomistic simulation. It has long been recognised that it is necessary to go beyond the assumption of pair-wise interactions, but this has only recently been achieved with the advent of simplified models which take account of the electron gas. For d-band metals, the tight-binding model is a useful picture and it can be applied at various levels of approximation. The simplest of these is the second-moment approximation, which is very rapid to compute. Other schemes, such as the embedded-atom method, are also very practical for large scale simulations. These schemes will be described and compared in terms of their physical basis.

§1. INTRODUCTION

It is a common assumption that the total energy of a metal consists of a sum of pair-wise interatomic potentials and a volume-dependent term. Although only roughly true for a particular class of metals, the simple s, p bonded ones, this has been a useful assumption for the progress of theoretical metallurgy, particularly in the field of atomistic simulation of defects. When one looks into the justification for such a simple model of the energetics of a complicated quantum-mechanical system, it rests on the expressions derived by the linear screening of weak pseudo-potentials in the simple, non-transition metals in which the bonding is of nearly free-electron type (Harrison 1966). For the purposes of atomistic simulation of defect energies, this pair-wise picture cannot be expected on theoretical grounds to predict the energies of defects such as vacancies or surfaces, even in those metals where linear screening is good for the perfect crystal, and this failure has been well documented in the literature. The internal inconsistency of a term in the energy which depends on the macroscopic volume of the crystal has also been widely discussed. Nevertheless, pair potentials have maintained a role in atomistic simulation of all metals, including transition metals, because there have been no better founded ways of specifying the energy as a function of configuration which at the same time would allow practical computations. They have also greatly extended our insight into the atomic configurations and processes which can occur in defects such as dislocations and grain boundaries, as will be discussed by others at this symposium.

Over the past fifteen years or so, more sophisticated representations of the energy have started to make an impact on atomistic simulation. Here we shall concentrate on the tight-binding model and the effective-medium models. They offer the possibility of treating realistically the energetics of internal cavities and surfaces, and also of understanding chemical trends in a series of alloys. It should be emphasized that these remain qualitative theories, while extending the range of qualities they can represent. Accurate first-principles calculations are the province of density-functional theory, which is computationally far more costly than the simpler models and until recently had been applied only to perfect crystals. With the advent of supercomputers, progress in atomistic simulation has included the introduction of self-consistent density-functional theory into the relaxation of defect structures, although so far only vacancies and simple interface structures have been treated in Si and Ge. Thus we are at last seeing a meeting of the fields of electron theory and atomistic simulation, which formerly had only a limited influence on one another. For example, the electron theorist saw only the glaring inadequacies of empirical potentials but was unable to deliver the tractable models required to improve the situation. It is fortunate that progress has increased the level of communication between the two camps.

It is still necessary to develop semi-empirical methods which bridge the gap between *ab initio* density-functional treatments and pair-potential descriptions in order to allow more realistic atomistic simulations of complex structures. A popular approach which goes beyond pair potentials is the second-moment approximation of tight-binding theory. This is closely related to the empirical *N*-body potentials and to the effective-medium or embedded-atom model which will be discussed in detail. Since others are describing applications of the empirical potentials, in this Paper we shall concentrate on how they are related to electron theory. Besides drawing attention to the approximations and simplifications which must still be made to obtain tractable models for large-scale atomistic simulation, this approach will also indicate where future developments can be made.

§ 2. FROM DENSITY-FUNCTIONAL THEORY TO ELECTRON-GAS MODELS

Density-functional theory, in its simplest spin-degenerate form, is here summarized. This development, principally the work of Hohenberg and Kohn (1964) and Kohn and Sham (1965), has been of enormous importance to solid-state physics by putting the single-particle picture on a sound theoretical footing. The equations also provide a basis for deriving more approximate schemes of total energy calculation, which is the main reason for introducing them here.

The solid is treated as a system of positive ions and electrons. The ions may be the bare nuclei, as in the first-principles calculations of Moruzzi, Janak and Williams (1978), or they may be pseudo-ions, in which the core electrons are frozen into an effective pseudo-potential. The latter procedure greatly reduces the dimensions of the problem, and in the case of simple s, p bonded elements the weakness of the pseudo-potential means that a basis of plane waves provides a useful way of solving the Schrödinger equation (Payne, Bristowe and Joannopoulos 1986).

The total energy is variationally minimum with respect to the electron density $n(r)$, and is written as a functional of it:

$$E = T[n] + F[n]. \tag{1}$$

To avoid cumbersome notation, r stands for the three-dimensional position, and integrals over r will be understood to be volume integrals. T is the kinetic energy of a system of hypothetical non-interacting particles whose density is the same as that of the actual electrons $n(r)$. It is commonly known as the kinetic energy of the electrons, and it is convenient to refer to it as such, although it is not in fact the expectation value of the many-body kinetic-energy operator. The non-interacting particles are in a potential V_{eff}, to be specified later. Their wavefunctions are solutions of the Schrödinger equation:

$$[-\tfrac{1}{2}\nabla^2 + V_{\text{eff}}(r)]\psi_n = \varepsilon_n\psi_n. \tag{2}$$

The charge density is constructed from the eigenfunctions

$$n(r) = \sum_n a_n\psi_n^*(r)\psi_n(r), \tag{3}$$

where a_n denotes the occupancy of the nth eigenfunction. Hence the kinetic energy functional takes the form

$$T[n] = \sum_n a_n\varepsilon_n - \int n(r)V_{\text{eff}}(r)\,\mathrm{d}r. \tag{4}$$

In extended systems, the eigenvalue sum is usually expressed as the integral over the density of states to the Fermi energy:

$$\sum_n a_n\varepsilon_n = \int^{\varepsilon_F} n(\varepsilon)\,\mathrm{d}\varepsilon. \tag{5}$$

The second part of the total energy in (1) consists of the classical electrostatic energy E_{es} and the correction for exchange and correlation E_{xc}:

$$F[n] = E_{\text{es}}[n] + E_{\text{xc}}[n], \tag{6}$$

where

$$E_{\text{es}}[n] = \tfrac{1}{2}\int n(r)\phi(r)\,\mathrm{d}r + \int n(r)V(r)\,\mathrm{d}r + E_{\text{ii}}, \tag{7}$$

where V is the potential of the bare ions, E_{ii} is their Coulomb interaction energy, and ϕ is the Hartree potential of the electrons,

$$\phi(r) = \int \frac{n(r')}{|r-r'|}\,\mathrm{d}r'. \tag{8}$$

To complete the description of the total energy, and as a basis for calculation, it remains to specify the effective potential V_{eff} and the functional E_{xc}. V_{eff} was shown by Kohn and Sham to be equal to

$$V_{\text{eff}}(r) = V(r) + \phi(r) + \mu_{\text{xc}}(r), \tag{9}$$

where the exchange-correlation potential μ_{xc} is the functional derivative of the exchange-correlation functional:

$$\mu_{\text{xc}} = \frac{\delta E_{\text{xc}}}{\delta n(r)}. \tag{10}$$

So far the theory is exact, but in order to make calculations the local-density approximation (LDA) is normally made, according to which E_{xc} is approximated by the volume integral of its value for a uniform electron gas (jellium) at the local density. As is by now well known, the resulting first-principles calculations of the properties of pure metals and alloys such as lattice parameter, bulk modulus and cohesive energy, are spectacularly successful, especially when magnetic effects are included in the theory (see for example Moruzzi, Janak and Williams (1978) or Williams and von Barth (1983)).

