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WORKSHOP ON
COMPUTATIONAL METHODS IN
MATERIALS SCIENCE AND ENGINEERING

"LMTO methods in electronic structure calculations"

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LMTO methods in electronic structure calculations

I. Basics of LMTO; LMTO-ASA

II. FP-LMTO for crystals
Example calculation: C in Si
Using ab-initio to improve a classical model

III. FP-LMTO for molecules and clusters

Basics of the LMTO method

Framework:

- Aim is accurate calculations for "small systems" 2 – 10 .. 20 .. 700 atoms (as opposed to semiempirical or classical methods)
- Density-functional Theory used to treat electron-electron interaction

In practice:

$$\left[-\Delta + V_{eff}(\vec{r})\right]\psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$

$$\rho(\vec{r}) = \sum_i a_i |\psi_i(\vec{r})|^2$$

$$V_{eff}(\vec{r}) = V_N(\vec{r}) + 2\int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' + \mu(\rho(\vec{r}))$$

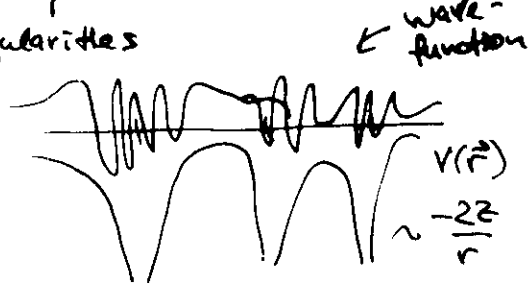
make self-consistent

$V_N(\vec{r})$: Nuclei; $2\int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}'$: Hartree potential; $\mu(\rho(\vec{r}))$: exchange-correlation-pot $\approx -C\rho^{1/3}$

Understanding:
"exchange-correlation hole"

To obtain reasonable results within DFT, must

- Solve Schrödinger's equation for an "unpleasant" potential with Coulomb singularities



- add together the output density $\sim \sum |\psi_i(\vec{r})|^2$
- make a new effective potential
  - ↳ Poisson equation $-\Delta V_H = 8\pi\, \delta(\vec{r})$
  - ↳ make xc-potential $\propto \delta^{+4/3}$

At end: evaluate total energy

$$E = \sum_i q_i \langle \psi_i | -\Delta | \psi_i \rangle + \int V_N \cdot \delta(\vec{r})\, d^3r + \int \frac{\delta(\vec{r})\delta(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r\, d^3r' + \int \varepsilon(\delta(\vec{r}))\delta(\vec{r})\, d^3r$$

Each substep by itself is already a difficult problem.

To solve the Schrödinger equation:
variational approach.

$$\psi = \sum_m C_m \varphi_m(\vec{r})$$

↑ basis functions

Make $S_{mn} = \langle \varphi_m | \varphi_n \rangle = \int \varphi_m^*(\vec{r}) \varphi_n(\vec{r})\, d^3r$

$H_{mn} = \langle \varphi_m | -\Delta + V_{eff} | \varphi_n \rangle$

C_m, ϵ from generalized matrix eigenvalue problem

$$HC = \epsilon S C \qquad C = \begin{pmatrix} C_1 \\ \vdots \\ C_m \\ \vdots \end{pmatrix}$$

Hamiltonian matrix — Overlap matrix

Effort: $\sim$ (matrix dimension)^3

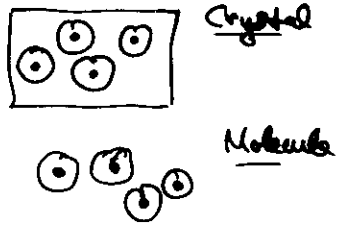
Approach here: try to define the basis set $\{\varphi_m(\vec{r})\}$ so that the required dimension is as small as possible.

What you pay: more complicated formulation (and computer programs).

Construction of the LMTO basis set

LMTO = "Linear muffin-tin orbital"
(O.K. Andersen 1975).

I. Split space into muffin-tin spheres and interstitial region



Motivation: character of potential is completely different in/outside spheres (Slater) 1953

Inside: almost spherical, very deep

Outside: smoothly varying, no special symmetry in general.

⇒ "Muffin-Tin geometry"

II. Basis functions in interstitial region:

"Solid spherical Hankel functions"

$$H_L(\vec{r}) = h_\ell(\kappa r)\, Y_L(\hat{r})$$

Y_L: spheric harmonic; h_ℓ: spherical Hankel fct.

These are centered on the nuclei, taken up to some L-cutoff, possibly different values of κ included

$$\Rightarrow \quad \{ H_{\nu L\alpha}(\vec{r}) = H_L(\vec{r} - \vec{R}_\nu) \}$$

site, ang. mom., decay; with $\kappa = \kappa_\alpha$

Why this choice makes sense:

1. Shape of H_L is similar to that of real wavefunction

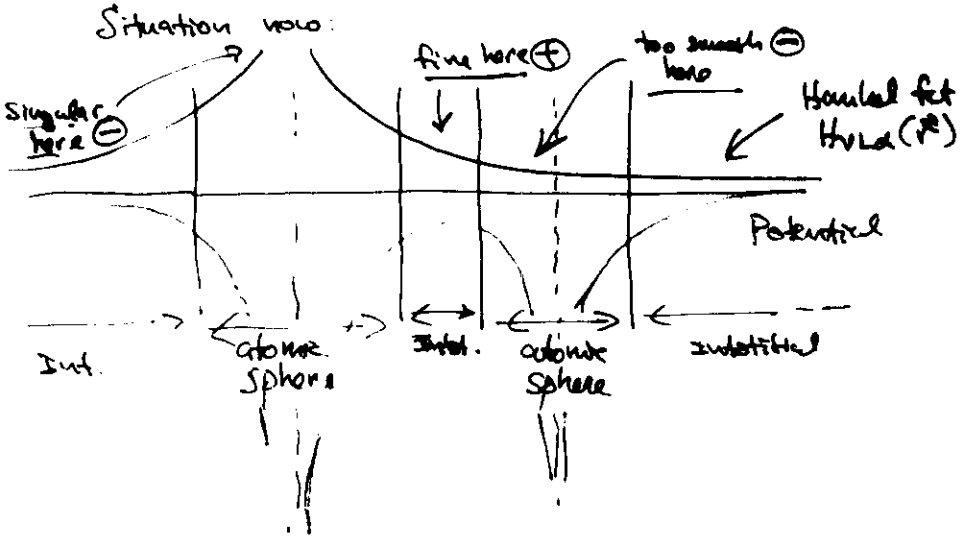
$$\boxed{\Delta H_L = -\kappa^2 H_L}$$ (Helmholtz equation)

cf. $\Delta\Psi = (V-\epsilon)\Psi$ Schrödinger equation

2. Useful properties for further steps follow from Helmholtz equation.

III. Basis function inside atomic spheres:

"augmentation" by numerical functions
(Slater 19yy)



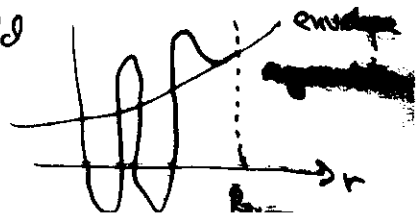
Aim: replace the analytical fct (Hankel "head" or "tail")
by numerical solution of the Schrödinger equation

$$\Psi(\vec{r}) = \sum_L \frac{u_L(r)}{r} Y_L(\hat{r})$$

$$u_L''(r) = \left[\frac{l(l+1)}{r^2} + V(r) - \epsilon\right] u_L(r)$$

radial Schrödinger equation

The numerical fuction should match smoothly onto the envelope function.

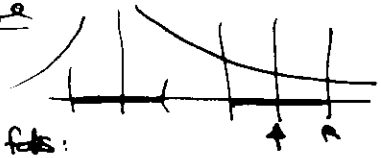


Augmentation in practice

1. To match smoothly to value and slope of envelope, must calculate these first.

Head: $H_L(\vec{r}) = h_l(\kappa r)\, Y_L(\hat{r})$
must match to $h_l(\kappa R)$ and $\frac{\partial}{\partial r} h_l(\kappa R)$ at R.

Tails: must augment a Hankel function centered somewhere else



had $\Delta H_L = -\kappa^2 H_L$
fundamental basis of non-singular fcts:

$$\boxed{J_L = j_l(\kappa r)\, Y_L} \quad \text{with } \Delta J_L = -\kappa^2 J_L$$

Inside a different MT sphere, $H_L(r - R_\mu)$ is smooth

$\Rightarrow$ expansion $\boxed{H_L(\vec{r} - \vec{R}_\nu) = \sum_{L'} B_{LL'}(\vec{R}_\nu - \vec{R}_\mu)\, J_{L'}(\vec{r} - \vec{R}_\mu)}$

"Structure constant" cf. KKR

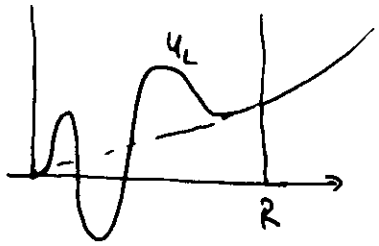
At site μ:
match each component $L' \rightarrow u_{L'}(r)$
. to reproduce $B \cdot j_{l'}(\kappa r)$, $\frac{d}{dr} B \cdot j_{l'}(\kappa r)$.

