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SPRING COLLEGES IN COMPUTATIONAL PHYSICS

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AB-INITIO ELECTRONIC STRUCTURE CALCULATIONS - III

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Hamiltonian for molecules and solids

$$H = \sum_{i=1}^{N} \frac{P_i^2}{2m} + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e^2}{|r_i - r_j|}$$

$$- \sum_{i=1}^{N} \sum_{\nu=1}^{n} \frac{Z_\nu e^2}{|r_i - R_\nu|}$$

$$+ \sum_{\nu=1}^{n} \frac{P_\nu^2}{2M_\nu} + \frac{1}{2} \sum_{\substack{\nu,\mu=1 \\ \nu \neq \mu}}^{n} \frac{Z_\nu Z_\mu e^2}{|R_\nu - R_\mu|}$$

n = # of atoms (2-100 for molecules, ∞ for solids)

N = # of electrons

$$H = T_e(p) + V_{ee}(r) + V_{eN}(r,R) + T_N(P) + V_{NN}(R)$$

Schroedinger eq.

$$H(r,p,R,P)\,\psi_i(r,R) = E_i\,\psi_i(r,R)$$

all properties can be derived from it

Al

```
 atomic number is 13.00
 lsd = 0 sic = 0 latt = 0 nsp = 0 ixc = 3  beta= .50 tr2=1.0E-14
 mesh = 421 r(mesh) =  51.16474 ibound = 0 xmin = -4.00 dx =  .02500

 n l     nl              e(nl)
 1 0     1s( 2.00)   -110.3120
 2 0     2s( 2.00)     -7.8681
 2 1     2p( 6.00)     -5.1266
 3 0     3s( 2.00)      -.5742
 3 1     3p( 1.00)      -.2055

 eps = 4.1E-15  iter = 21
  etot       ekin       encl       epse       ehrt       ecxc       evxt
-482.61801  481.32786-1154.41018     .00000  225.33907  -34.87477     .00000

 normalization and overlap integrals

 s(1s/1s) =  1.000000     <r> =   .12
 s(1s/2s) =   .000000
 s(1s/3s) =   .000000
 s(2s/2s) =  1.000000     <r> =   .63
 s(2s/3s) =   .000000
 s(2p/2p) =  1.000000     <r> =   .61
 s(2p/3p) =   .000000
 s(3s/3s) =  1.000000     <r> =  2.54
 s(3p/3p) =  1.000000     <r> =  3.44
```

$[R_y]$ [eV]

−1500.9
−107.1
−69.8
−7.8
−2.8

a_0

$1\,a_0 \approx 0.53\,\text{Å}$

Adiabatic Approximation

2 different "phases": electrons and atoms (ions)

$M_{ion} \approx 2000 - 100000\ m_e$

$Z_{eff\,ion} \approx 1$

$\Rightarrow \quad \hbar\omega_{ion} \sim 10\,meV \qquad \hbar\omega_{el} \sim 1\,eV$

$\hbar\omega_{ion} \ll \hbar\omega_{el}$

$T_{ion} \gg T_{el}$

On the time scale electrons need to readjust themselves ions essentially don't move

$$\Psi(r,R) = \chi(R)\,\varphi(r;R)$$

neglecting $\nabla_R \varphi(r;R)$

$$\frac{[T_e + V_{ee} + V_{en} + V_{nn}]\,\varphi(r;R)}{\varphi(r;R)} + \frac{T_n \chi(R)}{\chi(R)} = E$$

$$\begin{cases} [T_e + V_{ee} + V_{en} + V_{nn}]\,\varphi(r;R) = E(R)\,\varphi(r;R) \\ [T_n + E(R)]\,\chi(R) = E\,\chi(R) \end{cases}$$

knowledge of $E^{el}_{GS}(\mathbf{R})$ gives access not only to

- static ground state properties ($T=0$)
  crystal structure → phase diagrams ($P, T=0$)
  elastic constants, dielectric cons, piezoelectric cons.
  static susceptibilities

but also to

- dynamical properties
  Harmonic phonon spectra
  Anharmonic phonons → lattice expansion
  Low frequency dielectric response ($\omega <$ infrared)

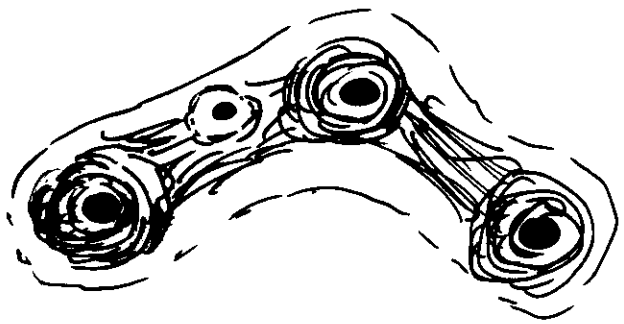
"High frequency static" dielectric constant: $\varepsilon_\infty = \varepsilon(\omega)$ when $E_{gap} >> \hbar\omega >>$ phonons

and

- Thermodynamical properties ($T \neq 0$)
  phase diagrams (T, x)

$$E^{(r)}_{q\text{-test}} = q\left[\sum_v \frac{Z_v e}{|R_v - r|} + \int \frac{-e\, n(r')}{|r' - r|}\right]$$

$q = -e$



$$E(r) = -\sum_v \frac{Z_v e^2}{|R_v - r|} + e^2 \int \frac{n(r') + \delta n(r')}{|r' - r|}\, d^3r'$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ion}(r) + e^2\int \frac{n(r')}{|r' - r|}\, d^3r + v_{Screen}(r)\right]\varphi_i(r) = \varepsilon_i\, \varphi_i(r)$$

electrons are Fermions

$$\psi(r_1, \ldots r_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_1(r_1) & \cdots & \varphi_1(r_N) \\ \vdots & & \vdots \\ \varphi_N(r_1) & \cdots & \varphi_N(r_N) \end{vmatrix}$$

$$n(r) = \sum_{i=1}^{N} |\varphi_i(r)|^2$$

Self Consistent Field

the screening [illegible] contributions [illegible] to

[illegible] (= charge) and [illegible]

[illegible] correlations

HARTREE-FOCK

variational approximation for E_{GS}

Ψ_{HF} = slater determinant

minimize

$$E[\Psi_{HF}] = \langle \Psi_{HF} | T_e + V_{ee} + V_{en} | \Psi_{HF} \rangle$$

$$E[\Psi_{HF}] = \sum_{i=1}^{N} \langle \varphi_i | -\frac{\hbar^2}{2m}\nabla^2 + V_{ion} | \varphi_i \rangle$$

$$+ \frac{1}{2} \sum_{i,j} \int |\varphi_i(r)|^2 \frac{e^2}{|r-r'|} |\varphi_j(r)|^2 d^3r\, d^3r'$$

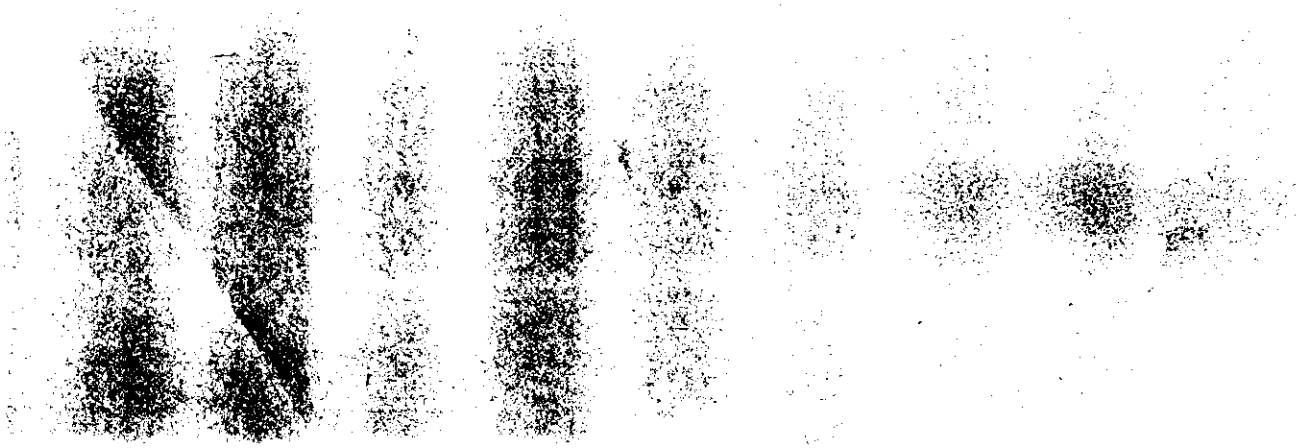
$$- \frac{1}{2} \sum_{i,j} \int \varphi_i^*(r)\, \varphi_j(r) \frac{e^2}{|r-r'|} \varphi_j^*(r')\, \varphi_i(r')\, d^3r\, d^3r'$$

orthogonality conditions $- \sum_{i,j} \lambda_{ij} \left(\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right)$

Hartree-Fock equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ion}(r) + e^2 \int \frac{n(r')}{|r-r'|} d^3r' + \hat{V}_x \right] \varphi_i(r) = \varepsilon_i \varphi_i(r)$$