2.1. *Charge density, density of states and the Green function*

Here we discuss some further formal results and notation which are of use in the subsequent discussion. We note that we have introduced the same symbol n for electronic charge density $n(r)$ and electronic density of states $n(\varepsilon)$. It is appropriate to do so because both quantities are contractions of the same operator. To see what is meant by this, and to arrive at useful expressions for later reference, let us introduce the local density of states $n(r,\varepsilon)$ such that

$$n(\varepsilon)=\int n(r,\varepsilon)\,\mathrm{d}r, \tag{11}$$

$$n(r)=\int^{\varepsilon_F} n(r,\varepsilon)\,\mathrm{d}\varepsilon, \tag{12}$$

where

$$n(r,\varepsilon)=\sum_m \psi_m^*(r)\psi_m(r)\delta(\varepsilon-\varepsilon_m). \tag{13}$$

It is useful to think of $n(r,\varepsilon)$ as the diagonal element $n(r,r,\varepsilon)$ of an operator in r-space, whose general elements are $n(r,r',\varepsilon)$. The latter quantity may be written as

$$n(r,r',\varepsilon)=-\frac{1}{\pi}\lim_{\delta\to 0+}\operatorname{Im}\sum_m \psi_m^*(r)\frac{1}{(\varepsilon+\mathrm{i}\delta-\varepsilon_m)}\psi_m(r'), \tag{14}$$

in which a standard expression for the delta function has been used. Equation (14) can be rewritten in the Dirac notation (which is clearer for subsequent derivations)

$$n(r,r',\varepsilon)=-\frac{1}{\pi}\lim_{\delta\to 0}\operatorname{Im}\sum_m \langle r|m\rangle\langle m|(\varepsilon+\mathrm{i}\delta-H)^{-1}|m\rangle\langle m|r'\rangle, \tag{15}$$

where H is the Hamiltonian operator, and with this notation the Schrödinger equation (2) takes the form

$$H|n\rangle=\varepsilon_n|n\rangle. \tag{16}$$

The operator $(\varepsilon-\mathrm{H})^{-1}$ is the one-electron Green function, called $G(\varepsilon)$, and the limit $\delta\to 0$ will be understood but not explicitly written in all subsequent equations involving the imaginary part of G. Noting that the eigenfunctions $|n\rangle$ are an orthonormal set

$$\langle n|m\rangle=\delta_{nm} \tag{17}$$

we can express (15) as

$$n(r,r',\varepsilon)=-\frac{1}{\pi}\operatorname{Im}\sum_m\sum_n\langle r|m\rangle\langle m|G(\varepsilon)|n\rangle\langle n|r'\rangle. \tag{18}$$

Noting further that they are a complete set, namely

$$\sum_n |n\rangle\langle n|=1, \tag{19}$$

we can write

$$n(r,r',\varepsilon)=-\frac{1}{\pi}\operatorname{Im}\langle r|G(\varepsilon)|r'\rangle. \tag{20}$$

This completes the connection between the densities $n(r)$, $n(\varepsilon)$ and the operator G.

In Dirac notation, the operators H and G are diagonal in the basis of eigenfunctions of H, and are written

$$H=\sum_n |n\rangle\varepsilon_n\langle n|, \tag{21}$$

$$G=\sum_n |n\rangle(\varepsilon-\varepsilon_n)^{-1}\langle n|. \tag{22}$$

Another useful operator is the density, of which $n(r)$ is the diagonal element in the r representation. The density operator may be written

$$n=\sum_n |\mathrm{n}\rangle \mathrm{a}_n\langle \mathrm{n}|, \tag{23}$$

or

$$n=-\frac{1}{\pi}\operatorname{Im}\int^{\varepsilon_F} G(\varepsilon)\,\mathrm{d}\varepsilon. \tag{24}$$

These operator concepts allow the terms entering the total energy to be written in a basis-independent form, convenient for manipulation. Thus an integral of the form

$$\int n(r)V(r)\,\mathrm{d}r \tag{25}$$

for example, becomes

$$\int\langle r|n|r'\rangle\langle r'|V|r\rangle\,\mathrm{d}r\,\mathrm{d}r', \tag{26}$$

noting that V is diagonal in the r representation. The integral over r' is analogous to the summation in a matrix product. The integral over r then gives the trace of the product of the n and V operators,

$$\operatorname{Tr} nV, \tag{27}$$

and in this form it is independent of the representation. Similarly

$$\sum_n a_n\varepsilon_n=\operatorname{Tr} nH. \tag{28}$$

In this way the total energy equation (1) can be written, by combining eqns. (4) and (6)-(9) as

$$E=\operatorname{Tr} nH-\operatorname{Tr} n(\tfrac{1}{2}\phi+\mu_{xc})+E_{xc}[n]+E_{ii}. \tag{29}$$

So far we have used two representations, with bases $\{|n\rangle\}$ and $\{|r\rangle\}$. A third, which is employed in the tight-binding model, uses a basis of localized atomic orbitals $\{|\phi_{j\alpha}\rangle\}$, where j labels the atom and α the orbital centred on that atom. In this case the traces in eqn. (29) become conventional matrix products.

2.2. *Local approximations and electron-gas models*

We have already introduced the local approximation for exchange and correlation, the LDA, which replaces the functional $E_{xc}[n]$ by

$$\int n(r)\varepsilon_{xc}(r)\,\mathrm{d}r, \tag{30}$$

in which $\varepsilon_{xc}(r)$ is the exchange and correlation energy per particle of a uniform electron gas of density $n(r)$. The LDA currently provides the most accurate total energy calculations for solids. It is an approximation which one might expect to be valid when the electron density varies little from a uniform value, or is slowly varying, so its high degree of success even for diatomic molecules is surprising. We are concerned here with what further simplifying approximations can be made.

The kinetic energy in eqn. (4) can also be cast into a form involving the integral of a 'local' kinetic-energy density,

$$T[n]=\int t(r,[n])\,\mathrm{d}r, \tag{31}$$

where

$$t(r,[n])=e(r,[n])-n(r)V_{\mathrm{eff}}(r), \tag{32}$$

$$e(r,[n])=\int^{\varepsilon_F}\varepsilon n(r,\varepsilon)\,\mathrm{d}\varepsilon. \tag{33}$$

It is understood that the kinetic-energy density $t(r,[n])$ and the local one-electron energy sum $e(r,[n])$ are really non-local quantities, being functionals of the entire electron density. If we approximate $t(r,[n])$ by a local function $t^{\mathrm{jellium}}(n(r))$ we obtain the Thomas–Fermi model, or rather since exchange and correlation are included, the family of Thomas–Fermi-like models, which can be improved by adding gradient terms to t.