Matching value and slope of some L-component

rad. eqn. $u_L'' = \left[\frac{l(l+1)}{r^2} + V - \epsilon\right] u_L$

To get prescribed values of $u_L(R)$ and $u_L'(R)$, ϵ cannot be chosen freely.

energy ϵ is function of
- number of nodes
- log. derivative $\frac{R u_L'(R)}{u_L(R)}$



Nodes $\leftrightarrow$ principal quantum number

Log.deriv $\leftrightarrow$ exactly one value of ϵ matches.

2 Ways to proceed

① "ASW method": must match either Hankel heads or Bessel tails.
For each, use corresponding energy (ϵ_H or ϵ_J)

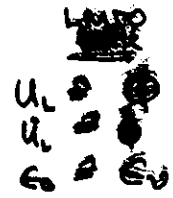
② LMTO: linearize ϵ-dependence around ϵ_0

$$u(\epsilon, r) \approx u(\epsilon_0, r) + (\epsilon - \epsilon_0)\, \dot{u}(\epsilon_0, r)$$

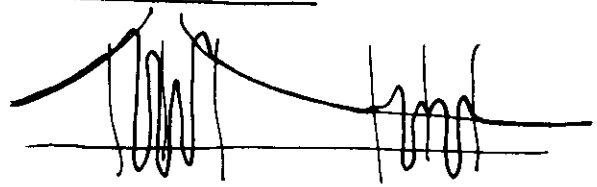
energy derivative

$\Rightarrow$ match $u_L(R), u_L'(R)$ by the proper linear combination of $u_L(\epsilon_0, r)$ and $\dot{u}_L(\epsilon_0, r)$

Put ϵ_0 where "most important".



Discussion of the LMTO basis set

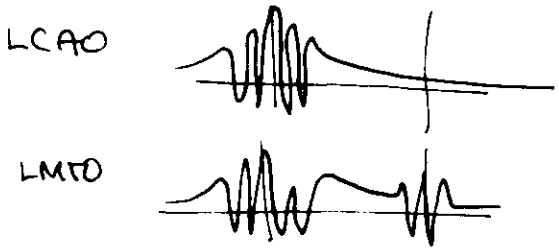


① Is this just some type of LCAO?
LCAO = Linear combination of atomic orbitals.

Differences:

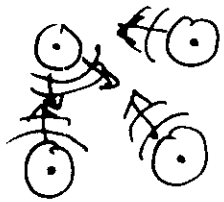
(minor) ▷ basis adapts to potential changes in spheres

(major) ▷ Any basis function depends on the positions of all atoms



② Multiple-scattering theory:
expansion in LMTO's is exact solution for muffin-tin potential.

Balance between incoming and outgoing wave satisfies MT scattering properties on all spheres simultaneously.



There is a strong relationship between KKR and LMTO.
LMTO $\approx$ linearized KKR.

Calculation of matrix elements in LMTO basis

Piecewise definition of basis functions
⇒ divide into integrals over spheres and Interstitial.

ie. $\langle \phi_{\nu L} | \phi_{\nu' L'} \rangle = \int_I \ldots d^3r + \sum_\mu \int_{S_\mu} \phi^*_{\nu L} \phi_{\nu' L'}$

$\phi_{\nu L}$: full LMTO = augmented Hankel fct

At site μ, expand both functions

$$\phi_{\nu L} = \sum_{L''} B^{\nu\mu}_{LL''} \tilde{J}_{\varepsilon L''}(r)$$

$$\phi_{\nu' L'} = \sum_{L'''} B^{\nu\mu}_{L'L'''} \tilde{J}_{\varepsilon L'''}(r)$$

$\phi, \dot{\phi}$ combination Wronski matches $j(\kappa r)$

Contribution to overlap matrix from S_ν

$$= \sum_{L''} B^{\nu\mu *}_{LL''} B^{\nu'\mu}_{L'L''} \langle \tilde{J}_{\varepsilon L''} | \tilde{J}_{\varepsilon' L''} \rangle_\mu$$

Structure constants → describe structure

Integral over sphere S_μ → atomic property

Special case: if $\mu = \nu$ (say): expand only $\phi_{\nu' L'}$; $\phi_{\nu L}$ is $\tilde{h}_L(r) Y_L(\hat{r})$

… get $\langle \tilde{h}_L | \tilde{J}_{\varepsilon L'} \rangle_\nu B^{\nu'\nu}_{L'L}$ ● (v)

other special case $\mu = \nu'$ (v) ●

get $B^{\nu\nu' *}_{LL'} \langle \tilde{J}_{\varepsilon L} | \tilde{h}_L \rangle_\nu$

Even more special case when $\nu = \nu'$, $L = L'$ from S_ν:

get $\langle \tilde{h}_L | \tilde{h}_L \rangle_\nu$ ●

Altogether for overlap matrix for all orbitals, contributions from inside spheres:

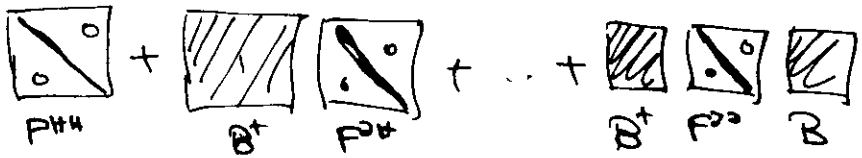
$$\sum_\mu \langle \phi_{\nu L} | \phi_{\nu' L'} \rangle_\mu \ldots$$

$$= F^{HH} + B^\dagger \cdot F^{JH} + F^{HJ} B + B^\dagger F^{JJ} \cdot B$$

B = matrix of all structure constants } structure

F^{HH} has elements $\langle \tilde{h}_L | \tilde{h}_L \rangle_\mu$

F^{JH} has elements $\langle \tilde{J}_L | h_L \rangle_\mu$ etc } specify atomic properties



So ① Easy and straightforward to calculate

② Nice separation into atomic and structural information.

More sphere contributions to matrix elements

Kinetic energy $\langle \phi_{vL} | -\Delta | \phi_{v'L'} \rangle$:

looks exactly the same. $F^{HH} = \langle \tilde{h}_\ell^\nu | -\Delta | \tilde{h}_{\ell'}^\nu \rangle_\mu$ etc

Potential energy $\langle \phi_{vL} | V | \phi_{v'L'} \rangle$:

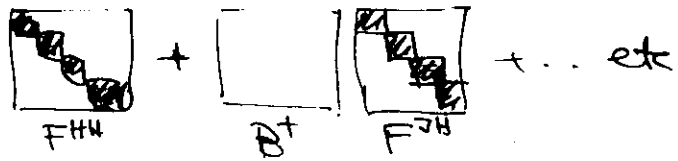
looks exactly the same if V_μ is spherical,

$$F^{HH} = \langle \tilde{h}_\ell | V_\mu | \tilde{h}_{\ell'} \rangle_\mu$$

$$F^{JJ} = \langle \tilde{j}_\ell | V_\mu | \tilde{j}_{\ell'} \rangle_\mu \quad \text{etc}$$

if V_μ has non-spherical terms :

get non-zero $\langle \tilde{h}_\ell | V_\mu | \tilde{h}_{\ell'} \rangle$ etc

$\Rightarrow$ 

ALTOGETHER

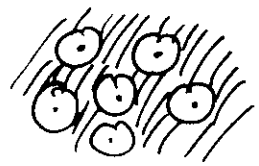
Contributions to the matrix elements from inside the muffin-tin spheres are easy.

They are all assembled in the same way out of the structure constants and simple integrals over the atomic spheres.

Interstitial contributions to matrix elements

In I, all basis functions are simply Hankels.

Overlap $\leftrightarrow$ Greens theorem



$$\Delta \phi_1 = -\kappa_1^2 \phi_1$$
$$\Delta \phi_2 = -\kappa_2^2 \phi_2$$

$$\nabla \cdot \{ \phi_1^* \nabla \phi_2 - \phi_2 \nabla \phi_1^* \} = \phi_1^* \Delta \phi_2 - \phi_2 \Delta \phi_1^*$$
$$= (\kappa_1^2 - \kappa_2^2)\, \phi_1^* \phi_2$$

so $\int_I \phi_1^* \phi_2 = \underbrace{\int_{\partial I} \{ \phi_1^* \nabla \phi_2 - \phi_2 \nabla \phi_1^* \} \cdot d\vec{a}}_{\text{Make from values and slopes of Hankels on spheres}} \frac{1}{\kappa_1^2 - \kappa_2^2}$

In this vein: do all required terms (even when $\kappa_1^2 = \kappa_2^2$ etc.)

