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SPRING COLLEGES IN COMPUTATIONAL PHYSICS

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ORDER N METHODS FOR ELECTRONIC STRUCTURE

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ORDER-N METHODS

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- OUTLINE -

1. INTRODUCTION : O(N) METHODS
2. LOCALISATION : GENERAL IDEAS
   - "NEARSIGHTEDNESS"
   - WANNIER FUNCTIONS
   - DENSITY MATRIX
3. FUNCTIONAL METHODS
   - DENSITY MATRIX FUNCIONALS
   - ORBITAL FUNCTIONALS
4. PROJECTION METHODS (FERMI FUNCT. AT FINITE T)
5. SPECTRAL METHODS
   - D.O.S. : MOMENTS METHODS
   - SELECTED EIGENVECTORS : "FOLDED SPECTRUM" METHOD
6. APPLICATION TO AB-INITIO CALCULATIONS
   - LCAO APPROACH
   - REAL SPACE GRIDS
   - "DIVIDE AND CONQUER" APPROACH

O(N) METHODS

- "CAR-PARRINELLO" METHODS (conjugate gradients)

  ☺ GLOBAL OPTIMIZATION
  MOLECULAR DYNAMICS

  ☹ N^2-N^3 SCALING
  "LOCAL" OPTIMIZATIONS

- GREEN'S FUNCTIONS METHODS – RECURSION

  ☺ LOCAL PROPERTIES
  TERMINATION ⟶ O(N) SCALING

  ☹ FORCES
  TOTAL ENERGY

"MODERN" ORDER-N METHODS ⟵
- MINIMIZATION (FUNCTIONALS)
- PROJECTION
- MOMENTS (D.O.S.)
- ...

COMBINE THE VIRTUES OF THE FORMER SCHEMES

OPTIMAL FOR ⟵
- PROPS. OF THE ENTIRE SYSTEM
  (ENERGY, MD THERMAL SIMULATION, GLOBAL RELAXATION)
- "LOCAL" PROPERTIES
  (LOCAL RELAXATIONS; PHONON CALCULATI

INGREDIENTS:
- NEW, UNCONSTRAINED FUNCTIONALS

⇒
- LOCALISATION
- INFORMATION RECONSTRUCTION

LOCALISATION :

W. KOHN : "Near-sightedness" [PRL, 76, 3168 (96)]

THE PROPERTIES OF A PART OF A SYSTEM ARE NOT AFFECTED BY CHANGES OF THE POTENTIAL AT DISTANT REGIONS.

CONSEQUENCES:

- $\rho(\vec{r}, \vec{r}') \xrightarrow[|\vec{r}-\vec{r}'|\to\infty]{} 0$

- Existence of Wannier functions :
  Localized (exponentially) functions which describe the ground state. (Kohn, Phys. Rev. 115, 809 (59))

$$\chi(\vec{r}) \xrightarrow[\vec{r}\to\infty]{} 0 \qquad \chi(\vec{r}-\vec{R}) = \frac{1}{V_0}\int d\vec{k}\, e^{-i\vec{k}\vec{R}}\, \psi_{\vec{k}}(\vec{r})$$

(occupied bands)

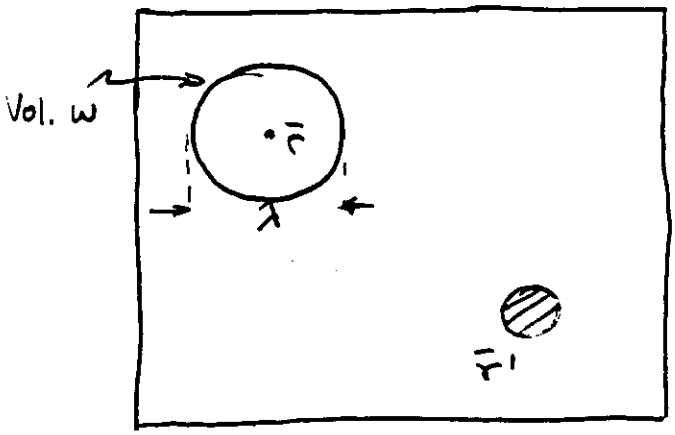
THE DECAY IS EXPONENTIAL IN INSULATORS; POWER-LAW IN METALS

(EXIST ALSO IN NON-PERIODIC SYSTEMS)

LOCALISATION APPROXIMATION :

$$\rho(\vec{r},\vec{r}') = 0 \quad |\vec{r}-\vec{r}'| > R_c \qquad \chi(\vec{r}) = 0 \quad |\vec{r}| > R_c .$$

* NEARSIGHTEDNESS * (W. Kohn, PRL 76, 3168 (96))