2.3. *The rigid-atom model*

The postulate that the electron density in a solid is composed of a superposition of atomic charge densities has long been a starting point for band-structure calculations, which may then go on to iterate the charge density to self-consistency. Recently Harris (1985) and Foulkes (1987) have made important progress by formulating an approximate expression for the total energy based on this, or a similar, zeroeth-order charge density. Let us denote the Hamiltonian associated with the overlapping atomic charge densities by H^{in}, in which the superscript is short for 'input'. The electrostatic and exchange-correlation potentials are also calculated from the superimposed zeroeth-order charges, thus

$$H^{\mathrm{in}}=-\tfrac{1}{2}\nabla^2+V^{\mathrm{in}}_{\mathrm{eff}}(r), \tag{34}$$

where

$$V^{\mathrm{in}}_{\mathrm{eff}}(r)=V(r)+\phi^{\mathrm{in}}(r)+\mu^{\mathrm{in}}_{xc}(r). \tag{35}$$

We suppose that the Schrödinger equation is solved with the Hamiltonian H^{in}, giving eigenvalues $\varepsilon^{\mathrm{out}}_m$, and from the eigenstates the density n^{out} is constructed. By expanding the energy (29) in powers of the deviation of the density from its self-consistent value n^{sc}, Harris (1985) and Foulkes (1987) have shown that

$$E=E^{\mathrm{rigat}}+O^2(n^{\mathrm{sc}}-n^{\mathrm{in}},n^{\mathrm{sc}}-n^{\mathrm{out}}), \tag{36}$$

where

$$E^{\mathrm{rigat}}=\sum_n a_n\varepsilon^{\mathrm{out}}_n-\int[\tfrac{1}{2}n^{\mathrm{in}}(r)\phi^{\mathrm{in}}(r)+n^{\mathrm{in}}(r)\mu^{\mathrm{in}}_{xc}(r)]\,\mathrm{d}r+E_{xc}[n^{\mathrm{in}}]+E_{ii}, \tag{37}$$

which in the notation introduced above becomes

$$E^{\mathrm{rigat}}=\mathrm{Tr}\,n^{\mathrm{out}}H^{\mathrm{in}}-\mathrm{Tr}\,n^{\mathrm{in}}(\tfrac{1}{2}\phi^{\mathrm{in}}+\mu^{\mathrm{in}}_{xc})+E_{xc}[n^{\mathrm{in}}]+E_{ii}. \tag{38}$$

Comparing this expression with the exact one, eqn. (29), we see that the sum of the eigenvalues, $\mathrm{Tr}\,nH$, has been replaced by the sum of the eigenvalues of the approximate Hamiltonian, and in the remaining electrostatic and exchange-correlation terms the input charge density has been used. The important point is that the correction terms are of second order in the error in the charge density, which is an effect of the variational principle. As a consequence, the approximation involved in neglecting these corrections is surprisingly accurate. Harris (1985) calculated the binding energies, bond lengths and vibration frequencies of a number of dimers, namely Be_2, C_2, N_2, F_2 and Cu_2 and compared the results from eqn. (37) with self-consistent calculations. Among all these quantities the worst error was 21%, which was for the binding energy of C_2, in its double π-bonded ground state. Nevertheless, its vibration frequency was only 6% too high. It should be pointed out that the approximate energy (37) or (38) is not simply the density functional (1) with an approximate density n^{in}, but includes n^{out} in its kinetic energy, which means that we do not have any guarantee from the variational principle that the approximate energy lies above the exact energy.

If we substitute for the sum of eigenvalues in eqn. (37) using

$$\sum_n a_n\varepsilon^{\mathrm{out}}_n=T[n^{\mathrm{out}}]+\mathrm{Tr}\,n^{\mathrm{out}}V^{\mathrm{in}}_{\mathrm{eff}}, \tag{39}$$

we can write

$$E^{\mathrm{rigat}}=E[n^{\mathrm{in}}]+\Delta E^{\mathrm{rigat}}, \tag{40}$$

where

$$E[n^{\mathrm{in}}]=T[n^{\mathrm{in}}]+\int[\tfrac{1}{2}n^{\mathrm{in}}(r)\phi^{\mathrm{in}}(r)+n^{\mathrm{in}}(r)V^{\mathrm{in}}_{\mathrm{eff}}(r)]\,\mathrm{d}r+E_{xc}[n^{\mathrm{in}}]+E_{ii}, \tag{41}$$

and

$$\Delta E^{\mathrm{rigat}}=T[n^{\mathrm{out}}]-T[n^{\mathrm{in}}]+\mathrm{Tr}\,(n^{\mathrm{out}}-n^{\mathrm{in}})V^{\mathrm{in}}_{\mathrm{eff}}. \tag{42}$$

The correction term of eqn. (42) can be shown to vanish to second order in the density differences $(n^{\mathrm{in}}-n^{\mathrm{sc}})$ and $(n^{\mathrm{out}}-n^{\mathrm{sc}})$ as follows. Neglecting second-order terms, eqn. (42) can be expanded in a Taylor series:

$$\Delta E^{\mathrm{rigat}}\approx\int\left(\frac{\delta T}{\delta n}+V^{\mathrm{in}}_{\mathrm{eff}}\right)(n^{\mathrm{out}}-n^{\mathrm{in}})\,\mathrm{d}r, \tag{43}$$

where the functional derivative of $T[n]$ is evaluated at n^{in}. Now we see by comparing with (1) and (6) (10) that the first factor in the integrand vanishes by the variational principle at $n = n^{\text{sc}}$, so this factor evaluated at n^{in} is of order $n^{\text{sc}} - n^{\text{in}}$. Hence ΔE^{Harris} is of order $(n^{\text{in}} - n^{\text{sc}})(n^{\text{out}} - n^{\text{sc}})$. Furthermore, since the variational principle tells us directly that

$$E[n^{\text{in}}] = E[n^{\text{sc}}] + O[(n^{\text{in}} - n^{\text{sc}})^2], \tag{44}$$

we have also proved the equivalence of E^{Harris} and $E[n^{\text{sc}}]$ to second order. Finally, we note that if we insert local approximations for T and E_{xc} into $E[n^{\text{in}}]$, we recover the formula for the energy of overlapping atomic charges proposed by Gordon and Kim (1972), and reviewed by Clugston (1978), which has several variants. Formulae of essentially this type were originally proposed for calculating interatomic forces by Jensen (1932, 1936) and Lenz (1932) and developed by Wedepohl (1967). The Gordon–Kim formula for a pair of atoms gives interatomic potentials which are especially useful for closed-shell systems, and they have been used to provide short-range repulsive potentials for atomistic simulation. Further references are given by Harding and Harker (1982) who have published a set of FORTRAN codes for implementing the scheme for any dimer, with various options for exchange-correlation and atomic configuration.