Kinetic energy: almost exactly the same

$$\langle \phi_1 | -\Delta | \phi_2 \rangle_I = \langle \phi_1 | -\Delta \phi_2 \rangle_I = \kappa_2^2 \langle \phi_1 | \phi_2 \rangle_I$$

Potential energy: same if potential is constant

$$\langle \phi_1 | V_0 | \phi_2 \rangle_I = V_0 \langle \phi_1 | \phi_2 \rangle_I .$$

If potential is not constant: real problems

Terms to calculate:

	Spheres	Interst'l
S	✓	✓
T	✓	✓
V	✓	✗

Interstitial potential matrix elements

$$V_{ij}^{(I)} = \int_I \phi_i^*(\vec{r})\, V(\vec{r})\, \phi_j(\vec{r})\, d^3r$$

... no straightforward or easy way to evaluate this for a potential of general shape.

Different LMTO methods ↔ handle $V_{ij}^{(I)}$ differently.

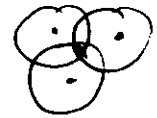
LMTO-ASA (atomic sphere approximation)	"ignore" $V_{ij}^{(I)}$
J. Wills, K-H. Weyrich } FP-LMTO	expand $V(\vec{r})$ in plane waves
our crystal FP-LMTO	interpolation technique
our cluster FP-LMTO	tabulation technique.

LMTO – ASA (atomic spheres approximation)

1. Set potential in interstitial to a constant
   V_0 = "muffin-tin zero".
2. Replace potential in spheres by spherical average

Muffin-tin potential

3. Increase size of atomic spheres until they fill all of space
   ⇒ overlapping atomic spheres.

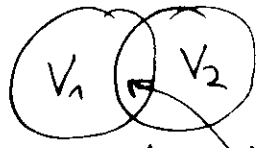


Or: approximate WS-cell by a WS-sphere.

Interstitial integrals: non-zero, correct partly for the sphere approximation ⇒ "combined correction terms"

ie. Potential $\int_{cell} \phi_i^* V_0 \phi_j + \sum_v \int_{S_v} \{\phi_i^* V_v \phi_j - \phi_i^* V_0 \phi_j\}$

So potential is



—maybe—

(4.) Leave away all interstitial terms
⇒ get ASA without "combined corrections".

Advantages and disadvantages of ASA

\+ Very simple formulation. Without CC,

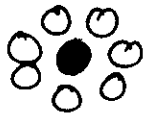
$$H = F^{HH} + B^{\dagger} \cdot F^{JH} + F^{HJ} \cdot B + B^{\dagger} \cdot F^{JJ} \cdot B$$

is already everything $\Rightarrow$ fast, efficient.

\+ Building on this simple Hamiltonian, can do analytical transformations to basis sets with useful properties
- "nearly orthogonal basis"
- localized "tight-binding" LMTO basis

Idea: modify LMTO by adding some amount of LMTO's on neighbors

$$\tilde{\varphi}_i = \varphi_i + \sum_{j \neq i} a_j \varphi_j$$



\+ small "minimal" basis
- metals (bulk) 9 functions / atom
- semiconductors 18 functions / atom.

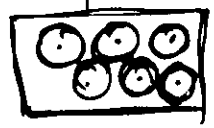
— need "empty spheres" for systems which are loosely packed (ie. Si)

— Cannot calculate energies reliably for non-isotropic distortions
- ECV: ok
- phonons, elastic constants etc: not ok.

Full-potential LMTO for crystals

using an interpolation technique for $V_I(\vec{r})$

➤ Use non-overlapping muffin-tin spheres.



➤ retain non-spherical potential terms inside the muffin-tin spheres.
→ slightly more complicated; no problem.

▷ Must choose a suitable representation for the interstitial potential $V_I(\vec{r})$ and the interstitial density $\rho_I(\vec{r})$.

Here: expand these quantities in a (different) set of atom-centered Hankel functions:

$$\rho_I = \sum_{JL\alpha} R_{JL\alpha} \chi_{JL\alpha}(\vec{r}) \quad \text{etc}$$

($R_{JL\alpha}$: coeff.; $\chi_{JL\alpha}$: Hankel fct.)

Reason: can solve the Poisson equation easily in the Hankel-fct basis.

$$\Delta V_H = -8\pi\rho$$

$$\hookrightarrow \Delta H = -\kappa^2 H$$

In the interstitial, there are two completely different Hankel-fct. basis sets:

① $\{\phi_{\nu L\alpha}(\vec{r})\}$ to expand the wavefunction — ≈ 20 functions per atom

ν: runs over all sites
L: goes up to $l=2$ typically
α: $\kappa^2 \approx -0.5$ Ry .. -2 Ry

For the crystal, $\phi_{\nu L\alpha}$ is really a Bloch sum for the wavevector $\vec{k}$

$$\phi_{\nu L\alpha}(\vec{r}) = \sum_{\vec{R}}^{!} e^{i\vec{k}\cdot\vec{R}}\, \phi^{(0)}_{\nu L\alpha}(\vec{r}-\vec{R})$$

② $\{\chi_{\nu L\alpha}(\vec{r})\}$ to expand the density and potential — ≈ 50 fcts per atom.

ν: all sites
L: up to $l=4$ or $l=6$
α: κ^2 $\approx -1, -3$ Ry

Crystal: $\chi_{\nu L\alpha}(\vec{r})$ is a periodic sum

$$\chi_{\nu L\alpha}(\vec{r}) = \sum_{\vec{R}}^{!} \chi^{(0)}_{\nu L\alpha}(\vec{r}-\vec{R}).$$

We must solve two related problems in the interstitial:

① calculate $\int_I \phi_i^* V_I(\vec{r})\, \phi_j(\vec{r})\, d^3r$

② bring the product $\phi_i^* \phi_j$ into a useful form, i.e., a sum of χ's,

because output density is $\sum_{ij}^{!} C_i^* C_j\, \phi_i^*(\vec{r})\phi_j(\vec{r})$

when $\psi(\vec{r}) = \sum_i^{!} C_i \phi_i(\vec{r})$.

So: the main problem is handling the product of two Hankel functions, e.g.

$$\phi_i^* \phi_j = \frac{e^{-\kappa r}}{r} \cdot \frac{e^{-\kappa|\vec{r}-\vec{R}|}}{|\vec{r}-\vec{R}|} = ?$$

$\Rightarrow$ Seek a (numerical) expansion

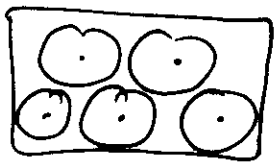
$$\phi_i^*(\vec{r})\,\phi_j(\vec{r}) = \sum_m C_m^{ij}\, \chi_m(\vec{r})$$

wavefunction basis — density basis

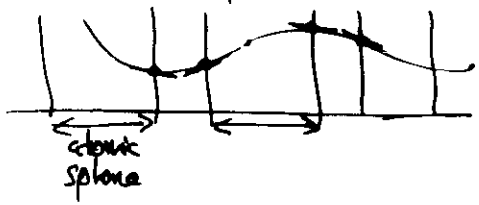
Interpolation technique to get expansion

$$\phi_i^* \phi_j = \sum_m C_m^{ij} \gamma_m(\vec{r})$$

Assume the sphere packing is good (must sometimes use empty spheres to attain this).



The interstitial is narrow
=> any well-behaved function is already essentially determined by its values and slopes on the sphere surfaces.



Adjust the coefficients C_m^{ij} until the values and slopes on the RHS reproduce those of $\phi_i^* \phi_j$ on all spheres simultaneously
=> must solve pretty large matrix inversion <u>once</u> for a given structure.

This is similar to numerical techniques, ie, Simpson integration etc.

<u>Interstitial potential matrix elements:</u>

Any interstitial function $f(\vec{r})$ is specified by its values and slopes

$$(\ldots f_{VL}(R_v), \ldots, f'_{VL}(R_v) \ldots) \times 50 \text{ number per atom.}$$

<u>Integrals</u> over f are linear in f_{VL}, f'_{VL}

$$\Rightarrow \int_I f(\vec{r}) V(\vec{r})\, d^3r = \sum_{VL} \{\alpha_{VL} f_{VL} + \beta_{VL} f'_{VL}\}$$

Apply to $f(\vec{r}) = \phi_i^*(\vec{r}) \phi_j(\vec{r})$:

- calculate $(\phi_i^* \phi_j)_{VL}$ and $\frac{d}{dr}(\ldots)$ using Clebsch-Gordan coefficients
- multiply these with α_{VL}, β_{VL} and sum.

This is more or less what must already be done to include the non-spherical potential terms inside the spheres => no extra effort here to get $\int_I \phi_i^* V_I \phi_j \, d^3r$.

Doing a FP-LMTO crystal calculation

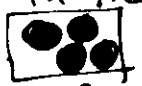
1. Choose sphere radii, basis sets

   Ie $\kappa^2 = -0.5$ s, p, d
   $\kappa^2 = -1$ s, p, d
   $\kappa^2 = -2$ s, p
   } 22 functions

   (For empty spheres: no functions entered here.)