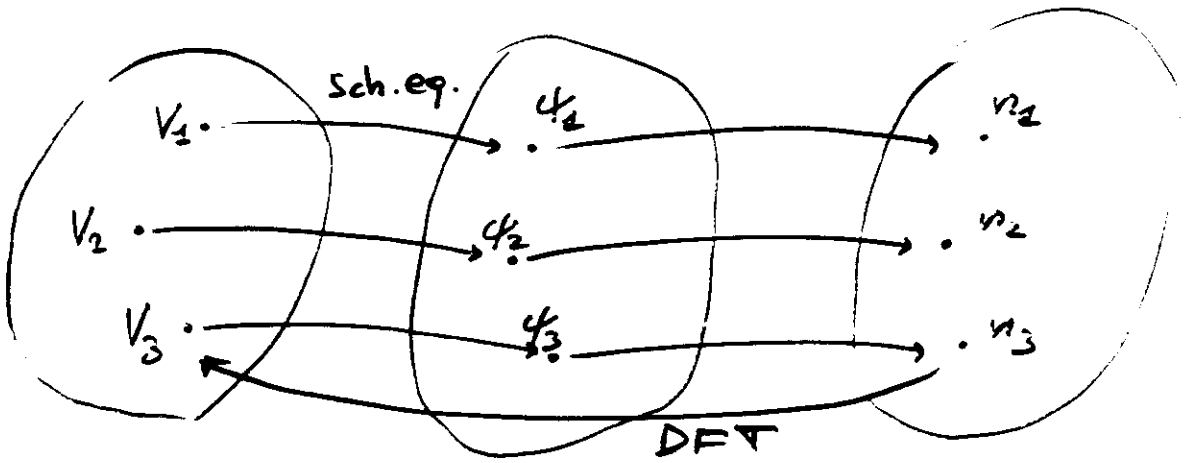
$\hat{V}_x$ exchange, no correlation



DENSITY FUNCTIONAL THEORY

the density as the basic variable (for GS properties)

$$[T_e + V_{ee} + V]\psi_{GS} = E_{GS}\,\psi_{GS} \quad ; \quad n(r) = \langle \psi_{GS} | \hat{n}(r) | \psi_{GS} \rangle$$



Hohenberg & Kohn Theorem Phy. Rev. 136 B864 (1964)

if $V'(r) \neq V(r) + \text{const}$ then $n'(r) \neq n(r)$

$\Rightarrow n(r) \rightarrow V(r) + \text{const} \longrightarrow \psi_{GS} \rightarrow E_{GS}, \ldots$

$$F[n] = \langle \psi_{GS}^{[n]} \,|\, T_e + V_{ee} \,|\, \psi_{GS}^{[n]} \rangle$$

$$E[n] = F[n] + \int V(r)\, n(r)\, d^3r$$

$F[n]$ is a well defined functional of $n(r)$

$E[n]$ is minimized by the true GS density

and $E[n_{GS}] = E_{GS}$

$F[n]$ is a very non-trivial functional of the density $n(r)$

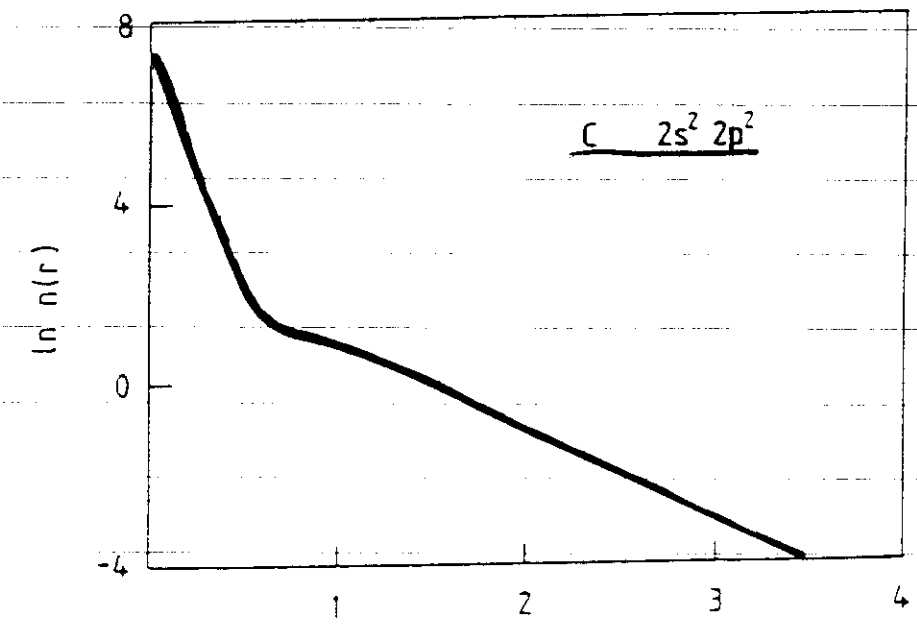


FIG. 1. Spherically averaged density $n(r)$ in ground state of carbon atom as a function of distance r from nucleus.

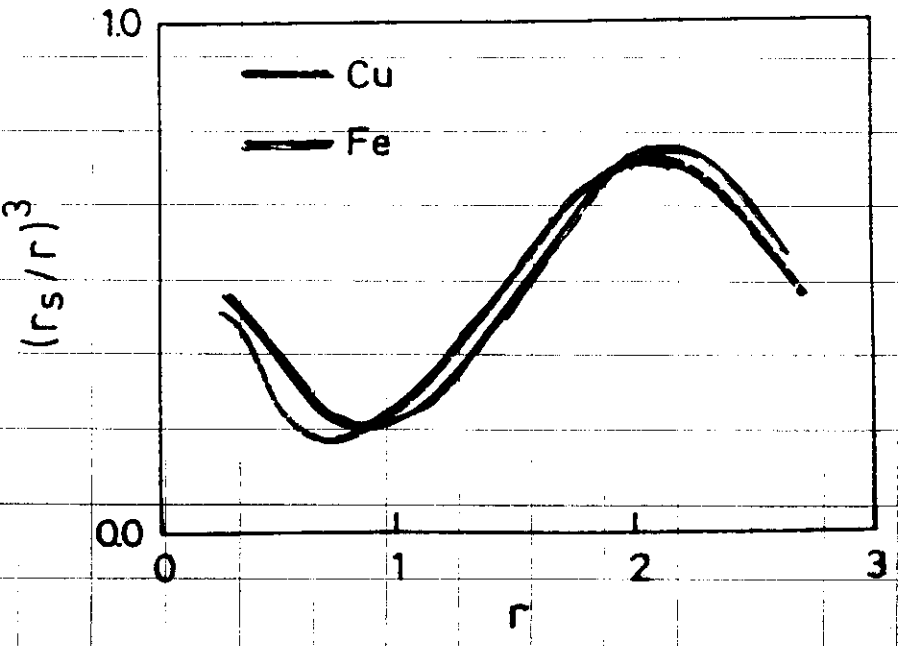


FIG. 6. Density of metallic Fe and Cu as a function of the radius r. The density n is expressed in terms of the parameter r_s, where $n=(4\pi r_s^3/3)^{-1}$.

It is useful to introduce a ficticious system of non-interacting electrons

$$\text{HK:} \quad n(r) \longrightarrow T_s[n] = \min_{\phi \to n} \langle \phi | \hat{T}_e | \phi \rangle$$

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n]$$

↑

definition of E_{xc}.

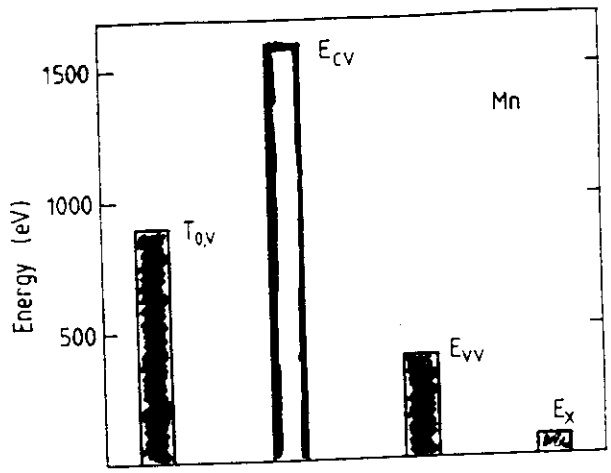


FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(r)\, n(r)\, d^3r$$

Kohn - Sham equations

the minimum condition for the interacting system is

$$\delta\left[F[n] + \int V_0(r)\, n(r)\, d^3r - \mu\left(\int n(r)\, d^3r - N\right)\right] = 0$$

$$\frac{\delta F[n]}{\delta n(r)} + V_0(r) - \mu = 0$$

$$\frac{\delta T_S[n]}{\delta n(r)} + e^2\int \frac{n(r')}{|r'-r|} d^3r' + \frac{\delta E_{xc}[n]}{\delta n(r)} + V_0(r) - \mu = 0$$

let V_{KS} be the potential of the NON-interacting system that gives $n(r)$

$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r)\right]\varphi_i(r) = \varepsilon_i \varphi_i(r)}$$

$$\psi(r_1,\dots,r_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_1(r_1) & \cdots & \varphi_1(r_N) \\ \vdots & & \vdots \\ \varphi_N(r_1) & \cdots & \varphi_N(r_N) \end{vmatrix}$$

$$\boxed{n(r) = \sum_i |\varphi_i(r)|^2}$$

$$\delta\left[T_S[n] + \int V_{KS}(r)\, n(r)\, d^3r - \mu\left(\int n(r)\, d^3r - N\right)\right] = 0$$

$$\frac{\delta T_S}{\delta n(r)} + V_{KS}(r) - \mu = 0$$

$$\boxed{V_{KS}(r) = V_0(r) + e^2\int \frac{n(r')}{|r'-r|} d^3r' + \frac{\delta E_{xc}[n]}{\delta n(r)}}$$

LOCAL DENSITY APPROXIMATION (LDA)

since $g(r,r',\lambda)-1$ is "short ranged"