§3. TIGHT-BINDING MODELS

Tight-binding models of the energy of solids have been extensively applied to describe the energetics of transition metals and their alloys, and have accounted for the trends across the periodic table of cohesive energy, bulk modulus, crystal structure and heats of alloy formation (see the reviews by Heine, Haydock, Bullett and Kelly (1980) and Pettifor (1983)). Also sp-bonded elements (Chadi and Cohen 1975) and compounds (Majewski and Vogel 1986) and pd-bonded compounds (Pettifor and Podloucky 1986) have been successfully treated. One does not pretend to be able to make quantitative predictions of delicate energy differences in these tight-binding models; the emphasis is on understanding trends. Such a limited goal is worthwhile; if for example it could be generally achieved in metallurgical systems it would be a scientific basis to guide alloy designers. With the advent of more powerful computers the application to atomistic relaxation, essential for describing defects, started to become feasible in the 1970s. Calculations in which atomic positions are relaxed have been made on vacancies (Allan and Lanoo 1976), dislocations (Masuda and Sato 1981, Masuda, Yamamoto and Doyama 1983, Legrand 1985) and surfaces (Tréglia, Desjonquères and Spanjaard 1983, Tréglia, Ducastelle and Spanjaard 1980, Terakura, Terakura and Hamada 1981, Masuda-Jindo, Hamada and Terakura 1984). The first surface relaxations with the tight-binding method were actually for the group IV semiconductors and GaAs (Chadi 1979 a, b), using a basis of four orbitals per atom.

A tight-binding model Hamiltonian represents the electron states in a localized energy-independent basis set $|\phi_{j\alpha}\rangle$, in which j labels the atomic site and α the orbital localized on that site. Normally for transition metals a basis of five distinct d orbitals is used. In fact the orbitals are never explicitly calculated, since the charge density is never sought in real space (the r representation), but rather Green functions and densities of states are expressed in the $j\alpha$ representation. Thus the integrals over r in §2 become summations over j and α, and, analogously to the local density of states $n(r, \varepsilon)$, there is a local density of states on a site and orbital $n^{j\alpha}(\varepsilon)$. From (24) we obtain density-matrix elements

$$n^{i\alpha j\beta} = -\frac{1}{\pi} \operatorname{Im} \int^{\varepsilon_F} G^{i\alpha j\beta}(\varepsilon)\, d\varepsilon. \tag{45}$$

The intersite elements of the density matrix are known as bond orders. The diagonal elements of the density matrix represent the electronic charge in a particular orbital on a particular site. Hence the charge on an atom is

$$q^i = \sum_{\alpha} n^{i\alpha i\alpha}. \tag{46}$$

Besides the simplification of an incomplete basis set, two other approximations are common to the tight-binding models concerned with energy calculations, namely

(i) three-centre terms in the matrix elements of H between orbitals on atoms i and j are neglected, and

(ii) the matrix elements of H between different orbitals on the same site are neglected, that is, $H_{i\alpha i\beta} = H_{i\alpha i\alpha}\delta_{\alpha\beta}$.

It is also often assumed for simplicity that the basis is orthonormal, which means assuming a diagonal matrix of overlap integrals.

3.1. *The tight-binding bond model*

The bond orders or density-matrix elements are the key quantities which enable one to make a more local and chemical description of the energy. Indeed the above definitions simply generalize to extended systems the ideas of bond order originally introduced by Coulson (1939) to described the chemical bond in hydrocarbon molecules. The sum of the eigenvalues in the site-orbital representation becomes, from eqn. (28):

$$\sum_n a_n \varepsilon_n = \sum_{i\alpha j\beta} n^{i\alpha j\beta} H_{i\alpha j\beta}. \tag{47}$$

The off-diagonal elements of the trace in eqn. (47) are a pair-wise summation which we shall call the covalent bond energy:

$$E_{\text{cov}} = \sum_{i\alpha \neq j\beta} n^{i\alpha j\beta} H_{i\alpha j\beta}. \tag{48}$$

An equivalent expression for the covalent bond energy is readily obtained in terms of the local density of states:

$$E_{\text{cov}} = \sum_{i\alpha} \int^{\varepsilon_F} n^{i\alpha}(\varepsilon)(\varepsilon - H_{i\alpha i\alpha})\, d\varepsilon. \tag{49}$$

Allan (1970) discussed defect energies using eqn. (49), in which the subtraction of the diagonal term was regarded as a correction for the double counting of the electron–electron interaction. It is the normal practice in the field to describe the remainder of the total energy as a sum of pair-wise repulsive terms, thus:

$$E = E_{\text{cov}} + E_{\text{rep}}. \tag{50}$$

The model goes on to assume that the elements of H are transferable between different situations, for example at defects, just as pair potentials were assumed to be transferable.

Sutton, Finnis, Pettifor and Ohta (1988) have arrived at the expression (50) by a different route. It has long been a criticism of empirical tight-binding theory that much effort goes into evaluating the sum of one-particle energies but that all the rest of the total energy is collected in an empirical pair-wise term, which is invariably assumed to be a sum of interatomic Born–Mayer repulsions. Thanks to the Harris and Foulkes analysis discussed in §2 we can now understand much better what this approximation means. Equation (6) shows that the part of the total energy not counted in the one-electron sum is indeed a classical pair-wise electrostatic interaction apart from the exchange and correlation terms. These can only be approximately pair-wise, for example as obtained by neglecting three-body terms in an expansion of the local exchange function $\rho^{4/3}$, where ρ is the superimposed atomic charge density, and it is hoped that the error is sufficiently small. There arises a problem because this identification of the pair-wise repulsive term as complementary to $\Sigma_n a_n \varepsilon_n$ does not appear to require the subtraction of the diagonal terms from (47). These diagonal terms include the crystal-field effects on the potential at a given atomic site, and it is very convenient to regard them also as included in the pair-wise term in order to write the energy in the form (50) rather than writing, as some authors have done,

$$E = \sum_n a_n \varepsilon_n + E_{rep}. \tag{51}$$

By losing the diagonal elements of H in this way we seem to be departing from the Harris model (38). However, we are probably doing less violence to the physical principles by subsuming the crystal-field terms in a pair-wise potential than we would be by simply ignoring their site-to-site variation in an imperfect crystal. Furthermore, we are led to a very simple form for the interatomic forces. To complete the specification of the model (50), which is what we have called the tight-binding bond (TBB) model, we add the condition that the atoms should be neutral in all environments, so that the q^i of eqn. (46) do not vary with the atomic configuration. This imposes a degree of self-consistency on the model, which in practice is achieved by varying the diagonal elements of H iteratively until the q^i converge to their initial constant values (Ohta, Finnis, Sutton and Pettifor 1987, Paxton 1987).