2. Invert the matrix for the interstitial part.

3. Overlap the free-atom densities to get the crystal density in the spheres.



4. Get values, slopes on spheres of density, $\varepsilon_{xc}(\vec{r})$, $\mu_{xc}(\vec{r})$.

5. Do interstitial fit to get $\delta(\vec{r})$, ε_{xc}, μ_{xc} in the interstitial.
   (Scale δ_I to make density neutral)

6. Solve Poisson equation.

7. Calculate α_{VL}, β_{VL}.

8. Set up and diagonalize matrices $HC = \epsilon SC$

9. Assemble output density inside spheres.

↳ Loop

Advantages and disadvantages of the crystal FP-LMTO procedure

\+ Fast for one fixed geometry.
After the setup step, speed is more-or-less like the ASA.

\+ For well-packed systems, the accuracy is as good (or better ↔ convergence) as the FLAPW method.

\+ The method can be applied equally well to any element in the periodic table.
Transition metals
Oxides etc
Good for materials science.

— Need empty spheres for many systems.
Some systems cannot be packed reasonably.

— Cannot move the atoms quickly.
Move atoms → re-do setup step.

— Forces are not available.

Example application :
Substitutional carbon in silicon.

The aim is to show the following:

- How the FP-LMTO method is applied in practice.
- What the method can/cannot do.
- The usefulness of combining ab-initio calculations with a suitable classical model.

(done with : H. Richter, W.J. Osten).

Topic: substitutional carbon in silicon.

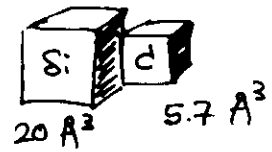
Why is this interesting?

① Strong covalent bonding
⇒ C, Si have "4 arms"
⇒ strong forces try to keep the carbon atom in the silicon lattice.

② C is much smaller than Si

Bond lengths:

Volume per atom:



So: the carbon atoms tend to occupy substitutional lattice sites, but are surrounded by large (energetically unfavorable) strain fields.

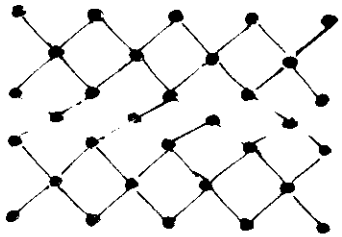
What are the consequences of these conflicting tendencies?

C in Si: dilute alloy versus ordered structures.

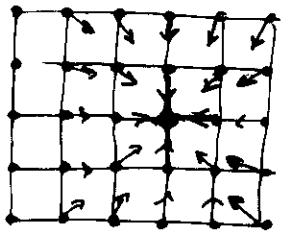
Idea: high local C concentrations could be possible for specific ordered structures.

Main problem: permit relaxation of the short C–Si bond

For some structures, this is easy.



Embedded C monolayer:
bond length can relax
(but strong angle distortion)



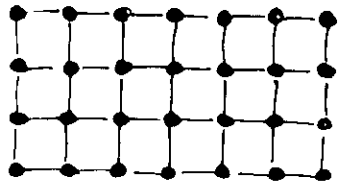
C point defect:
lattice perturbed
over large volume

For other, more complicated structures,
bond-length relaxation could be possible
without excessive angle distortion.

Plan: systematically try "all" possible arrangements of C atoms on Si lattice.

Needed: fast & accurate procedure to obtain the total energy.

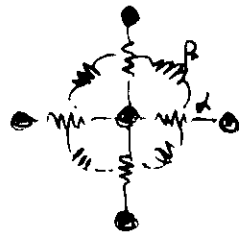
lattice-gas problem →



Contributions to total energy:

- elastic energy: ← most important term
  bond-bending and bond-stretching energy
- chemical energy: C–Si bond stronger than C–C and Si–Si
- electrostatic energy: charge transfer Si → C

Use keating model to get elastic energy.
Other terms by tuning keating parameters.



Keating model for elastic energy

$$W = \sum_{i,j} \frac{\alpha}{a_0^2} (\Delta r_{ij}^2)^2 + \sum_{\substack{i,j \\ k \neq j}} \frac{\beta}{a_0^2} (\Delta(\vec{r}_{ij} \cdot \vec{r}_{ik}))^2$$

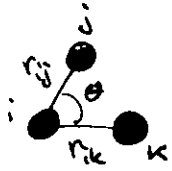
α = bond-stretching force constant

β = bond-bending force constant.

Generalization to anharmonic model:

$$\alpha_{ij} = \alpha_{ij}(r_{ij})$$

$$\beta_{ijk} = \beta_{ijk}(r_{ij}, r_{ik}, \theta_{ijk})$$



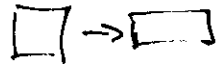
Aim: get suitable functional expressions using ab-initio calculations for a wide range of crystal volumes.

Anharmonic terms are needed because the Si-C bonds are stretched by a large amount in the Si-C alloys.

Step 1: get change in β when lattice constant changes.

Tetragonal distortion which maintains bond lengths

$$\varepsilon_1 = \varepsilon_2 = \sqrt{1+\delta} - 1, \quad \varepsilon_3 = \sqrt{1-2\delta} - 1, \quad \varepsilon_4 = \ldots = \varepsilon_6 = 0$$



then $\frac{2}{3V} \frac{d^2W}{d\delta^2} = \frac{4a}{a_0^2} \beta(a)$

⇒ get $\beta(a)$ from hardness of this distortion.

Result: β scales as a^{-7}

Step 2: get change in α with lattice constant.

Ab-initio: get $E(a)$ - bonding curve

Reproduce using Keating with $\beta \sim a^{-7}$ and $\alpha \sim a^{-4}$

Final Keating model with anharmonic terms:

$$\alpha_{ij} = \alpha_{ij}^0 \left(\frac{r_{ij}^0}{r_{ij}} \right)^4$$

$$\beta_{ijk} = \beta_{ijk}^0 \left(\frac{r_{ij}^0}{r_{ij}} \right)^{7/2} \left(\frac{r_{ik}^0}{r_{ik}} \right)^{7/2}$$

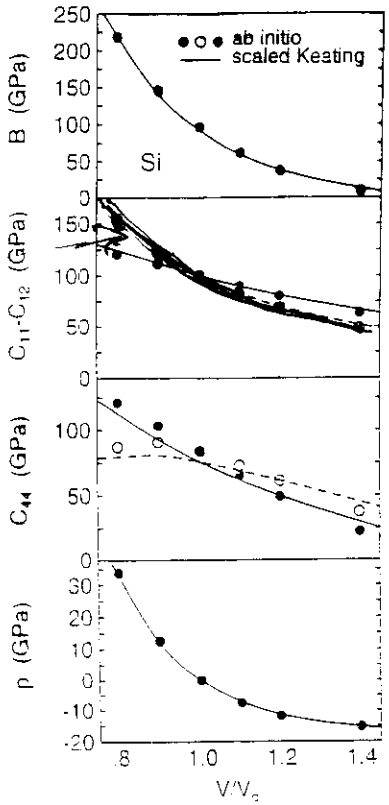
Test on $E(V)$, $\omega_{TO}(\Gamma)$, elastic constants.

Tests of anharmonic keating model for Si

bulk modulus

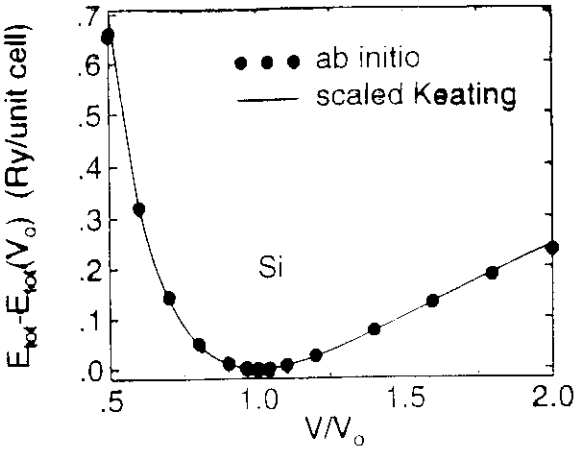
shear constants
bond-length
conserving
distortion

pressure

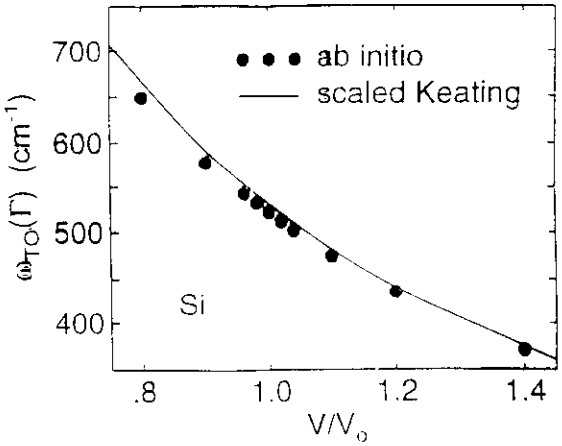


Anharmonic keating model for Si

energy-volume curve



optical phonon

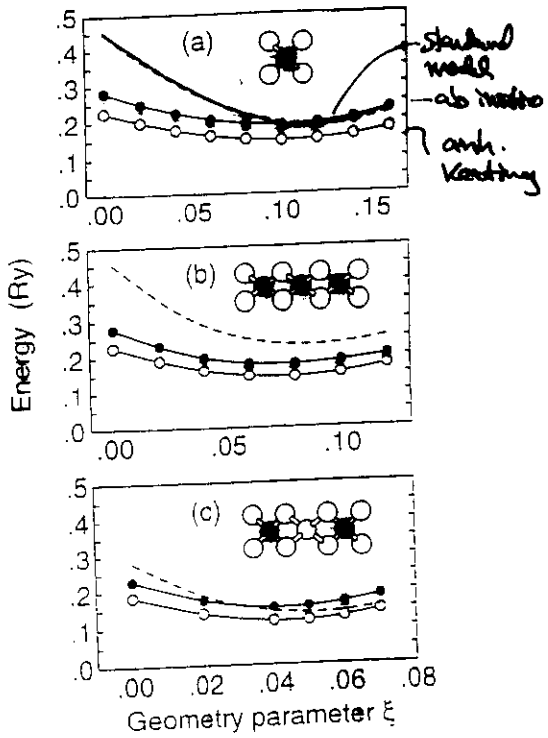


Test of anharmonic keating model
for mixed Si–C structures

isolated impurity
(32 atom supercell)