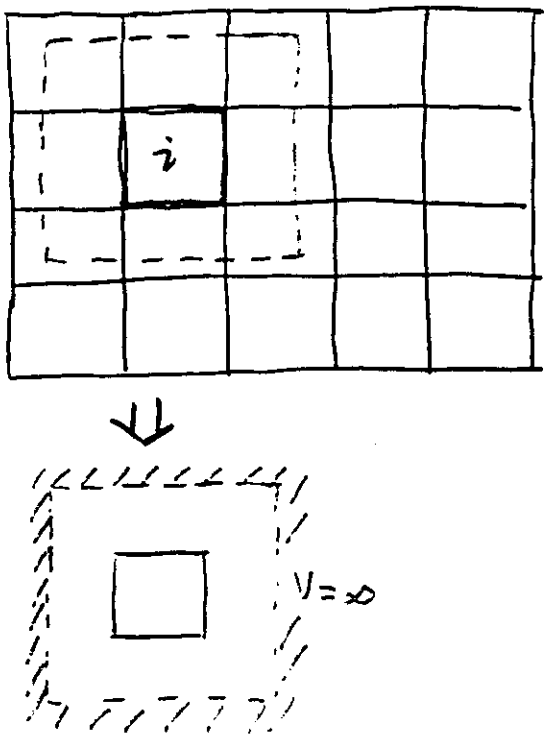
FIXED μ.

$F(\bar{r}_1, \ldots, \bar{r}_N)$ $\bar{r}_1, \ldots, \bar{r}_N \in \omega (\propto \lambda^3)$

Pot. change $\Delta v(\bar{r}')$ (arbitrarily large)

$F(\bar{r}_1, \ldots, \bar{r}_N)$ is unchanged if $|\bar{r} - \bar{r}'| \gg \lambda$

NEAR-SIGHTEDNESS $\Rightarrow$ $\exists$ $O(N)$ ALGORITHMS !!



(1) DIVIDE SYSTEM IN CUBES OF VOL. ω

(2) EXTRACT $\omega' = m\lambda^3$ (say $m = 3$) FOR EACH ω_i

(3) SOLVE ω' WITH HARD WALL BOUNDARIES $O(1)$

(4) REPEAT FOR EACH $\omega_i \rightarrow O(N)$

"Divide and conquer Approach"

W. Yang, PRL 66, 1438 (91)

LOCALIZED WAVE FUNCTIONS

$$\hat{H}\,\Psi_i = \varepsilon_i\,\Psi_i \qquad E_{BS} = \sum_i^{occ} H_{ii} = \sum_i^{occ} \langle \Psi_i \mid \hat{H} \mid \Psi_i \rangle$$

Ground State: SUBSPACE of the Hilbert Space
Occupied Eigenstates: BASIS of this Subspace

Unitary Transform.

$\{|\Psi_i\rangle\} \longleftrightarrow \{|\chi_i\rangle\}$

Eigenstates — **Localized Wave Functions**

GENERATE THE SAME SUBSPACE

$$E\left[\{\Psi_i\}\right] = E\left[\{\chi_i\}\right]$$

$|\chi_i\rangle$ are orthonormal and localized in space
(like the Wannier functions in crystals)

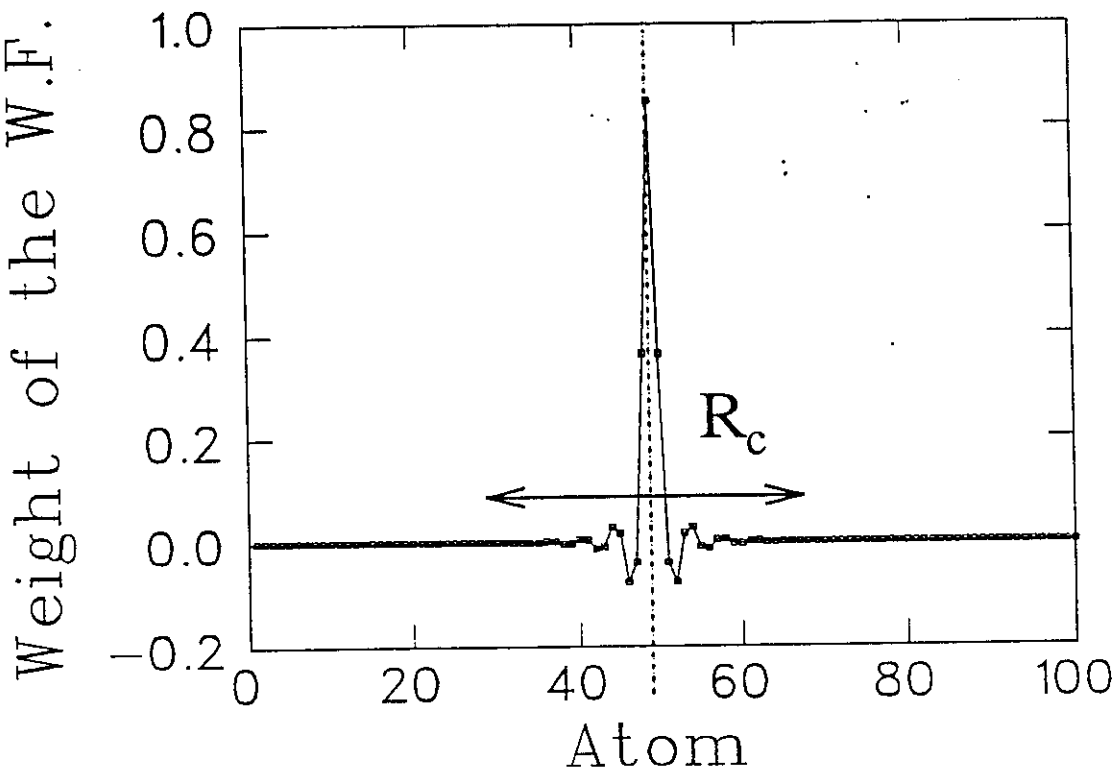
$\chi_i(r) \longrightarrow 0$ as $r \longrightarrow \infty$