In the two-centre approximation the overlap integrals $H_{i\alpha j\beta}$ are a function only of the vector $\mathbf{R}_{ij}$ between atoms i and j. Slater and Koster (1954) discussed and tabulated the transformation rules for $H_{i\alpha j\beta}$ under arbitrary rotations according to the s, p or d symmetry of the orbitals α and β. For applications it is also necessary to know the radial dependence of the overlap integrals. In the tight-binding calculations referred to, H and its radial dependence are fitted to band-structure calculations or are obtained from canonical band theory (Andersen 1975). To illustrate these ideas we will describe some covalent bond energy calculations using the canonical d-band Hamiltonian (Pettifor 1977) which is adequate to explain the trends in crystal structure across the transition-metal series, namely h.c.p. b.c.c. h.c.p. f.c.c., although it incorrectly predicts b.c.c. as the stable structure near the end of the series. With the z axis along the bond the matrix elements of the Hamiltonian H take the simple form (Slater and Koster 1954)

$$\left.\begin{aligned} H_{11} &= H_{44} = \mathrm{dd}\delta, \\ H_{22} &= H_{33} = \mathrm{dd}\pi, \\ H_{55} &= \mathrm{dd}\sigma, \\ H_{\alpha\beta} &= 0; \quad \alpha \neq \beta. \end{aligned}\right| \tag{52}$$

The suffixes label atomic d orbitals $|\alpha\rangle$; $\alpha = 1, 2, 3, 4, 5$, which have the following symmetry:

Orbital	Symmetry
1	xy
2	yz
3	zx
4	$\frac{1}{2}(x^2 - y^2)$
5	$\frac{1}{2\sqrt{3}}(3z^2 - r^2)$.

The overlap parameters vary as the inverse fifth power of the interatomic distance R according to

$$\left.\begin{aligned} \mathrm{dd}\sigma &= -6W\left(\frac{2}{5}\right)\left(\frac{S}{R}\right)^5, \\ \mathrm{dd}\pi &= +4W\left(\frac{2}{5}\right)\left(\frac{S}{R}\right)^5, \\ \mathrm{dd}\delta &= -1W\left(\frac{2}{5}\right)\left(\frac{S}{R}\right)^5, \end{aligned}\right\} \tag{53}$$

where S is the Wigner–Seitz radius, and W is the nominal bandwidth, which we use as the unit of energy. We assume that the range of the overlaps is limited to nearest neighbours in the f.c.c. and h.c.p. structures and to second-nearest neighbours in the b.c.c. structure. We have not, of course, recovered a truly pair-wise description of the energy, because the bond orders depend on the local atomic configuration. The TBB-model picture of the energy as a classical pair-wise term, mostly electrostatic in origin, plus a quantum-mechanical bonding term is still a great simplification, albeit a more physical one than the pair-wise force model.

3.2. *Interatomic forces in the TBB model*

For details of the derivation of the expression for forces and other details of the TBB model we refer the reader to Sutton, Finnis, Pettifor and Ohta (1988), where the general case of non-orthogonal orbitals is treated. A similar expression for orthonormal orbitals has been derived by several authors (Moraitis and Gautier 1979, Chadi 1984, Sankey and Allen 1986, Pollman, Kalla, Kruger, Mazur and Wolfgarten 1986), and originally by Coulson (1939). We simply state the result here for the force on an atom k:

$$\frac{\partial E}{\partial x_k} = \sum_{j \neq k} 2n^{k\alpha j\beta} \frac{\partial H_{j\beta k\alpha}}{\partial x_k} + \frac{\partial E_{rep}}{\partial x_k}. \tag{54}$$

The attraction of this formula for atomistic simulation is that it does not require the derivatives of the density matrix, which are not readily available, but only the derivatives of H, which are easy to calculate within the model. The reason for this lies in the variational principle, which tells us that the energy is stationary with respect to variations in the charge density, together with the condition of atomic charge neutrality.

It is also attractive that eqn. (54) expresses the force on an atom as a sum of interatomic or bond forces. The alternative which has been used in previous work would be to evaluate the force on an atom numerically by numerical differentiation of the total energy. This procedure requires the evaluation of densities of states on all atoms affected by the atom under consideration, which is normally more than the nearest neighbours involved in the explicit force formula (54).

To illustrate the concept, we return to the simple d-band model, in which the covalent bond energy (47) is a sum of individual covalent bond energies of the form

$$E^{ij}_{\text{cov}} = 2\text{dd}\sigma(n^{i5j5}) + 2\text{dd}\pi(n^{i2j2} + n^{i3j3}) + 2\text{dd}\delta(n^{i1j1} + n^{i4j4}). \tag{55}$$

From eqn. (54), the radial force associated with this bond is

$$F^{ij}_{\text{cov}} = -(5/R_{ij})[2\text{dd}\sigma(n^{i5j5}) + 2\text{dd}\pi(n^{i2j2} + n^{i3j3}) + \text{dd}\delta(n^{i1j1} + n^{i4j4})]. \tag{56}$$

This force is in the sense of shortening the bond distance, in other words it is an attractive force. In general there would also be a transverse component of the interatomic force, due to the angular derivatives of H, but this vanishes by symmetry in the perfect lattice.

3.3. *Calculations*

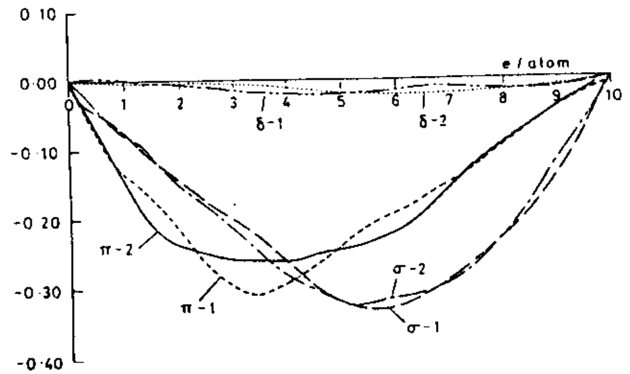
We turn now to consider some general aspects of methods used for implementing the tight-binding models discussed above, without going into the details of numerical and programming techniques which form a large field in their own right. There are many technical differences between methods, but they all broadly fall into k-space or real-space classes. In k-space the calculations have to be done on a periodic system, which can nevertheless contain over 100 atoms, whilst in real space the recursion method is favoured. The essential feature of real-space methods is that the calculation of the local density of states, or more generally the Green-function matrix elements, only includes the effect of the immediate environment of the atom or bond. For systems involving a large number N of atoms, the matrix inversion, which is the expensive part of a k-space calculation, will require $\sim N^3$ operations, whereas the time for the equivalent recursion-method calculation will be proportional to N. However we do not presently know at what value of N the real-space approach becomes cheaper. With the recursion method, Green-function matrix elements can be obtained in the form of continued fractions, as described for example by Haydock, Heine and Kelly (1972). It can be shown that if n shells of neighbours are included, then the first $2n+2$ moments, $\mu_0 \ldots \mu_{2n+1}$, of the density of states can be obtained exactly. Precisely how the density of states is then approximated is related to the problem of terminating the moment expansion (Cyrot-Lackmann 1968) or the continued fraction representation of a Green-function matrix element or resolvant, and has been investigated in detail by many authors (see for example the articles and references in Pettifor and Weaire (1985)). Although the moments are not normally explicitly calculated, it is helpful to realise that μ_n is simply a sum of products of n Hamiltonian matrix elements, the sum being over all paths of length n which start at the given orbital and hop to other orbitals before finally returning, with a matrix element multiplied in for each step. Thus for example, if $|0\rangle$ is the orbital whose local density of states we want, then its second moment would be

$$\mu_2 = \sum_{i\alpha} \langle 0|H|i\alpha\rangle\langle i\alpha|H|0\rangle. \tag{57}$$

The summation extends only to the range of H, which normally means the nearest neighbours in f.c.c. or the first- and second-nearest neighbours in b.c.c.