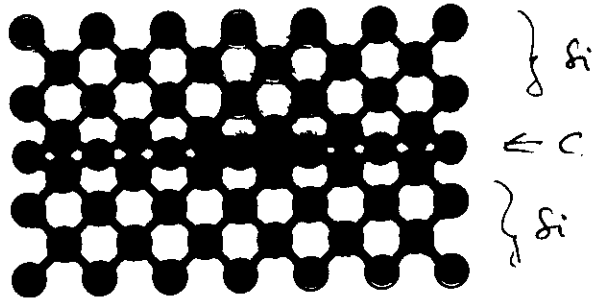
embedded monolayer

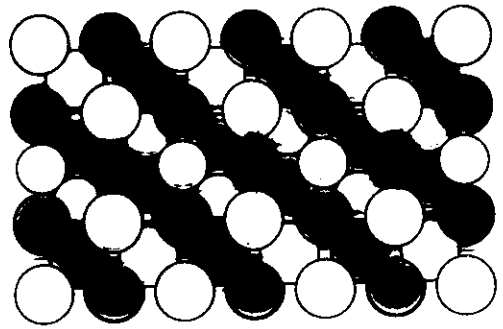
embedded
high - monolayer



Results: good reproduction of the energy surface.
Systematic shift is due to <u>compromise</u>
for SiC:
cannot get $\omega(\Gamma)$ and $C_{44} - C_{12}$ right
at same time.

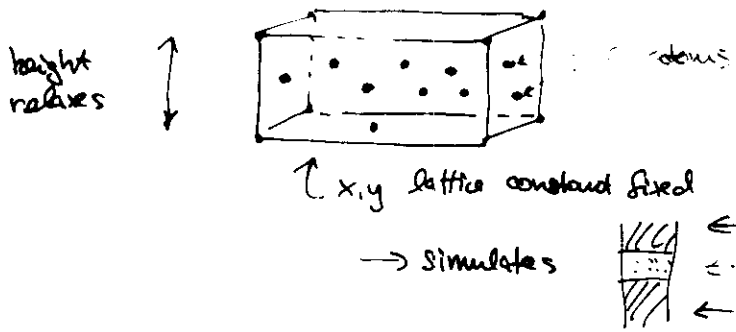
Sphere packings for embedded monolayer





Systematic search for low-energy structures

- distribute C atoms over Si lattice sites
- relax with anharmonic Keating model
- do final ab-initio calculations for low-energy structures.

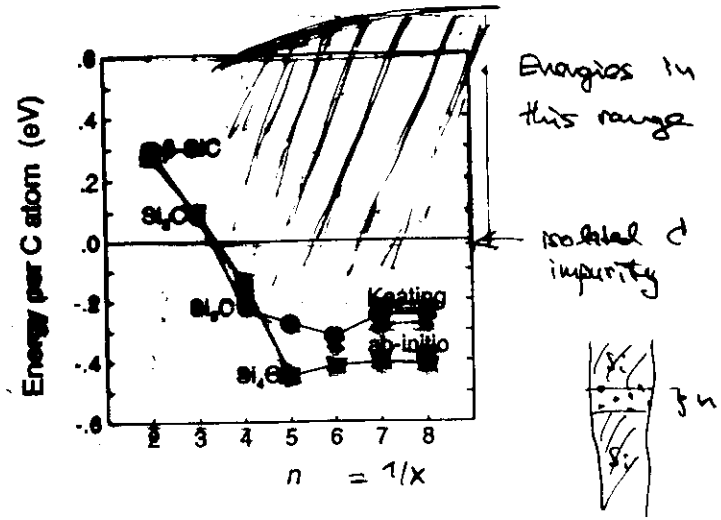


➡ Include all stoichiometries $Si_{n-1}C$ with $n = 2, 3 \ldots 8$ (i.e. Carbon concentration is $1/n$);

➡ all possible arrangements with up to two formula units per unit cell

➡ don't permit nearest-neighbour C-C pairs.

Energies of the optimal $Si_{n-1}C$ Structures



1. Energy lies <u>below</u> isolated impurity for some cases
2. Only specific structures have low energy
3. Looks like C-concentrations to 20% are possible in specific structures.

Experimental search for highly-concentrated structures:

Problem: the $Si_{1-x}C$ structures can all gain
> 1 eV/atom by collapsing to SiC and Si.

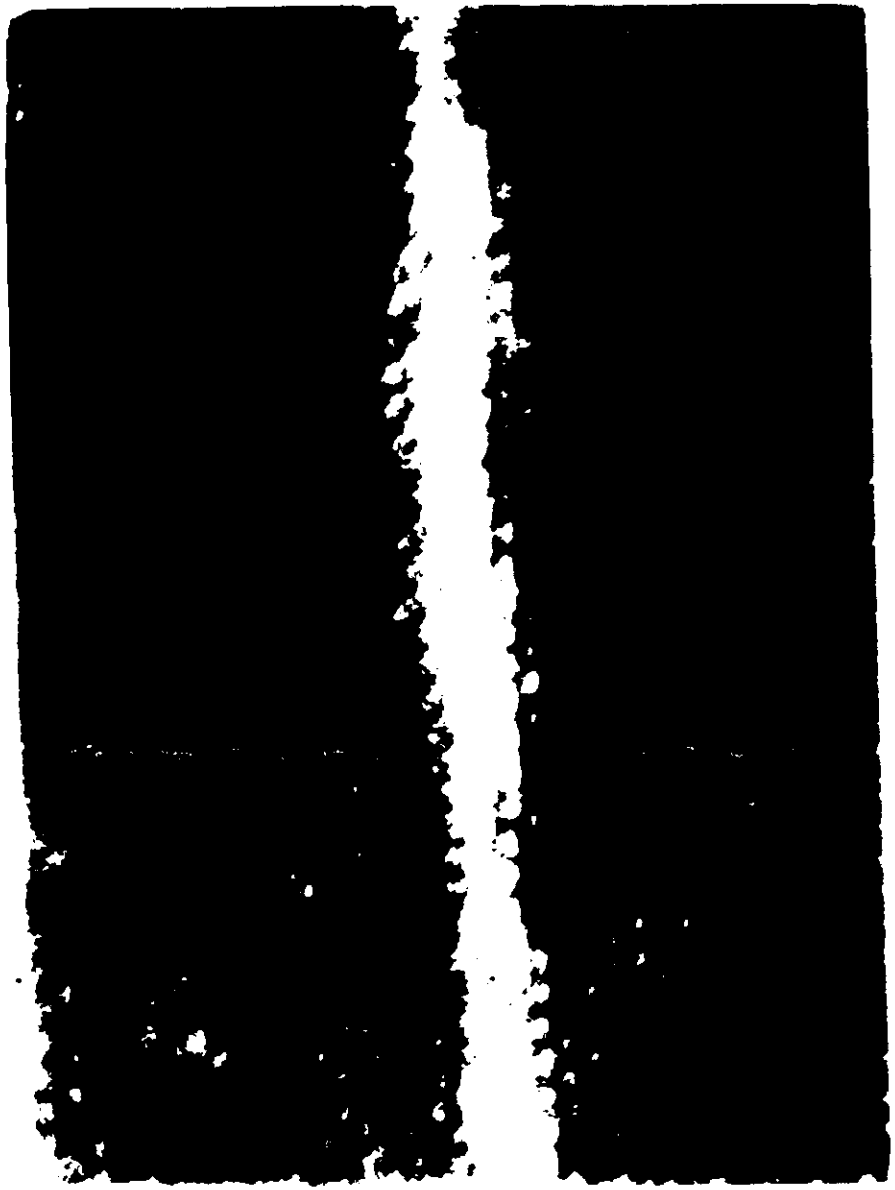
The Keating model cannot determine whether this happens
(bond-breaking, dangling bonds...)

⇒ need experiment here.

MBE

- p-Si (001) substrate
- growth at 600°C, 0.05 nm/s
- growth interruption, then deposit
  about 1 ML of carbon ...etc.
- Important: no coevaporation of C and Si

Investigation by high-resolution TEM.