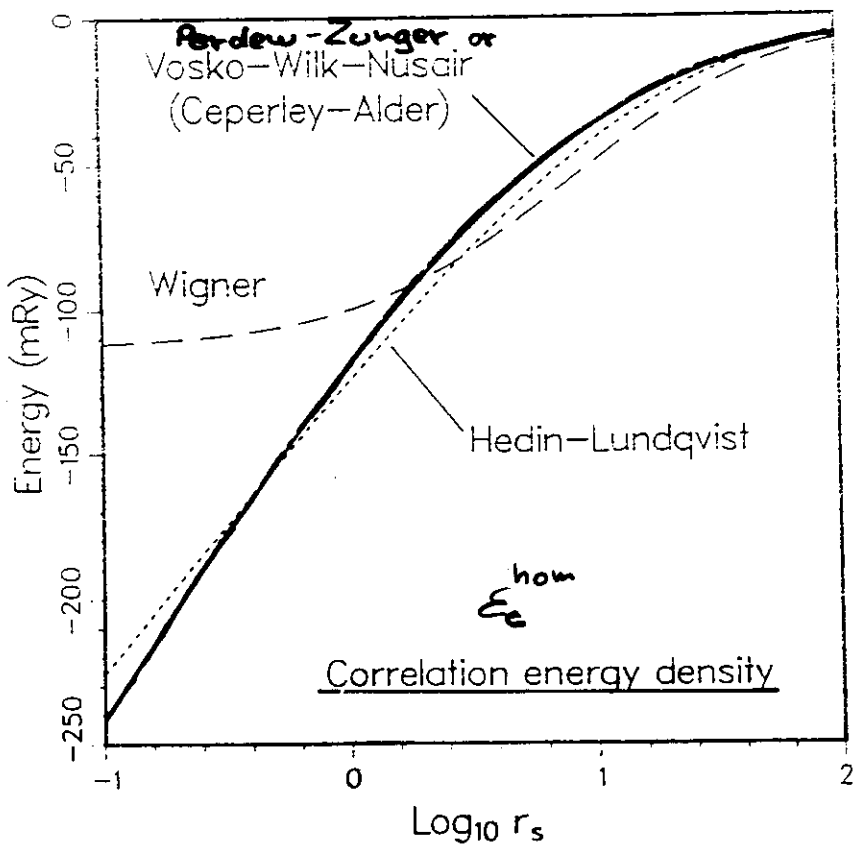
$n_{xc}(r,s) \cong n_{xc}^{hom}(r,s; n=n(r))$

$$E_{xc}^{LDA} = \int d^3r \; n(r)\, \varepsilon_{xc}^{hom}(n(r))$$

$$\varepsilon_{xc}^{hom}(n) = \varepsilon_x^{hom}(n) + \varepsilon_c^{hom}(n)$$

$$\varepsilon_x^{hom}(n) = -\frac{3}{4\pi} e^2 (3\pi^2 n)^{1/3}$$

$\varepsilon_c^{hom}(n)$ from accurate DMC data Ceperley-Alder
Phys. Rev. Lett 45, 566 (1



$$n = \frac{1}{\frac{4}{3}\pi r_s^3}$$

$$V_{xc}^{LDA}(r;[n]) = \frac{\delta}{\delta n(r)} E_{xc}^{LDA}[n] = \left.\frac{d(n\cdot\varepsilon_{xc}^{hom}(n))}{dn}\right|_{n=n(r)}$$

ZERO PARAMETER THEORY!

LOCAL SPIN DENSITY

$F[n]$ contains all the needed information but it may be useful to consider $F[n_\uparrow, n_\downarrow]$

$$F[n_\uparrow, n_\downarrow] = T_S[n_\uparrow, n_\downarrow] + E_H[n_\uparrow + n_\downarrow] + E_{xc}[n_\uparrow, n_\downarrow]$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}^\sigma(r)\right]\varphi_i^\sigma(r) = \varepsilon_i^\sigma \varphi_i^\sigma(r) \qquad \sigma = \uparrow, \downarrow$$

$$n_\sigma(r) = \sum_{\varepsilon_i^\sigma < \varepsilon_F} |\varphi_i(r)|^2$$

$$V_{KS}^\sigma(r) = V_0(r) + V_H(r) + \frac{\delta E_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(r)}$$

LSD approximation

$$E_{xc}^{LSD}[n_\uparrow, n_\downarrow] = \int (n_\uparrow(r) + n_\downarrow(r))\, \varepsilon_{xc}^{hom}(n_\uparrow, n_\downarrow)\, d^3r$$

$$v_{xc}^{LSD\,\sigma}(r) = \frac{d\left[(n_\uparrow + n_\downarrow)\varepsilon_{xc}^{hom}(n_\uparrow, n_\downarrow)\right]}{d n_\sigma(r)}$$

Ground State of the Electron Gas by a Stochastic Method

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(Received 16 April 1980)

An exact stochastic simulation of the Schroedinger equation for charged bosons and fermions has been used to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the stability at intermediate densities of a ferromagnetic fluid of electrons.

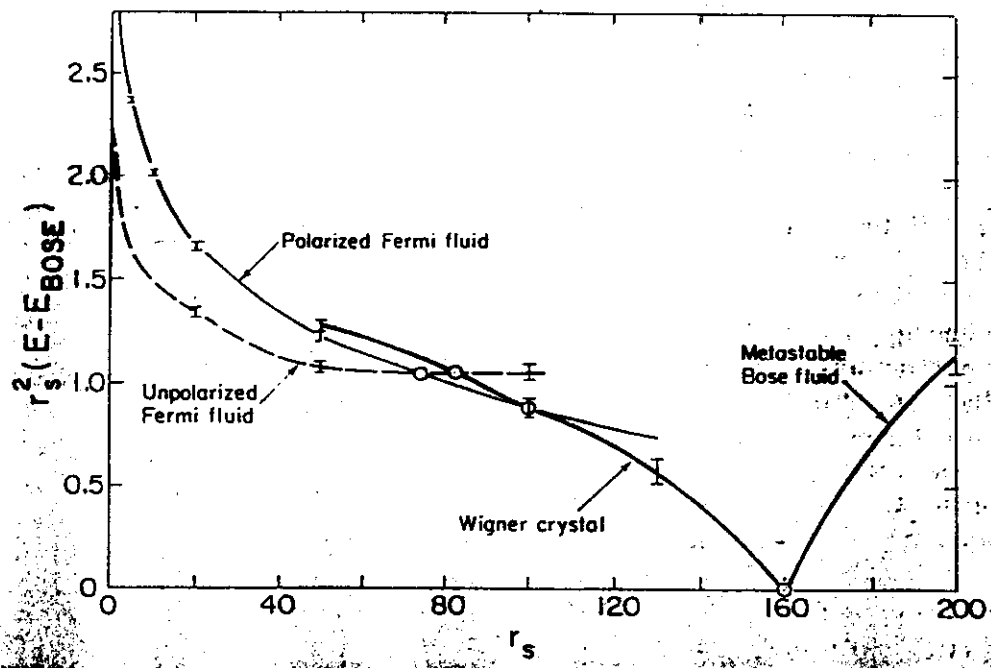
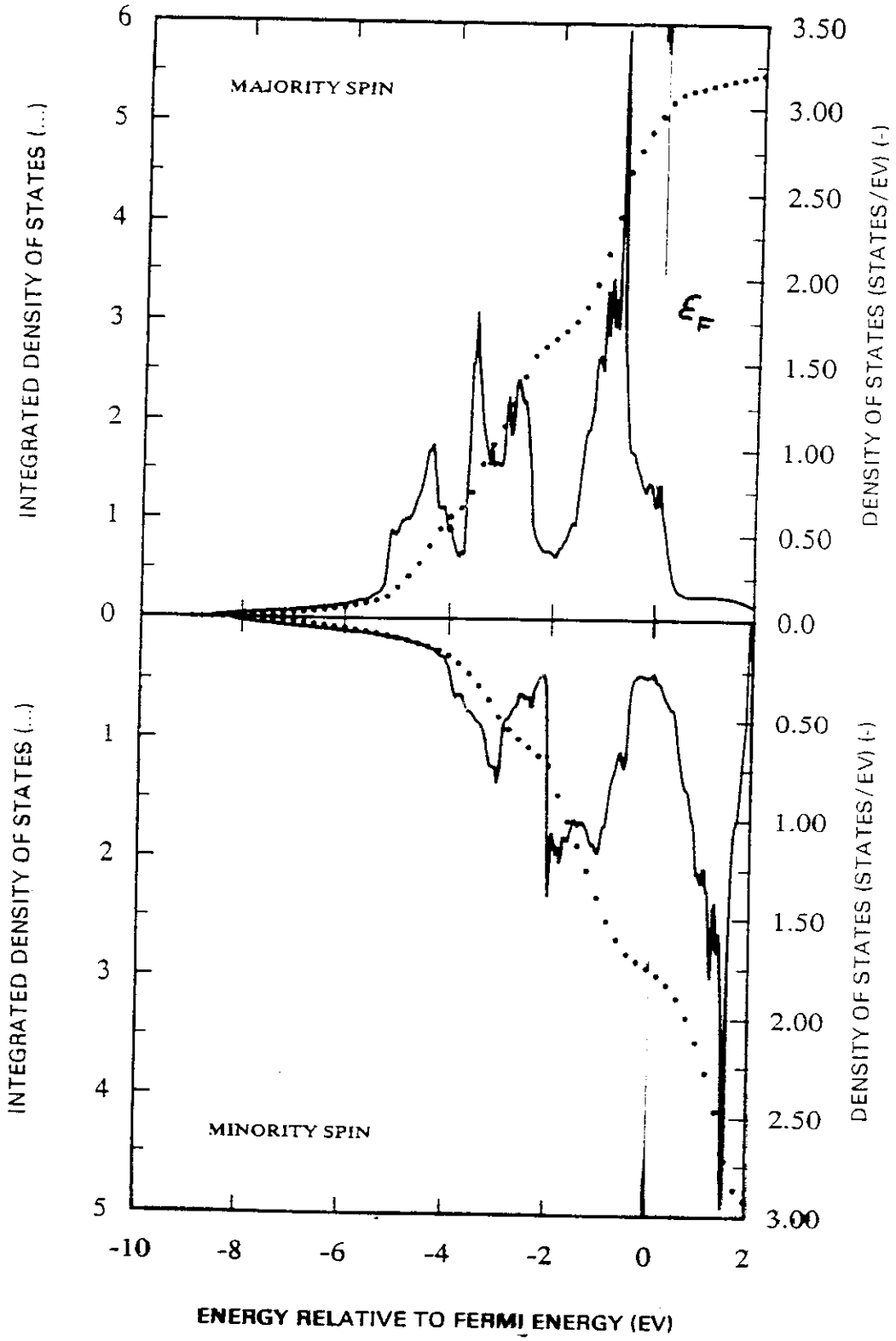