Figure 1 shows calculated covalent bond energies in an ideal h.c.p. lattice with the above canonical d-bond model, using the recursion method on a cluster of fifteen shells about the bond, which is large enough to ensure that the small energy differences between the bonds are reasonably well represented. These calculations used the method of Beer and Pettifor (1985) to terminate the continued fraction. The size of the cluster is a major consideration in implementations of the method, because a balance must be struck between accuracy and computer time, and this calculation which effectively includes μ_{29} is much bigger than one would contemplate as part of a full-scale atomistic relaxation. The covalent bond energies are broken down according to the σ, π or δ symmetry of the orbitals, just as the three terms in eqn. (55). We see that the two kinds of nearest neighbours, those in and out of the basal plane, have slightly different bond energies, since they have different atomic environments, which would not of course be seen by pair potentials. Furthermore, if we look in particular at the band filling corresponding to the real hexagonal metals Ti and Zr, namely 1 2 electrons, the out-of-plane π bond has a significantly lower energy than the basal plane π bond. This would explain why the observed c/a ratio of these metals is less than the ideal value assumed in the calculation. Looking at the bond force, eqn. (56), we see that the calculated electronic contribution of the π bond is such as to pull more strongly on the out-of-plane neighbours, thus tending to reduce the c/a ratio.

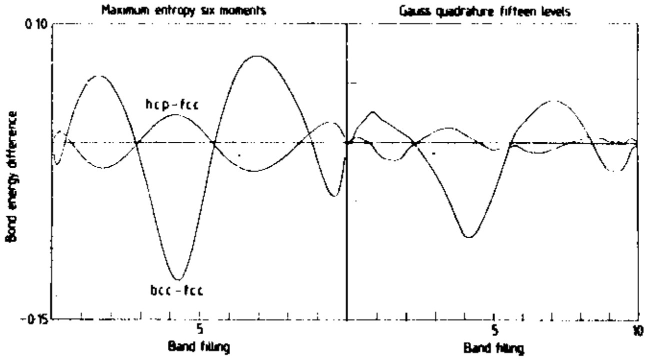
Fig. 1



The ddσ, ddπ and ddδ contributions to the bond energies, in arbitrary units, for a h.c.p. crystal of ideal axial ratio, using the canonical d-band parameters given in §3. Labels 1 and 2 denote neighbours in and out of the basal plane respectively.

The h.c.p. case raises another point of interest. If only one shell of neighbours of an atom is considered, h.c.p. and f.c.c. structures are very similar, each having twelve equivalent nearest-neighbour bonds. Thus the second and third moments, μ_2 and μ_3, of the local densities of states are identical. In both f.c.c. and h.c.p. structures the second shell consists of six equidistant neighbours, lying at the same distance in each structure although disposed differently according to the cubic or hexagonal symmetry. A purely pair-wise potential model would therefore have to extend beyond second neighbours to see any difference in energy between the structures. The different bond angles between the neighbours are only reflected in μ_4, which distinguishes the structural energies with the first and second shell of neighbours. However, to get a converged structural energy difference between h.c.p. and f.c.c. it has proved

Fig. 2

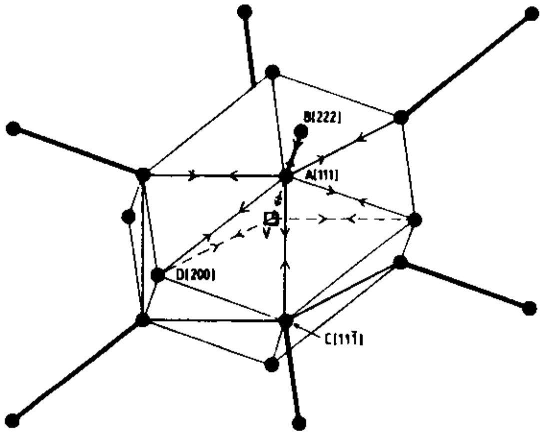


b.c.c.–f.c.c. and h.c.p.–f.c.c. bond energy differences, with the canonical d-band model using only six moments (up to μ_5) of the Green functions (left-hand graph) compared to the more exact Gaussian quadrature from fifteen recursion levels (up to μ_{29}; right-hand graph). After Glanville *et al.* (1988, to be published). The maximum-entropy method was not competitive with Gaussian quadrature for more than six moments.

necessary to include at least μ_5 of the local density of states (Legrand 1985). The effect of the number of exact moments on the calculation of structural energy differences has recently been studied by Glanville, Paxton and Finnis (1988), who also compared various methods of recovering the structural energy from the limited number of moments or recursion levels of the bonding and antibonding densities of states. The methods studied included the square-root terminator of Beer and Pettifor (1985), the maximum-entropy method recently used in this context by Brown and Carlsson (1985) and the Gaussian quadrature method of Nex (1978), which appears to be the best method for proceeding if more than four levels of recursion can be done (μ_6 or more; see fig. 2).

A purely bond-breaking model predicts that the vacancy formation and cohesive energies are the same (apart from the relatively small effect of relaxation), which among the elements is only the case (approximately) in the rare gases. Relaxation of the electronic charge is essential to an explanation of why observed vacancy formation energies in metals are much less than the cohesive energy; typically the vacancy formation energy is about one-third of the cohesive energy. Tight-binding calculations of covalent bond energy show explicitly how bond energies and interatomic forces are modified at defects. For example around a vacancy, there is considerable strengthening of the bonds compared to their bulk values (Ohta, Finnis, Pettifor and Sutton (1987); see fig. 3). This vacancy-induced bond energy strengthening is readily understood at the level of μ_2. For the electron energies obtained by integrating $\varepsilon n(\varepsilon)$ to the Fermi level, μ_2 will scale in any model of the density of states roughly as $\sqrt{\mu_2}$, and as we see from eqn. (57), μ_2 is proportional to the atomic coordination z. Thus the energy per bond scales as $1/\sqrt{z}$, and this is strengthened by reducing z, as around a vacancy. The converse effect as z goes to $z+1$ has been suggested as a mechanism of the weakening of metal–metal bonds by hydrogen (Sayers 1984).

Fig. 3



The vacancy-induced changes in the bond strengths in Mo. All the bonds become stronger, to an extent which is indicated by the thickness of the lines drawn between the atoms. The bonds not indicated by lines are little affected by the vacancy. The pair of arrows →·← stands for the interatomic force becoming more attractive or less repulsive, and the pair of arrows ←·→ stands for the interatomic force becoming less attractive or more repulsive.