Arrangement of C atoms in optimal structures

C: ● ▲ ■ ◆

Si: ○ ◇ □ △

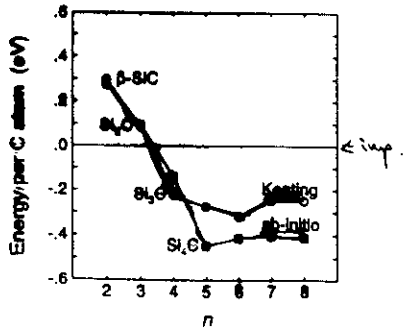
Layer ◆ 1 2 3 4

○ ◇ △ □

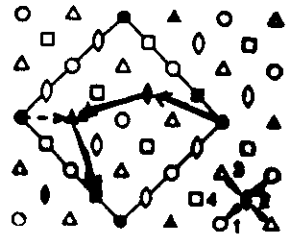
Characteristic property:

C atoms in successive planes connected by "knights move"

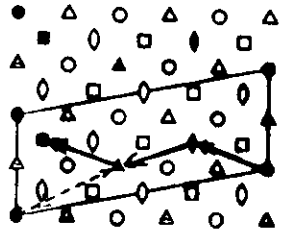
→ third-nearest neighbors



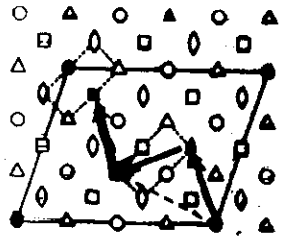
n=4 (Si_3C)



n=5 (Si_4C)

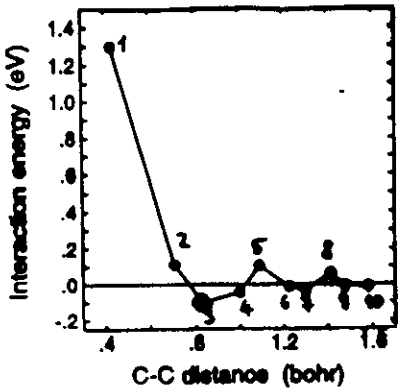


n=6 (Si_5C)

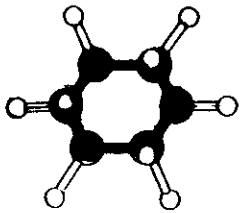


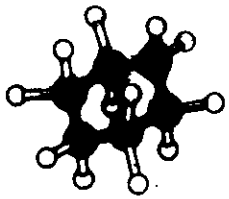
Interaction between substitutional C impurities

- ▷ Keating model.
- ▷ 2000 atom supercell with 2 C atoms
- ▷ Oscillations correspond to different directions



Energy gain for third-nearest-neighbors.
⇒ six-fold ring with C at opposite points



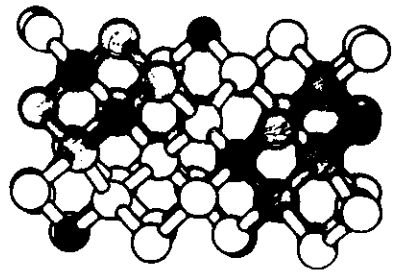


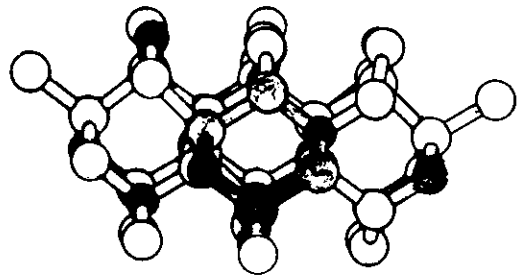
Low energy structures: maximal 3nn pairs without 1nn, 2nn pairs

n	2	3	4	5	6	7	8
N_2	12	4	2	0	0	0	0
N_3	0	4	6	4	4	3	3

Optimal structure for stoichiometry Si_4C

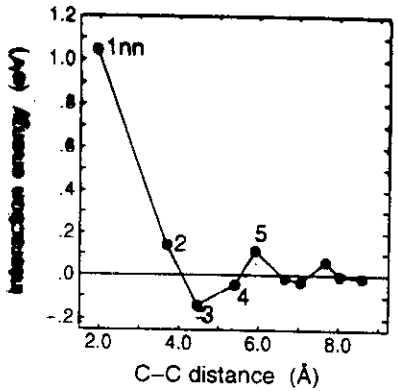
- Very symmetric structure
- 4 3nn C-C neighbors
- unit cell with 10 atoms





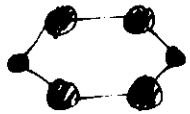
Local vibrational modes in dilute Si-C alloys.

Those confirm directly the C-C pair interaction



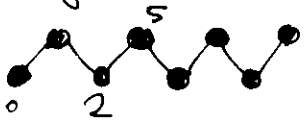
Low-energy configuration (ie. third-n-n)

- shorter Si-C bond
- bond harder
- higher frequency



Unfavorable (high-energy) configuration:

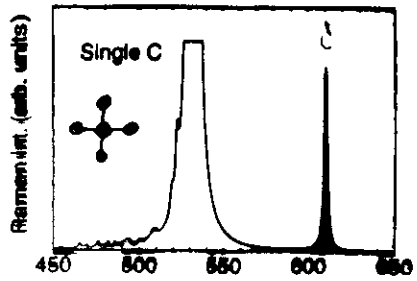
long, soft bond,
. lower frequency.

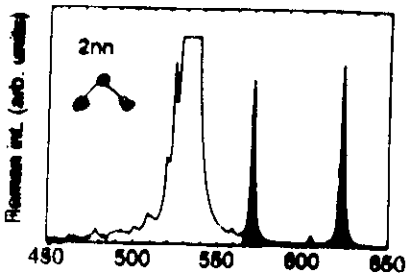


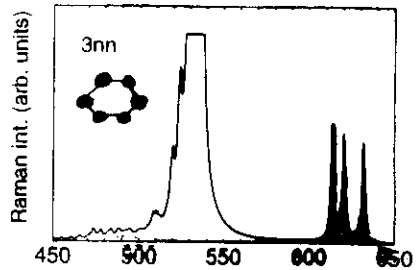
Calculated modes
(anharmonic coupling)

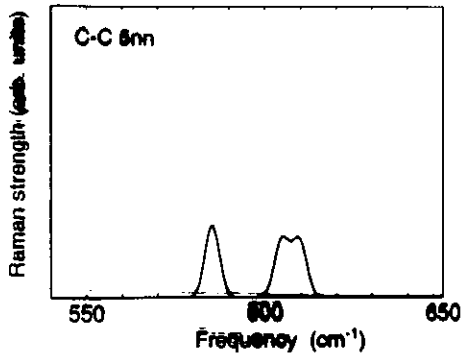
Direct diagonalization of dynamical matrix,
2 C atoms in
2000-atom supercell.

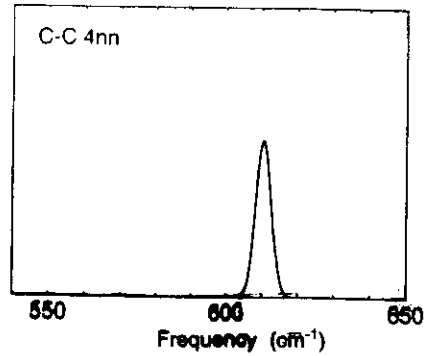
(Raman selection rules)





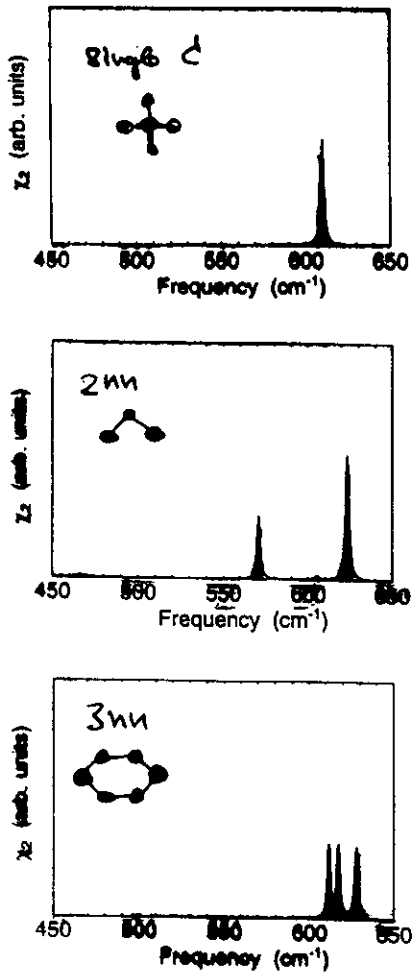






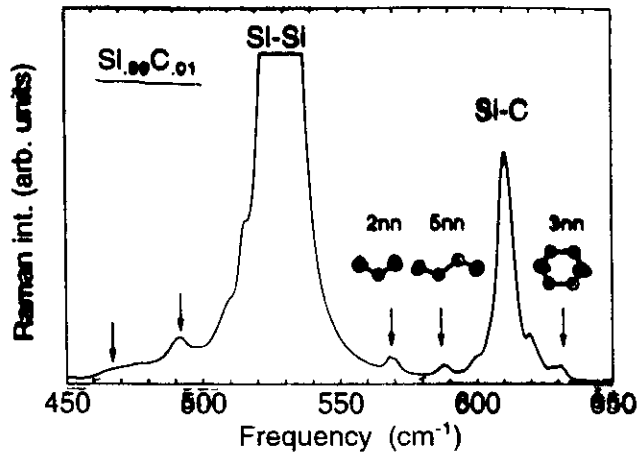
Calculated frequencies

(Infrared selection rules)



For random occupation of lattice sites:

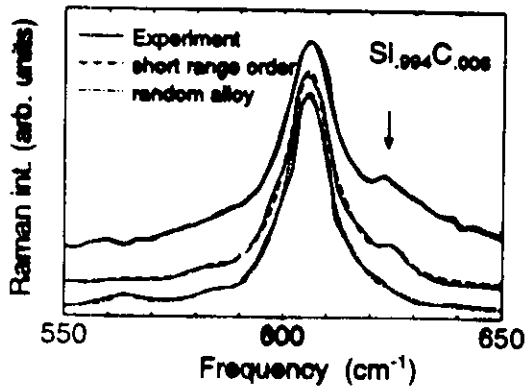
get spectrum by summing over pair spectra with suitable weights.