FIG. 2. The energy of the four phases studied relative to that of the lowest boson state, versus r_s in Bohr radii. For $r_s = 160$ the Bose fluid is the most stable phase, while above $r_s = 76$ the Wigner crystal is stable. The energies of the polarized and unpolarized Fermi fluid are set equal at $r_s = 100$. The ferromagnetic Fermi fluid is the normal above

Iron $Z = 26$



$$\vec{\mu}_s = -g_s \frac{e}{mc} \vec{S}$$

$$= -\frac{g_s}{2} \mu_B (N_\uparrow - N_\downarrow)$$

$= 2.15\ \mu_B$/atom

exp: 2.2 μ_B/atom

LSD calculation

Moruzzi
Janak
Williams

Calculated Electronic Properties of Metals,
Pergamon 1978

Choice of the basis set

A periodic solid is a collection of atoms in periodically repeated positions

$R + \tau_s$ → position inside the unit cell
↓
lattice vector $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r)\right]\varphi_{k,\nu}(r) = \varepsilon_{k\nu}\varphi_{k\nu}(r)$$

$V_{ext}(r)$, $n(r)$ ($\rightarrow V_H(r)$, $v_{xc}(r)$) are periodic functions

$V_{ext}(r+R) = V_{ext}(r)$ $\quad n(r+R) = n(r)$

$$V_{ext}(r) = \sum_{R,s} V_s(\vec{r} - (\vec{R}+\vec{\tau}_s)); \quad V_s(\vec{r}) = -\frac{e^2 Z_s}{|\vec{r}|}$$

To solve the problem a basis set is introduced in order to expand the wavefunctions (in Bloch form)

$$\varphi_{k\nu}(r) = \sum_{i=1}^{N_b} c_{k\nu}^i \, b_i^k(\vec{r})$$

b_i^k → basis function
$c_{k\nu}^i$ → expansion coefficient

This brings the eigenvalues problem to matrix form

$$\left[H_{KS}^{(r,p)} - \varepsilon_{k\nu}\right]\varphi_{k\nu}(r) = 0$$

↓

$$\sum_{j=1}^{Nb}\left[H_{ij}^{(k)} - \varepsilon_{k\nu}S_{ij}^{(k)}\right]c_{k\nu}^j = 0$$

$$H_{ij}^{(k)} = \langle b_i^{(k)} | H | b_j^{(k)} \rangle$$

$$S_{ij}^{(k)} = \langle b_i^{(k)} | b_j^{(k)} \rangle$$

A natural choice for a periodic system is given by the **Plane Wave basis set**

$$b_i^{(k)}(\vec{r}) = \langle r | k+G_i \rangle = \frac{1}{\sqrt{V}} e^{+i(k+G)r}$$

with $\vec{G}_i = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$ $\qquad \vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$

reciprocal lattice vectors

PW's form an infinite (and complete) orthogonal basis set. A finite basis set is selected requiring

$$\frac{\hbar^2}{2m}(k+G_i)^2 < E_{cutoff}$$

It has several advantages

- It is unbiased: has the same spatial resolution in every point and for every configuration
- Can be improved easily and systematically by increasing Ecutoff
- Matrix elements are very simple to calculate

$$\langle k+G | -\frac{\hbar^2}{2m}\nabla^2 | k+G' \rangle = \frac{\hbar^2}{2m}(k+G)^2 \delta_{GG'}$$

$$\langle k+G | V(r) | k+G \rangle = \frac{1}{V}\int V(r) e^{-i(G-G')r} d^3r = \tilde{V}(G-G')$$

- Allows the use of FFT to go back and forth between direct and reciprocal space

$$\nabla^2 V_H(r) = -4\pi e^2 n(r)$$

$$n(r) \xrightarrow[N\ln N]{FFT} n(G) \xrightarrow[N]{} V_H(G) = \frac{4\pi e^2}{G^2} n(G) \xrightarrow[N\ln N]{FFT} V_H(r)$$

$$(H\varphi)(k+G): \quad T\varphi = \frac{\hbar^2}{2m}(k+G)^2 \varphi(k+G) \quad N_\varphi$$

$$\varphi(k+G) \xrightarrow[N\ln N]{FFT} \varphi(r) \xrightarrow[N]{\cdot} V(r)\varphi(r) \xrightarrow[N\ln N]{FFT} [V\varphi](k+G)$$

However a straightforward use of PW's is frustrated by the very large numbers needed to describe core electron wavefunctions

$$\langle r_{1s} \rangle \sim 1/Z \sim \lambda_{min}$$

$$G_{max} \sim \frac{2\pi}{\lambda_{min}} \sim 2\pi Z$$

$$E_{cutoff} \sim \frac{\hbar^2}{2m} G_{max}^2 \sim (2\pi Z)^2 \text{ Ryd}$$

but core electrons do not participate to chemical bonding and are almost unchanged with respect to the atomic case

The region around the nuclei can and must be treated in a special way to make the size of the problem tractable there are 2 strategies

- All-electrons methods: (F)LAPW, (F)LMTO, KKR

APW: the space is separated in atomic spheres and the interstitial region. The basis set is given by plane waves in the interstitial region matched to atomic-like solutions on the spheres.

$$\mathcal{A}(\mathbf{p}, \mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} a_{lm} Y_{lm}(\theta, \varphi) R_l(E, r) \eta(r_s - r) + e^{i\mathbf{p}\cdot\mathbf{r}} \eta(r - r_s)$$

In this basis the secular equation becomes

$$\langle \mathcal{A}_{\mathbf{k}_i} | H - E | \mathcal{A}_{\mathbf{k}_j} \rangle = \left(\frac{\hbar^2}{2m} \mathbf{k}_i \cdot \mathbf{k}_j - E \right) \delta_{ij}$$

$$+ \frac{4\pi r_s^2}{\Omega} \left\{ \left(\frac{\hbar^2}{2m} \mathbf{k}_i \cdot \mathbf{k}_j - E \right) \frac{j_1(|\mathbf{k}_i - \mathbf{k}_j| r_s)}{|\mathbf{k}_i - \mathbf{k}_j|} \right.$$

$$\left. + \sum_{l=0}^{\infty} (2l + 1) P_l(\cos\theta_{ij}) j_l(k_i r_s) j_l(k_j r_s) \left[\frac{R_l'(E, r_s)}{R_l(E, r_s)} - \frac{j_l'(k_j r_s)}{j_l(k_j r_s)} \right] \right\}$$

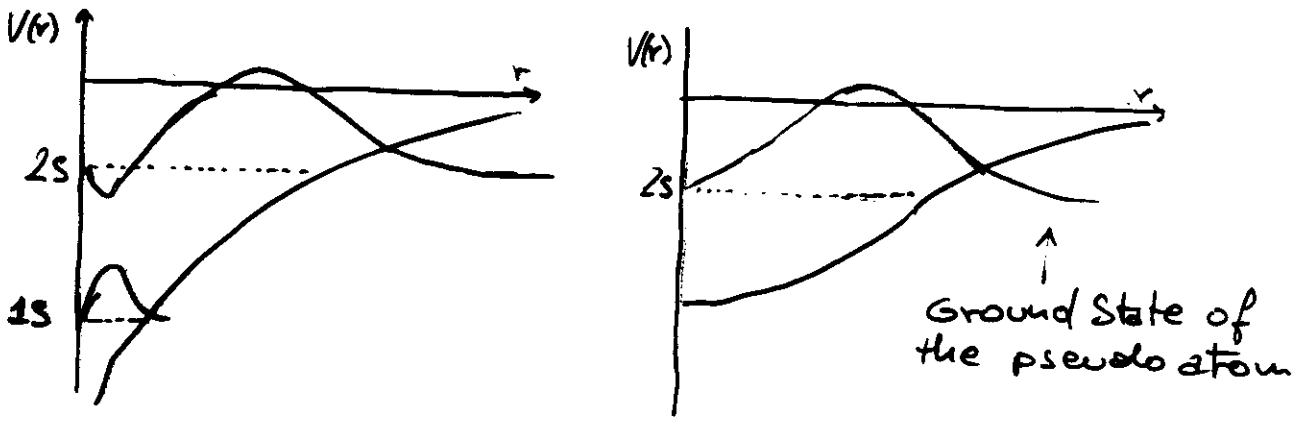
match of logarithmic derivative at the sfere boundary

② PSEUDOPOTENTIALS

Hamman, Schlüter and Chiang PRL 43 1494 (1979)