§4. *N*-BODY POTENTIALS

Motivated by the separation of a cohesive, electronic energy and a pair-wise repulsive energy which appears in tight-binding models, Finnis and Sinclair (1984) took an empirical approach to describing the total energy, by writing

$$E=\sum_i f(\rho_i)+E_{\text{rep}}. \tag{58}$$

(In the original paper a factor A was included before f.) By analogy with the second-moment approximation, ρ_i was understood as a measure of the coordination of atom i, a generalization of the discrete quantity z. Likewise f was taken to be the square-root function. The coordination or local density of atoms was written

$$\rho_i=\sum_j \phi(R_{ij}), \tag{59}$$

where the function ϕ was assumed pair-wise, and E_{rep} took the pair-wise form

$$E_{\text{rep}}=\tfrac{1}{2}\sum_{ij} V(R_{ij}). \tag{60}$$

From then on the approach was entirely empirical. Simple short-ranged functional forms were assumed for ϕ and V and fitted to cohesive energy, lattice parameter, elastic constants, and roughly to the vacancy formation energy, for the b.c.c. elements V, Cr, Fe, Nb, Mo, Ta and W. The cores of the potentials were subsequently calculated from an electron-gas model, which ensured stability of the models under high pressure (Ackland and Thetford 1987). Similar modifications have been proposed by Rebonato, Welch, Hatcher and Bilello (1987).

Empirical pair potentials alone could never predict the elastic constants correctly together with the observed atomic volume because in a purely pair-potential model the Cauchy relation holds, which in cubic crystals is

$$C_{12}-C_{44}=0. \tag{61}$$

However, in most real metals the Cauchy relation is violated. A common approach is to add a term in the energy which is a function of the total volume of the crystal. This only has any justification for simple (non-transition) metals. The N-body potential is an important improvement over such empirical pair potentials in that the Cauchy discrepancy $C_{12}-C_{44}$ is described without recourse to any such volume term in the energy. Such a volume term presented problems when surfaces or cavities were considered, since the surface energies could not be well described. Furthermore a term in the energy depending on the total volume leads to inconsistencies between the longitudinal elastic constants or bulk modulus as calculated by the method of long waves (constant total volume) and as calculated by imposing a homogeneous deformation.

If the function $f(\rho)$ is expanded about some average or perfect-lattice value of ρ, which we call ρ^0, then the linear term gives a pair potential which we could add to the pair potential in E_{rep} to obtain an effective pair potential

$$V_{\text{eff}}=V(R)+2f'(\rho^0)\phi(R). \tag{62}$$

Terms if $f''(\rho^0)$ and higher-order derivatives contribute to many-body forces. It is instructive to write the elastic constants for the b.c.c. crystals in terms of this effective pair contribution and the second-derivative terms. The independent elastic constant may be expressed as the two shear constants and the Cauchy discrepancy (or Cauchy pressure) thus:

$$\Omega C_{44}=\tfrac{8}{9}V_{\text{eff}}'(R_1)R_1+\tfrac{4}{9}V_{\text{eff}}''(R_1)R_1^2+V_{\text{eff}}'(R_2)R_2, \tag{63}$$

$$\Omega(C_{11}-C_{12})=\tfrac{4}{3}V_{\text{eff}}'(R_1)R_1+V_{\text{eff}}''(R_1)R_1^2, \tag{64}$$

$$\Omega(C_{12}-C_{44})=f''(\rho^0)[\tfrac{8}{3}\phi'(R_1)R_1+2\phi'(R_2)R_2]^2, \tag{65}$$

where Ω is the atomic volume and R_1 and R_2 are the first and second neighbour distances. The expressions for the two shear constants could be derived as in the old pair-potential models, as if the pair potential V_{eff} completely described the constant-volume distortions. On the other hand, the Cauchy discrepancy is directly proportional to $f''(\rho^0)$, which is a measure of the many-body nature of the forces. The experimental sign of the Cauchy pressure is positive, which is consistent with the concave behaviour of the negative square-root function assumed for f.

We do not expect this short ranged N-body model to give particularly good dispersive properties, such as phonon frequencies, for which longer-range forces play an obvious role. For example, particularly in the phonon-dispersion curves in Nb, there are anomalies that are ascribed to interatomic force constants at sixth and further neighbours. A simple tight-binding model can account for these (Varma and

Weber 1979, Finnis, Kear and Pettifor 1984), and it is certainly necessary to include more than μ_2. The phonon-dispersion curves with the N-body potentials therefore leave something to be desired in b.c.c. metals, as the calculations of Rebonato and Broughton (1987) show. The N-body potentials should rather be applied to simulations in which cohesive properties or surface energies are important, for example in radiation damage involving voids and bubbles or in crack simulations. Although the detailed surface reconstructions seen on the b.c.c. transition metals are not predicted by these models, as they have been with tight-binding, the general feature of an inward surface layer relaxation is (Ackland and Finnis 1986).

A major advantage of the N-body potentials for atomistic simulation is that they do not give rise to significantly longer computation times than classical pair potentials, whereas the more sophisticated tight-binding models give rise to times longer by a factor of one-thousand at least. In many studies, for example on the possible behaviour of grain boundaries and dislocation cores, insights could be gained by using simple pair potentials, but the N-body potentials and the closely related embedded atom models now offer a somewhat more satisfactory description of the elastic properties, and a further test of the sensitivity of possible configurations to the interatomic force laws. Further applications are described in detail by Matthai and Bacon (1985), Maysenhoelder (1986) and Harder and Bacon (1987). Similar potentials have been developed for the noble metals and Ni by Ackland, Tichy, Vitek and Finnis (1987), and for Au by Ercolessi, Tosatti and Parrinello (1986).

§5. EFFECTIVE-MEDIUM MODELS

An expression identical in form to eqn. (58) is the basis of the effective-medium method, a form of which is also referred to as the embedded-atom model, which was first applied to a metallic system in a simulation study of hydrogen embrittlement of Ni by Daw and Baskes (1983). The model has subsequently been applied in numerous studies, for example of surface (Daw and Baskes 1984, Daw 1986, Jacobsen and Nørskov 1987), phonon spectra (Daw and Hatcher 1985), liquid metals (Foiles 1985a), dislocations (Daw, Baskes, Bisson and Wolfer 1985), properties of alloys (Foiles 1985b, Foiles, Baskes and Daw 1986, Foiles and Daw 1987) and their grain boundaries (Baskes, Foiles and Daw 1987). In the EAM the empirical fitting is done with a somewhat different philosophy to that of the Finnis–Sinclair potentials, as we now describe.

In the embedded-atom model one regards ρ_i as the electronic charge density at atomic site i due to a superposition of atomic charge densities from the other atoms. These atomic charge densities are the free-atom densities as calculated from Hartree–Fock theory by Clementi and Roetti (1974). Fitting to experimental data and to an empirical pressure–volume curve of the kind suggested by Rose, Smith, Guinea and Ferrante (1984) are carried out in the most recent versions of the method, thereby determining the functions f and V. The function $f(\rho)$ is then described as the 'embedding function', and thought of as the energy change on introducing an atom into an electron gas of density ρ. The original concept of embedding was developed by Scott and Zaremba (1980) and independently by Nørskov and Lang (1980) and Nørskov (1982) with an electron-gas effective medium to describe the energetics of light impurities before being adopted in the way outlined above for the metal–metal interaction. A thorough discussion of the link between the effective-medium or embedded-atom picture and density-functional theory has recently been given by Jacobsen, Nørskov and Puska (1987) which enables one to appreciate the limitations of the effective-medium model and its connection to the μ_2 picture of the energy which in the end gives a similar looking model.