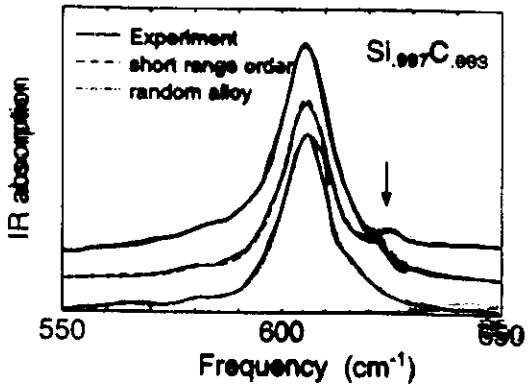


Comparison to experiment:

must artificially increase 3d-n-n frequency for reasonable agreement

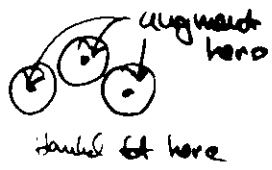
- Experiment
- Theory: random
- Theory: increase 3nn × 4, decrease 5nn / 4, 2nn / 4





FP-LMTO for molecules and clusters

Similarities to crystal FP-LMTO:



- exactly same LMTO basis set (but no Bloch sums)
- two sets of interstitial Hankel functions:

  $\{\phi_{\nu L\alpha}\}$ for wavefunction

  $\{\chi_{\nu L\alpha}\}$ for density and potential.
- Central point: expand product of ϕ's

$$\phi_i \phi_j \approx \sum_m^{\cdot} C_m^{ij} \chi_m(\vec{r})$$

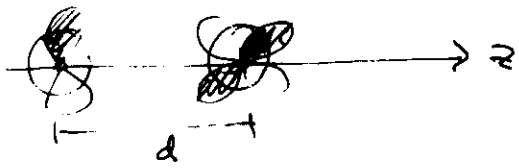
Main difference to crystal program:

- how to get the expansion.

Final result:
- no empty spheres
- get forces out
- can do molecular dynamics (two steps/step for each geometry).

Getting the expansion $\phi_i \phi_j \approx \sum C_{ijm} \chi_m$

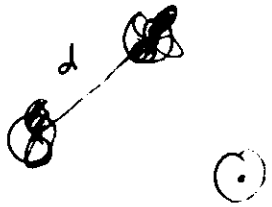
Step 1: put two atoms along z-axis.
Make an accurate numerical expansion by least-squares fit for various distances.



Step 2: Tabulate the coefficients $C^{ij}_m(d)$ as function of the distance.

---------- end of setup ----------

For general geometry:



Step 1: Look up in table for distance d.

Step 2: Rotate using Slater-Koster matrices

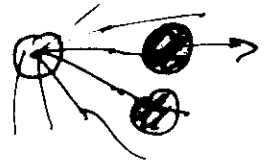
$$Y_{\ell m}(R\hat{r}) = \sum_{\ell'} D_{\ell\ell'}(R)\, Y_{\ell' m}(\hat{r})$$

mixes $\phi_{\ell m}$'s and $\chi_{\ell m}$'s.

Final result: very fast procedure to get the expansion for an arbitrary geometry whenever needed.

Forces in the cluster FP-LMTO program

Problem: Pulay terms are impossibly difficult to calculate directly.
Basis set changes in complicated manner when an atom is moved.



Harris functional:

$$E_H[\rho] = \sum \epsilon_i[V_{eff}(\rho)] - \int \rho V_{eff}[\rho] + U[\rho] + E_{xc}[\rho]$$

Atoms move along paths $R_\nu(\tau)$,
want force at $\tau = 0$.

Take any $\rho_{guess}(\tau)$ with $\rho_{guess}(0) = \rho_{sc}(0)$

Define $\tilde{E}(\tau) = E_H[\rho_{guess}(\tau)]$

Then: $\tilde{E}(0) = E_{KS}(0)$

$$\frac{\partial \tilde{E}}{\partial \tau}(0) = \frac{\partial E_{KS}}{\partial \tau}(0) = \text{Force}$$

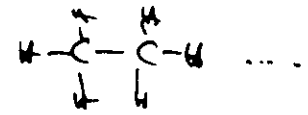
It is much easier to differentiate $\tilde{E}(\tau)$ if ρ_{guess} is chosen properly.
This gives a force theorem which looks completely different from

$$F = F_{\text{Hellmann-Feynman}} + \text{Pulay}.$$

Properties of cluster FP-LMTO method

+ No empty spheres are needed.
  Can make initial tabulation as accurate as needed.
+ Forces are available
  ⇒ molecular dynamics, simulated annealing etc.
+ Fast: small LMTO basis is used.
+ Can be applied to any material:
  transition metals, oxides, ...
+ No supercells are needed.
− Method is still pretty complicated.

Doing a calculation for a molecule

Say: some hydrocarbon  ....

1. Choose radii and Hankel-function basis sets for each species
   C: $R_{MT} = 1.0$; spd functions
   H: $R_{MT} = 0.7$; sp functions.
2. Set up tables for two-center ints:
   C–C ← can also be used for N, O, B..
   C–H ← can be used for N–H, O–H etc.
   H–H

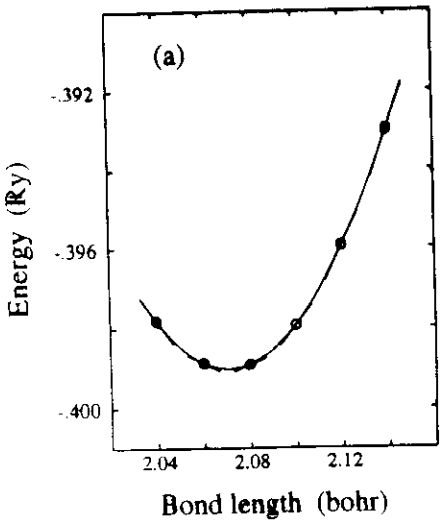
——— end of setup ———

3. Load all tables
4. Overlap free-atom densities
5. Set up and diagonalize Hamiltonian
6. calculate energy and forces.
7. Move nuclei by Verlet algorithm
8. Decompose density at old positions, mix, shift, re-overlap at new positions

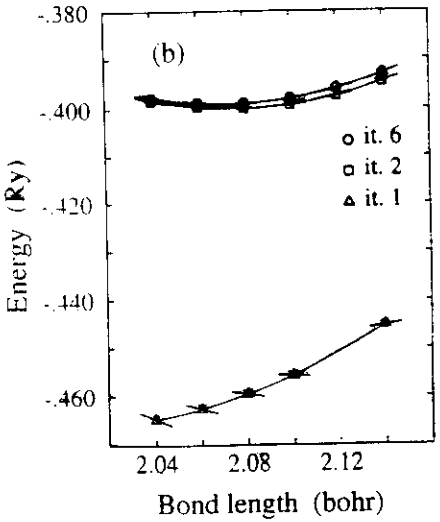
Loop over time steps.