It is possible to eliminate completely the core states and modify the external atomic potential in such a way that the valence wfc are smooth and nodeless inside the core sphere and are matched with the same scattering properties at the sphere boundary.

ex: Berillium: $[1s^2]2s^2$ ⟶ Pseudo Be: $2s^2$



Orthogonality to core states is "equivalent" to a repulsive term in the potential

Price to pay: Non-locality in the core region
(wfc's with diff. l have diff. orthogonality conditions)

Norm-Conserving Pseudo Potentials

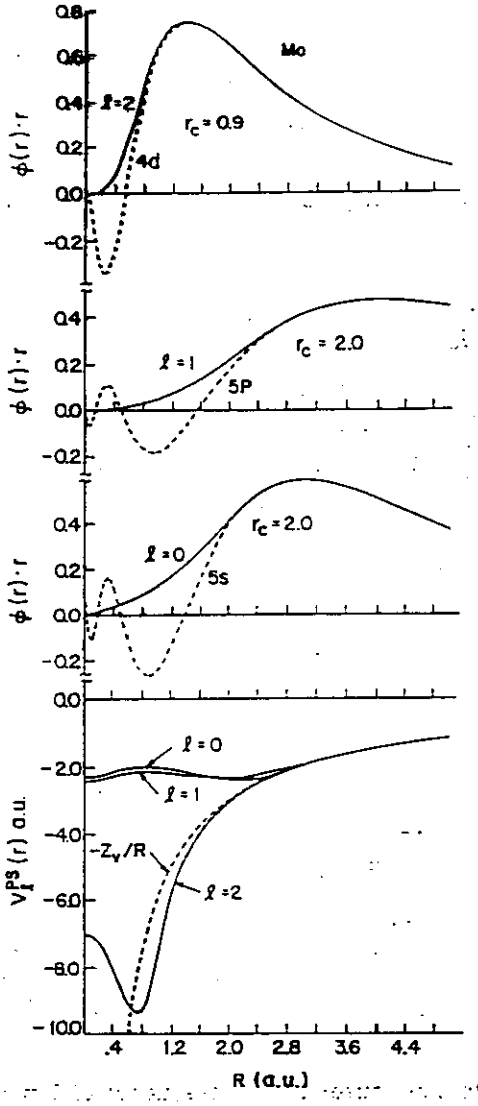


FIG. 1. Comparison of pseudo wave functions (solid lines) and *ab initio* full-core atomic valence wave functions (broken lines) for Mo. The lower panel shows the corresponding bare-ion pseudopotentials.

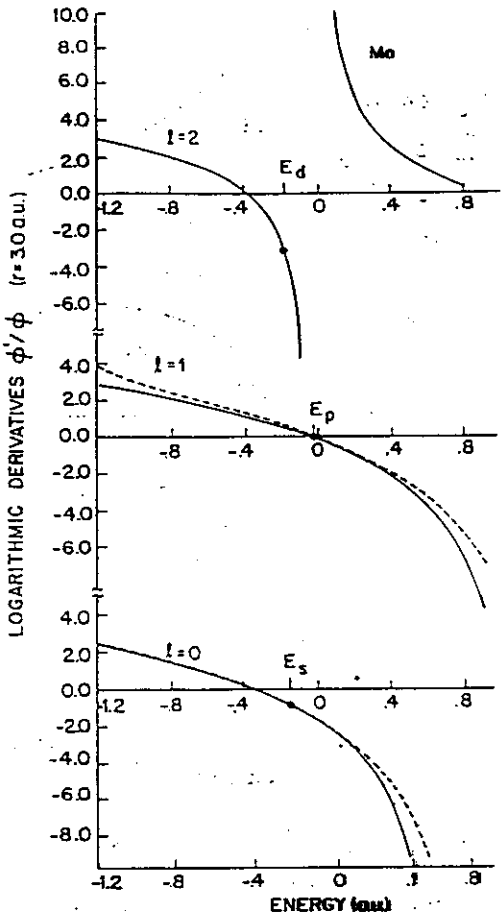


FIG. 2. Energy dependence of logarithmic derivatives at $r = 3.0$ a.u. for Mo *ab initio* full-core atomic wave functions (broken lines) and pseudo wave functions (solid lines) as shown in Fig. 1.

TABLE I. Atomic eigenvalues in atomic units for pseudopotentials constructed with $r_{cl} = 0.75 r_{ml}$. Δ denotes the deviations from the corresponding full-core *ab initio* results. The Wigner exchange approximation is used.

	Energy			Δ		
Configuration	s	p	d	s	p	d
O $2s^1 2p^5$	−0.8818	−0.34[illegible]	---	−0.0011	−0.0003	---
O $2s^2 2p^3$	−1.4337	−0.8[illegible]	---	0.0005	−0.0005	---
O $2s^2$[illegible]	−2.[illegible]	−1.5[illegible]	---	−0.0001	−0.0037	---
[illegible]	−0.[illegible]	−0.1[illegible]	---	−0.0018	0.0001	---
[illegible]	−0.[illegible]	−0.2[illegible]	---	0.0007	0.0004	---
[illegible]	−1.[illegible]	−0.7[illegible]	---	0.0031	0.0025	---
[illegible]	−0.21[illegible]	−0.0[illegible]	−0.[illegible]	≅0	−0.[illegible]	0.0025
[illegible]	−0.3[illegible]	−0.2[illegible]	−0.[illegible]	≅0	[illegible]	[illegible]0016
[illegible]	−0.55[illegible]	−0.2[illegible]	0.77[illegible]	[illegible]0013	[illegible]	−0.0006

TOTAL ENERGY PER UNIT CELL

$$\frac{E}{N_{cell}} = \frac{1}{N_{cell}}\left(T_e + E_H + E_{xc} + \int V(r) n(r) d^3r + V_{nn} \right)$$

the three electrostatic contributions diverge if taken separately. They give a finite result if take together (charge neutrality of the system)

$$\frac{1}{N_{cell}}\left(E_H + \int V(r) n(r) d^3r + V_{nn}\right) = \frac{1}{N_{cell}} \frac{1}{2} \sum_G{}' \frac{4\pi}{G^2} \left| \rho_{ion}(G) + \rho_0(G) \right|^2$$

$$\rho(G) = \frac{1}{\Omega} \int_\Omega \rho(r) e^{-iGr} d^3r$$

Hartree $$\frac{1}{N_{cell}} E_H = \frac{\Omega}{2} \sum_G{}' \frac{4\pi e^2}{G^2} |n(G)|^2$$

Ext. Pot. $$\frac{1}{N_{cell}} E_{ext} = \Omega \sum_G V^*_{ext}(G)\, n(G)$$

$$V_{ext}(G) = \frac{1}{\Omega} \int_\Omega \sum_{Rs} \frac{-Z_s e^2}{|r - R - \tau_s|} e^{-iGr} d^3r = -\frac{4\pi e^2}{G^2} \frac{\sum_s Z_s e^{-iG\tau_s}}{\Omega}$$

V_{nn} Ewald Sum

$$\frac{1}{N_{cell}} V_{nn} = \frac{e^2}{2} \sum_{Rss'}{}' \frac{Z_s Z_{s'}}{|R + \tau_s - \tau_{s'}|} = \frac{1}{2} \frac{4\pi e^2}{\Omega} \sum_G{}' \frac{\left|\sum_s Z_s e^{-iG\tau_s}\right|^2}{G^2} - \text{self. en.}$$

$$\frac{1}{r} = \frac{\operatorname{erf}(\sqrt{\alpha} r)}{r} + \frac{1 - \operatorname{erf}(\sqrt{\alpha} r)}{r} = \varphi_1(\sqrt{\alpha} r) + \varphi_2(\sqrt{\alpha} r)$$

$$\frac{4\pi}{G^2} = \frac{4\pi}{G^2} e^{-G^2/4\alpha} + \frac{4\pi}{G^2}\left[1 - e^{-G^2/4\alpha}\right]$$

$$E_{EWALD} = \frac{1}{2} \frac{4\pi e^2}{\Omega} \sum_G{}' \frac{e^{-G^2/4\alpha}}{G^2} \left|\sum_s Z_s e^{-iG\tau_s}\right|^2 - \frac{\pi e^2}{2\Omega\alpha} \left|\sum_s Z_s\right|^2 - e^2 \sum_s Z_s^2 \sqrt{\frac{\alpha}{\pi}}$$

$$+ \frac{e^2}{2} \sum_{Rss'}{}' Z_s Z_{s'} \varphi_2(\sqrt{\alpha} |R + \tau_s - \tau_{s'}|)$$

$$\frac{E}{N_{cell}} = \frac{1}{N_k} \sum_v \sum_k \langle \varphi_{kv} | -\frac{\hbar^2}{2m} \nabla^2 | \varphi_{kv} \rangle + \int_\Omega V_{ext}(r)\, n(r)$$

$$\frac{1}{N_k} E_H + \int_\Omega \varepsilon_{xc}^{(n)} n(r)\, d^3r + E_{EWALD}$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ext} + V_H + V_{xc} \right] \varphi_{kv} = \varepsilon_{kv} \varphi_{kv}$$

Band Structure energy

$$\frac{1}{N_{cell}} E_{bs} = \frac{1}{N_k} \sum_v \sum_k \varepsilon_{kv}$$

$$= \frac{1}{N_k} \sum_v \sum_k \langle \varphi_{kv} | -\frac{\hbar^2}{2m} \nabla^2 | \varphi_{kv} \rangle + \int_\Omega \left[V_{ext} + V_H + v_{xc} \right] n(r)\, d^3r$$

$$\frac{E}{N_{cell}} = \frac{E_{bs}}{N_{cell}} - \frac{E_H}{N_{cell}} + \int \left[\varepsilon_{xc}^{(n)} - v_{xc}^{(n)} \right] n(r) + \frac{E_{EWALD}}{N_{cell}}$$