The way Jacobsen *et al.* (1987) proceeded with examining the possible justification of the effective-medium model is suggested by the discussion of density-functional theory and approximate charge densities in §2. One would firstly like to isolate a term in the total energy which represents the embedding of an atom in jellium. This can be calculated from first principles in the local-density approximation, and for metals and hydrogen it gives a concave function suggestive of the form required of $f(\rho)$. The idea then would be to show that the remaining terms in the total energy could reasonably be represented as a pair potential. The first problem one encounters is that the effective medium model, at least in the form known as the embedded-atom model, refers to the charge density ρ_i at a point, whereas the terms in eqn. (29) require integrals of functions of n over all space. This is dealt with by replacing ρ_i by the average value of n within a Wigner–Seitz cell at site i in the absence of the atom there. Following Jacobsen *et al.* (1987), let us call this $\bar{n}_i$. It is likely to be easier to derive an effective medium model based on $\bar{n}_i$ rather than ρ_i because the exact charge at any point differs from $\bar{n}_i$ by an amount which vanishes on average, which will help to reduce electrostatic errors. The other pillar of the derivation is the variational principle which allows us to use an approximate charge density as input to the Kohn–Sham equations and to obtain second-order accuracy in the energy without the need to reconstruct a charge density from the wavefunctions. In the spirit of relating to the jellium embedding energy, Jacobsen *et al.* took as the input charge density not the atomic charge densities, but the charge densities induced by the isolated atoms in jellium, which we call pseudo-atomic charge densities. The procedure then is complicated in detail, but amounts to rearranging the terms in the total energy functional so as to expose the jellium embedding term. Their result for the binding energy is (eqn. 4.16 of Jacobsen *et al.* (1987))

$$\Delta E=\sum_i E_{c,i}(\bar{n}_i)+\sum_i\int_{a_i}[\Delta e_i-\Delta\tilde{e}_i]+\text{corrections.} \tag{66}$$

The first term is related to the embedding energy in jellium $\Delta E_i^{\text{hom}}(\bar{n})$ by

$$E_{c,i}(\bar{n}_i)=\Delta E_i^{\text{hom}}(\bar{n}_i)-\alpha_i\bar{n}_i, \tag{67}$$

where α_i is the mean Hartree potential in cell a_i of the charge of pseudo-atom i. The quantities $\Delta\tilde{e}_i$ are the changes in the sum of occupied one-electron energies (eqn. (33)) comparing the complete solid to the solid with vacancy plus free atom, $\Delta\tilde{e}_i$ is the same quality, but for the atom in jellium. The integral projects onto cell a_i the difference in the one-electron energy sum between the crystal in which atom i finds itself embedded and the isolated atom i in jellium. The 'corrections' are terms involving the differences between integrals over tails of neighbouring pseudo-atoms within cell a_i and the tail of pseudo-atom i outside cell a_i, together with electrostatic terms that vanish in the atomic-sphere approximation. All these correction terms have been derived by Jacobsen *et al.*, who showed that they are small.

Armed with eqn. (66), we are now better able to understand the relation of the effective medium model to the μ_2 approach. In a d-band metal such as Cr, one commonly considers that most of the cohesive energy comes from the one-electron sum, and indeed Jacobsen *et al.* showed that it is the second term in eqn. (66) which is most important in this case. It is this part which $f(\rho)$ represents in the empirical N-body potential, or the μ_2 model, and which is described by $E_{c,i}$ in the more sophisticated TBB model. In these cases the fitted pair potential corresponds more to the density dependence of the $E_{c,i}$ term. Of course, in an empirical fitting procedure we can only take this physical picture as a guide to the functional forms used, since these terms and the corrections referred to will be absorbed in the fitting in a non-unique way. On the other hand in a simple s,p-bonded metal such as Al or Na, we know that the changes in the one-electron energies at constant volume are described by a pair potential, so the non-pairwise embedding function $f(\rho)$ would be describing $E_{c,i}$, as originally intended. The noble metals fall somewhere in between, their cohesion depending on the lowering of energy levels due to s–d hybridization (Christensen and Heine 1985), and the pair-wise status of this one-electron part is doubtful. On the other hand, we expect a strong pair-wise repulsion between the filled d shells in the noble metals. One hopes that the fitted $f(\rho)$ terms represent the many-body nature of the one-electron energy changes besides simply representing an embedding function $E_{c,i}$.

§ 6. Conclusions

The empirical approaches to modelling interatomic forces in transition metals, in particular the tight-binding model, can now be partially justified *ab initio*. We have reviewed some recent progress in this direction in order to provide a framework for appreciating the status of these models. The starting point is the density-functional theory with the local-density approximation to exchange and correlation. A key step, due to Harris (1985) is to write the charge density as a superposition of atomic, or atom-like, charge densities, and to invoke the variational principle to show that an energy functional of this trial density will be a reasonable approximation to the exact density. In the Harris scheme, described in §2, the energy functional derived is actually a mixture of electrostatic, exchange and correlation energies of the superimposed atom charge densities together with the one-electron energies obtained from the Kohn–Sham equations. Besides justifying the pair-wise repulsive potential used in tight-binding, this picture enables one to understand the success of electron-gas models.

For the computation of minimum-energy configurations of complicated defects, even the simple tight-binding method is more than one-thousand times more demanding computationally than merely using pair-wise potentials. The second-moment approximation in the tight-binding method leads to a functional form which has been used in an empirical fitting scheme to yield an N-body potential. This is formally the same as the effective-medium or embedded-atom model in that a pair potential is supplemented by a cohesive term $\Sigma_i f(\rho_i)$ which is a function of the radial distribution of neighbours (but not their angular distribution), and these schemes are as rapid to compute with as are pair potentials.

The relation of the effective-medium or embedded-atom model to the concept of embedding an atom in jellium has been described, following Jacobsen *et al.* (1987). In the density-functional theory, the jellium embedding energy can be separately identified. However, the empirical $f(\rho)$ cannot simply be thought of as the jellium embedding energy, and indeed in the d-band metals it is in the function $f(\rho)$ that the one-electron energies are represented.

While they may be based on various physical pictures, the different $f(\rho)$ schemes have one shortcoming in common, which arises from their neglect of the dependence of the energy on the relative bond angles. This precludes their giving a physical description of the structural energy differences in the transition metals, where we have seen for example that six moments of the density of states are required to account for the relative f.c.c. h.c.p. stability, whereas an $f(\rho)$ scheme is only modelling μ_2. Structural stability is an important property of the potentials which should be established in the fitting procedure, but it must be recognised that the resulting third-neighbour forces required to achieve this in f.c.c. and h.c.p. will be unphysical. The higher moments depend on paths extending beyond second neighbours, not only on the neighbour distances. Nevertheless, these are likely to remain the best available energy functions for large-scale atomistic simulation of transition metals until more elaborate tight-binding schemes become computationally cheaper.

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