Cluster - LMTO for N_2 dimer

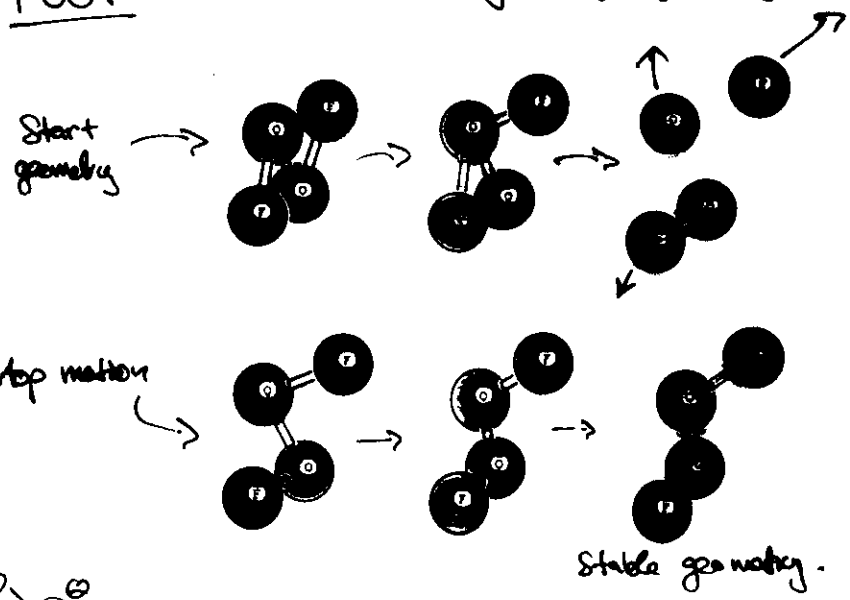
bonding curve →

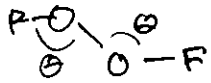


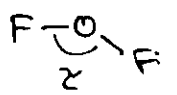
convergence of forces →



FOOF simulated annealing to get geometry.

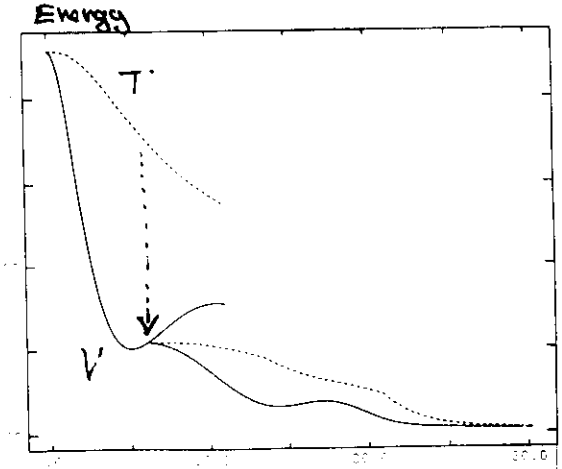






	F-O	O-O	
Exp	1.58	1.22	(9)
HF	1.36	1.31	
TCF	1.54	1.20	

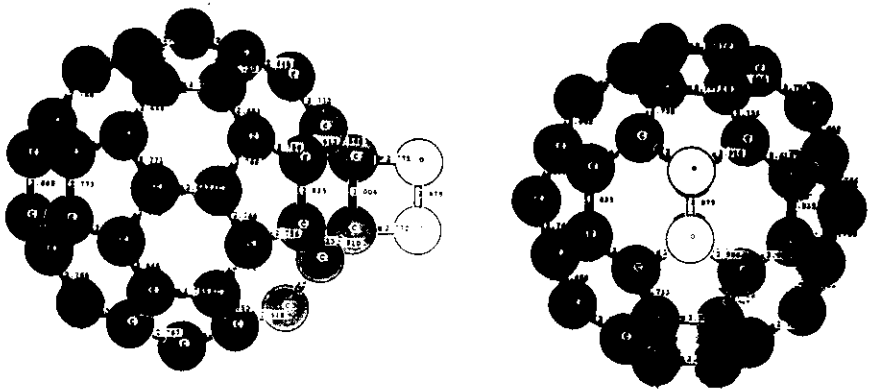
	θ	χ	(degrees)
Exp	110	88	
H-F	106	86	
TCF	110	87	



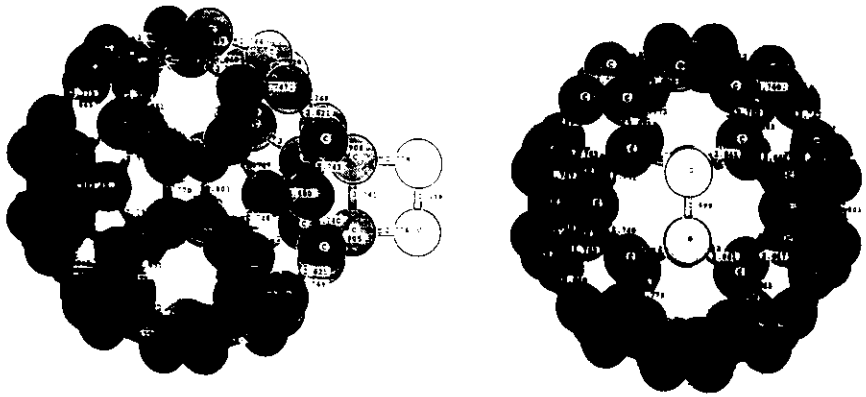
Bonding of O_2 to C_{60}

(R. Kuhlmann, M. Schäffler, Jordan)

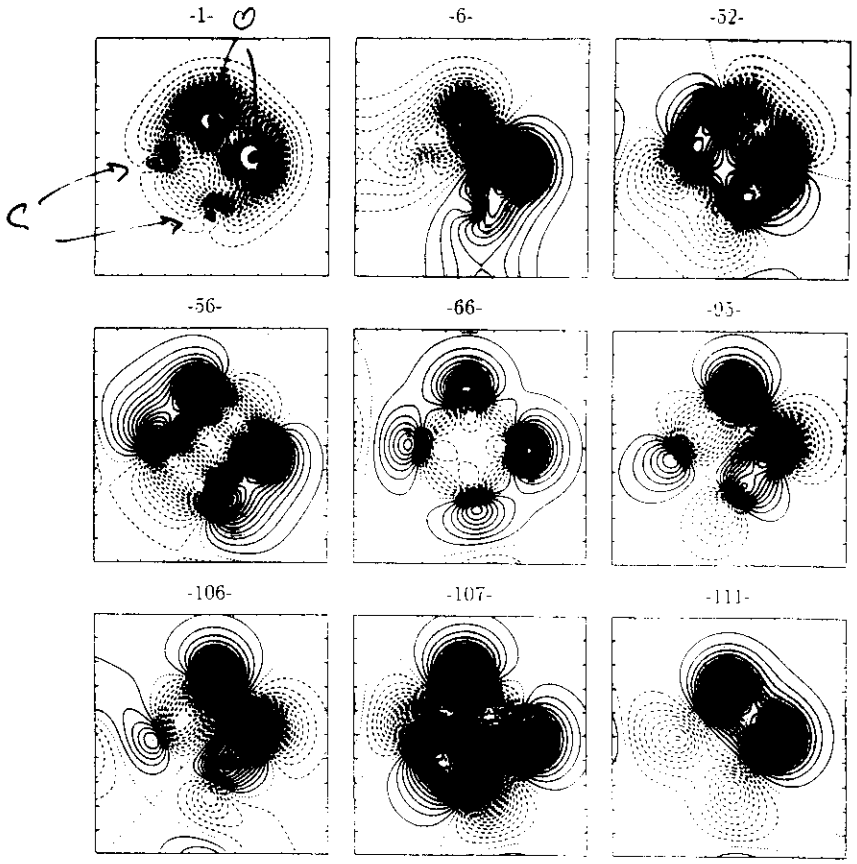
Stable geometry: over double bond



Metastable: over single bond.

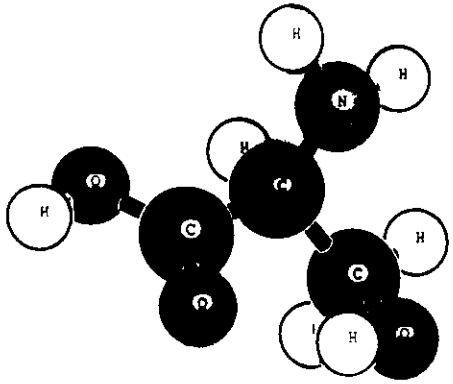


Wavefunctions with contribution on O_2 in $C_{60}O_2$

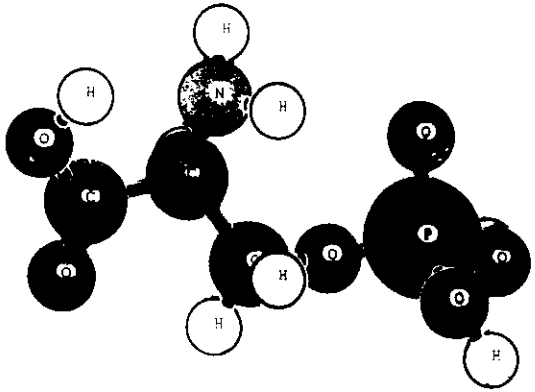


Serine : relaxed geometries in vacuum.

Ser



Ser-P



Summary

1. LMTO is a certain way to define a basis set to represent the wavefunction.
   LMTO = augmented Hankel function.

2. All sphere parts are easy to handle. In the interstitial, only the potential makes problems.

3. LMTO – ASA : "forget" interstitial
   fast, useful, cannot do non-isotropic distortions.

4. Crystal FP-LMTO :
   interpolation to treat V_I.
   Fast and accurate; needs empty spheres, no forces.

5. Cluster FP-LMTO :
   tabulation to treat V_I ; $\Phi_i \Phi_j = \sum_m C_m \chi_m$
   Fast, accurate, no empty spheres, has forces.