Special Points for BZ integration

several times integrals over the whole BZ are needed

$$E_{bs} = \frac{1}{\Omega_{BZ}} \int d^3k \sum_{\nu,\sigma} \varepsilon_\nu^\sigma(k) = \frac{1}{N_k} \sum_{k_i} w(k_i) \sum_{\nu,\sigma} \varepsilon_\nu^\sigma(k_i)$$

k_i, w_i determined using the symmetry of the BZ in order to minimize their number

Baldereschi Phys. Rev. B 7 5212 (1973)
Chadi & Cohen Phys Rev B 8 4547 (1973)
Monkhorst & Pack Phys. Rev B 13 5188 (1976)

in metals one should integrate inside the FS

Special points + smearing

C-L Fu & KM Ho Phys. Rev. B 28 5480 (1983)
M. Methfessel & AT Paxton Phys Rev B 40 3613 (1989)

Tetrahedron Method

J. Rath and A.J. Freeman Phys. Rev B 11, 2109 (1975)

Kohn-Sham eqs. are self consistent eqs.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}^{(in)}(r)\right]\varphi_i(r) = \varepsilon_i \varphi_i(r)$$

$$n(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}^{(out)}(r) = V_0(r) + e^2\int \frac{n(r')}{|r-r'|} d^3r' + v_{xc}^{LDA}(n(r))$$

$$V_{KS}^{(in)} \longrightarrow V_{KS}^{(out)}$$

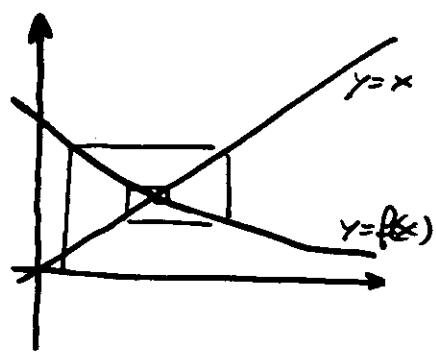
the solution is obtained when $V^{out} = V^{in}$

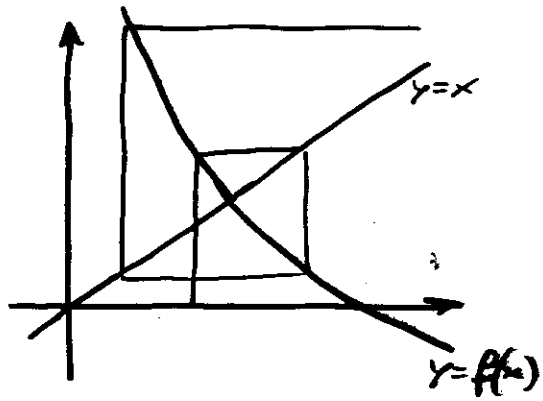
it is a fixed point problem

$$x = f(x)$$

procedure: $x_{n+1} = f(x_n)$

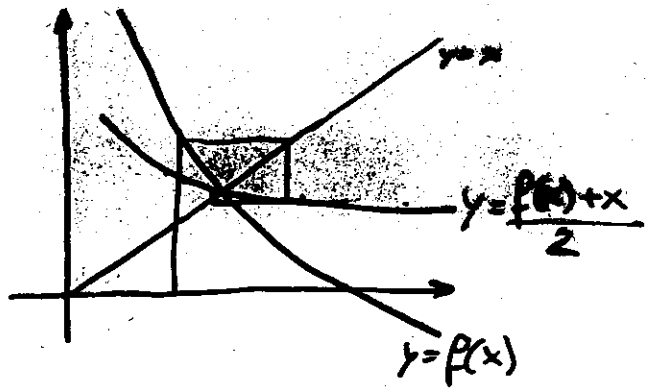
IF the sequence converge the limit is the solution





add a dumping term

$$x_{n+1} = \alpha f(x_n) + (1-\alpha)x_n$$



Computer Physics Reports 9 115-198 (1989)

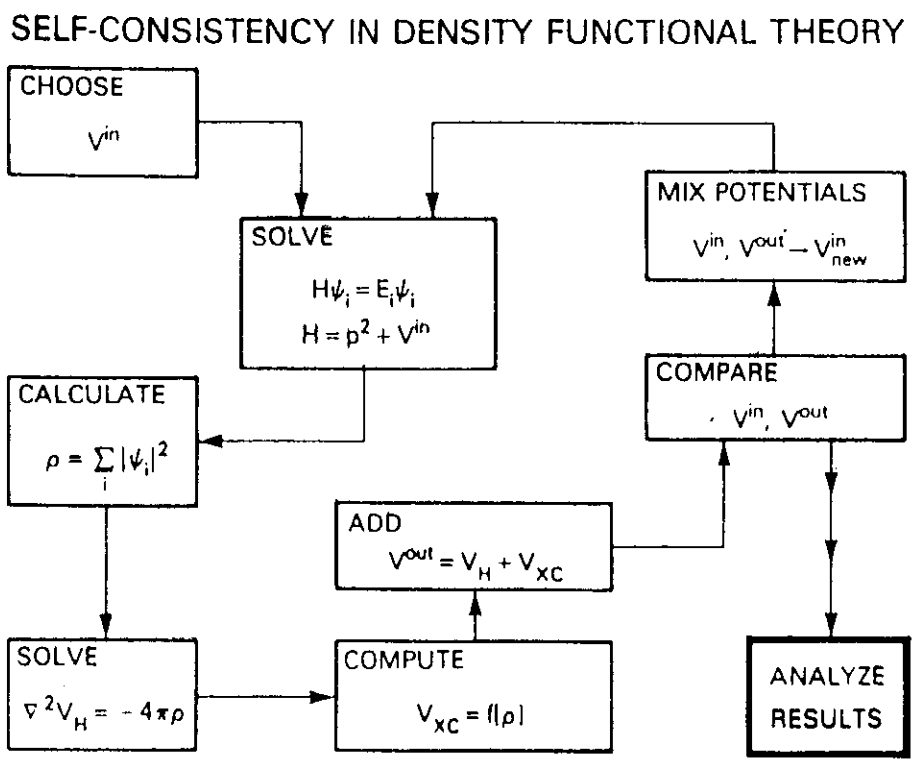


Fig. 5. Schematic diagram showing the steps in attaining self-consistency in Kohn–Sham density functional theory. To begin (upper left) a starting potential V^{in} is chosen, and inserted in the Hamiltonian H. The lowest N eigenfunctions (for an N-electron system) provides the electron density, which lead to the Hartree (V_H) and exchange-correlation (V_{xc}) potentials via Poisson's equation and a simple, usually local, functional, respectively. These potentials are combined to form the output screening potential, which is compared to the input potential. If the output potential is sufficiently close to the input potential, the system is self-consistent and analysis of results can proceed. Otherwise the output potential is mixed with the input potential to form a new input potential, and the procedure is iterated until convergence is attained.

FORCES ON ATOMS

$$V_{ext}(r;\{\tau_s\}) \longrightarrow n(r)$$

for every set of positions $n(r)$ is such that

$$E[\{\tau_s\}] = F[n] + \int V_{ext}(r;\{\tau_i\})\, n(r)\, d^3r + E_{ewald}$$

is minimized: $\dfrac{\delta E}{\delta n(r)} - \mu = 0$

Hellmann - Feynman Forces

$$\vec{F}_s = -\frac{dE[\{\tau_s\}]}{d\vec{\tau}_s} = -\left[\int \frac{\partial V_{ext}(r;\{\tau_i\})}{\partial \vec{\tau}_s} n(r)\, d^3r + \frac{\partial E_{ewald}}{\partial \vec{\tau}_s} + \int \frac{\delta E}{\delta n(r)} \frac{\partial n}{\partial \tau_s} d^3r\right]$$

$$= -\int \frac{\partial V_{ext}(r;\{\tau_s\})}{\partial \vec{\tau}_s} n(r)\, d^3r - \frac{\partial E_{ewald}}{\partial \vec{\tau}_s} - \mu \cancel{\frac{\partial N_{el}}{\partial \tau_s}}$$

All-electrons methods are more complex

$$E[\{\tau_s\}] = E[V_{ext}, \{c_i\}, \{b_i(\vec{k})\}]$$

$$\vec{F}_s = -\frac{dE[V_{ext}, \{c_i\}, \{b_i(\vec{k})\}]}{d\vec{\tau}_s}$$

$$= -\left[\int \frac{\partial V_{ext}}{\partial \vec{\tau}_s} n(r)\, d^3r + \frac{\partial E_{ewald}}{\partial \vec{\tau}_s} + \cancel{\sum_i \frac{\partial E}{\partial c_i} \frac{\partial c_i}{\partial \vec{\tau}_s}} + \sum_i \left[\frac{\partial E}{\partial b_i(r)} \frac{\partial b_i(r)}{\partial \tau_s}\right]\right]$$

H.F. force — Pulay force

R. Yu D.J. Singh and H. Krakauer Phys. Rev B 43 6411 (1991)

J.M. Soler and A.R. Williams Phys. Rev B 40 1560 (1989)

B. Kohler S. Wilke M. Scheffler R. Kouba C. Ambrosh-Draxl Comp. Phys. Comm. 94 31 (1996)

W. E. Pickett Comp. Phys. Reports 9 115 (1989)

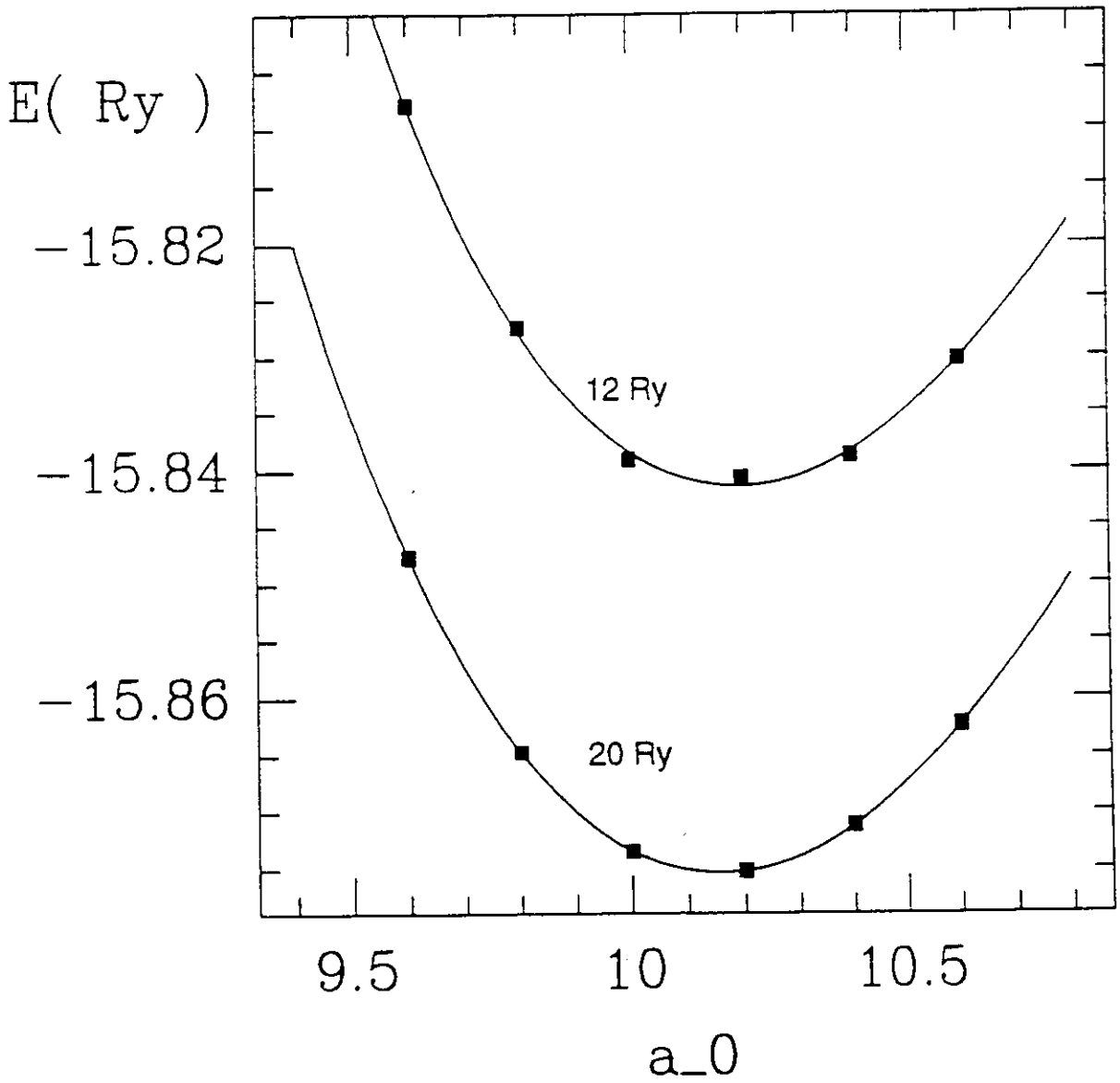
PWSCF CODE

A. Dal Corso in

"Quantum-Mechanical Ab-initio Calculation of the Properties of Crystalline Materials" p. 155

C. Pisani Ed. (Springer 1996)

$$E(\Omega) = \frac{\Omega_0 B_0}{B_0'}\left[\frac{1}{B_0'-1}\left(\frac{\Omega_0}{\Omega}\right)^{B_0'-1} + \frac{\Omega}{\Omega_0}\right] + const$$

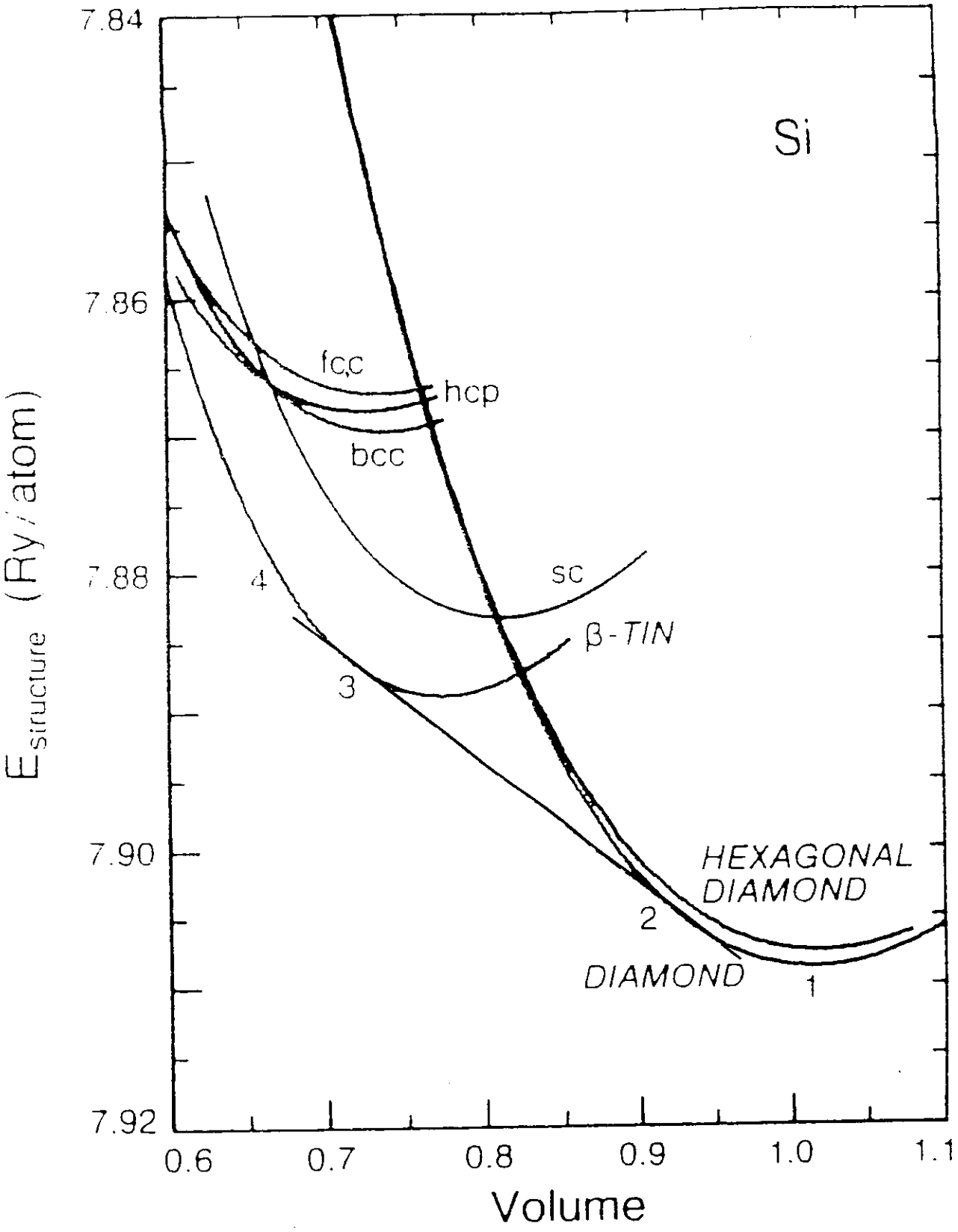


Th: $a_0 = 10.16$ a.u. $= 5.38$ Å $B = 0,96$ Mbar

Exp: $a_0 = 10.26$ a.u. $= 5.43$ Å $B = 0.99$ Mbar

igure 1. Total energy of silicon for different values of the lattice constant. he numerical values (squares) are interpolated with a Murnaghan equation :ontinuous lines). The two curves correspond to a cutoff of 12 and 20 Ry.

A. Dal Corso in "Quantum-Mechanical Ab-initio Calculation of the properties of Crystalline Materials" Ed. C. Pisani (Springer 1996)



M.T. Yin and M.L. Cohen Phys. Rev. B26 5668 (1982)

$P_T \sim 80$ kbar Exp 103–125 kbar

R. Car and M. Parrinello
Phys. Rev. Lett. 55 2471 (1985)

DFT + MD

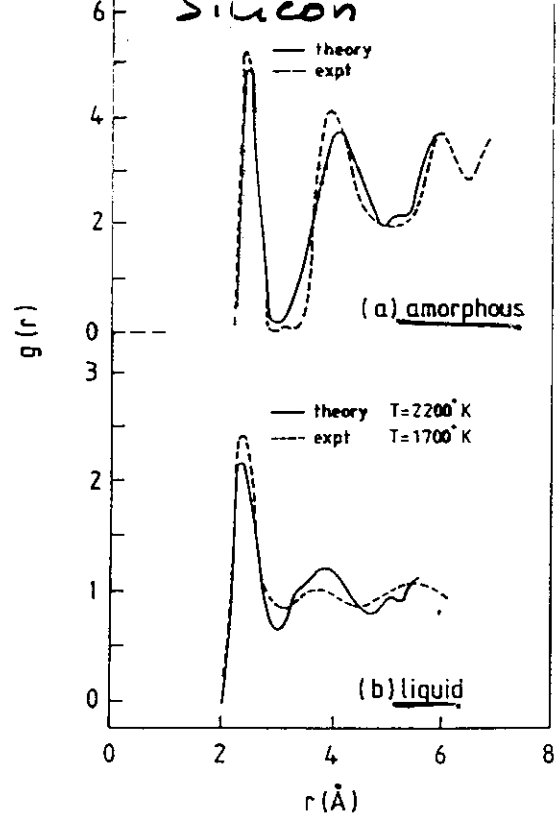


FIG. 25. Pair correlation function g(r) for (a) amorphous and (b) liquid Si (after Car and Parrinello, 1987).

Proc. 18th ICPS, p. 1165

S_7O

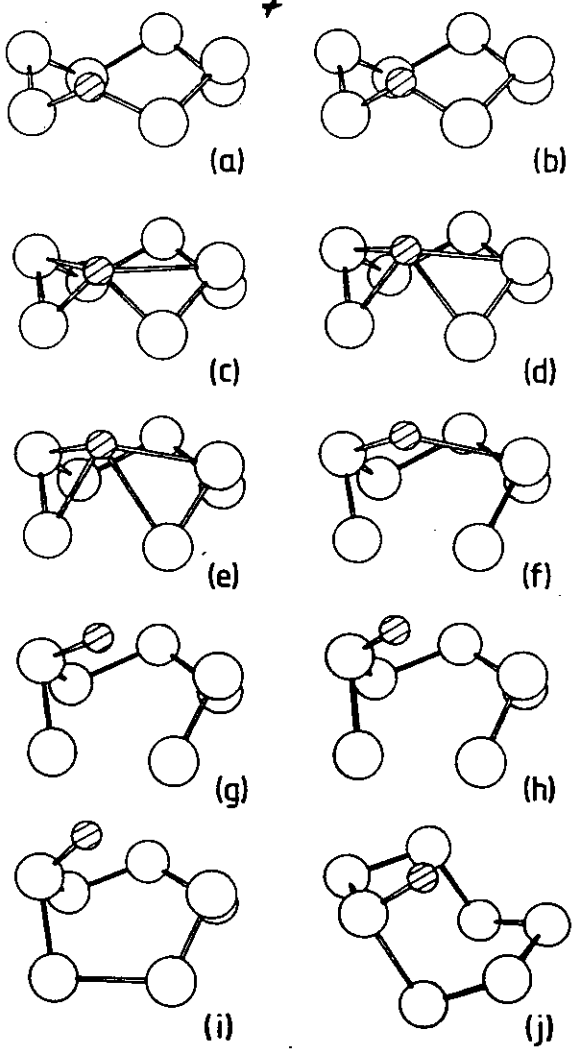


FIG. 27. Structural changes in S_7O at T=2000 K. (a)–(i) Evolution of the "ring" structure into the "intermediate" structure (Hohl *et al.*, 1989). The interval between each frame is 150 time steps, each of 1.7×10^{-16} sec. (j) The ground-state structure in the same perspective.

Hohl, Jones, Car, Parrinello
J. Am. Chem. Soc. 111 825 (1989)

Se_5

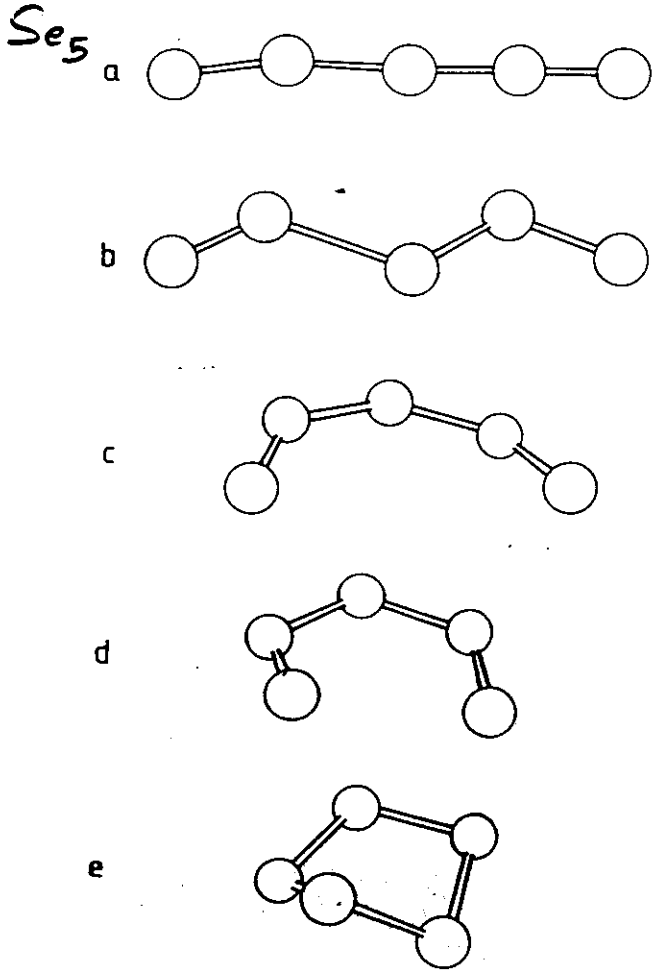
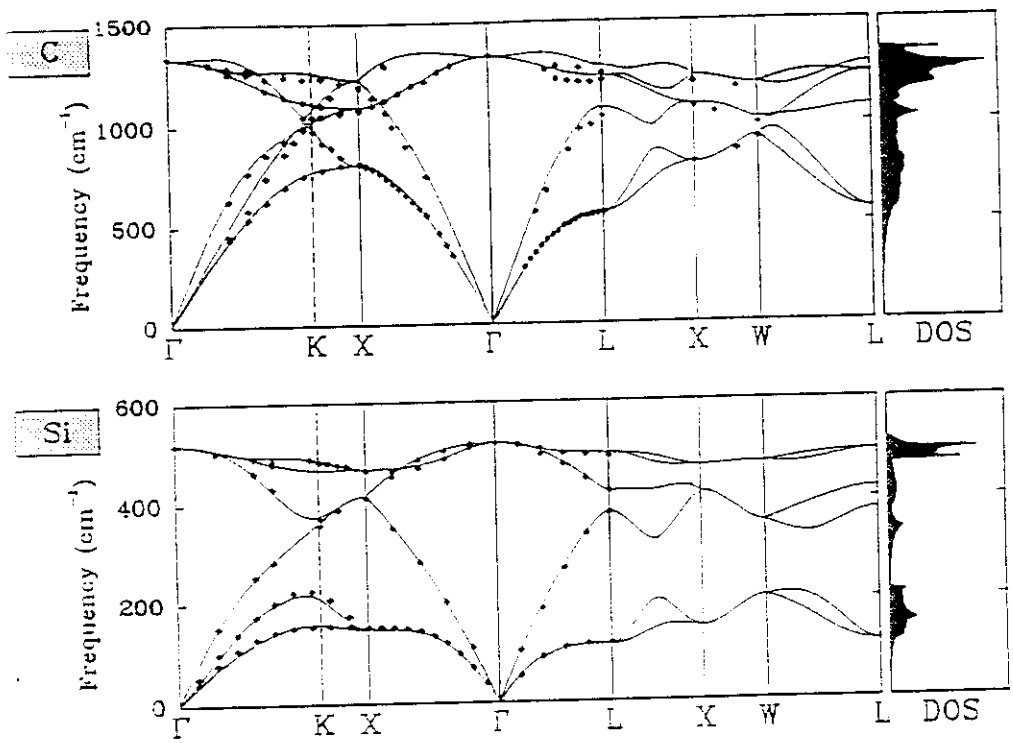


FIG. 26. Deformation of Se_5 linear chain to the calculated ground-state structure (Hohl *et al.*, 1987b).

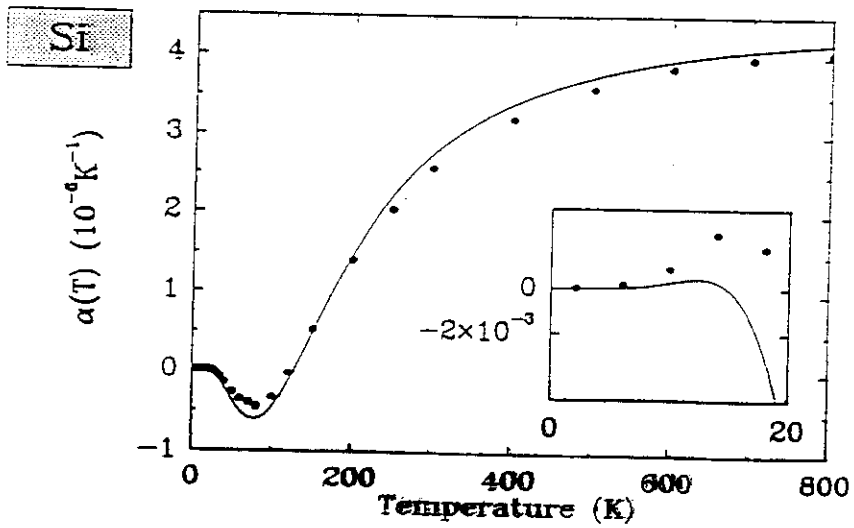
RO. Jones and O. Gunnarsson Rev. Mod. Phys 61, 689 (1989)

Lattice Dynamical Properties



P. Giannozzi, S. de Gironcoli, P. Pavone and S. Baroni PRB 43 7231 (91

Thermal Expansion



P. Pavone SISSA-PhD Thesis 1991