- Exponentially (insulators)
- Power law (metals)

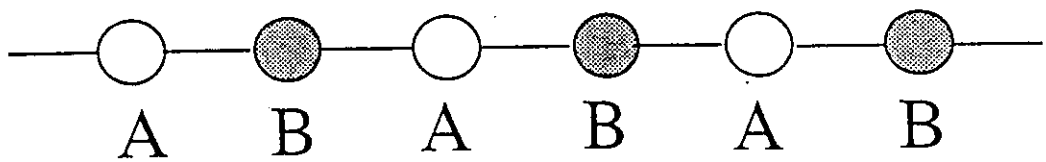
W. Kohn, Phys. Rev. 115, 809 (1959)

Note: Occupied States (Ψ_i or χ_i) expanded in a basis set:

$$\Psi_i = \sum_{\mu=1}^{M} c_{i\mu}\,\phi_\mu$$



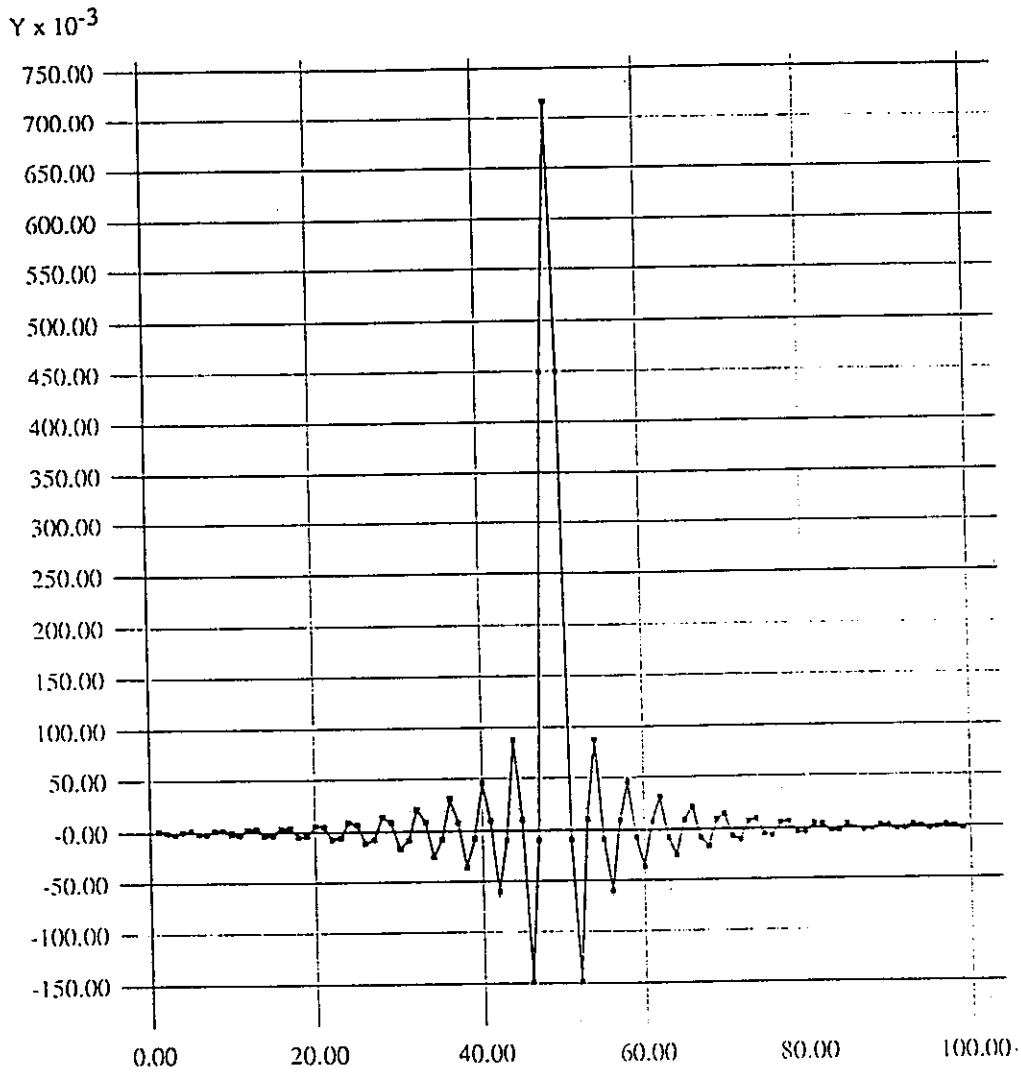
1-D Tight-Binding Hamiltonian (s orbitals)



ε_A= -5 eV V = -1 eV

ε_B= -4 eV S = 0

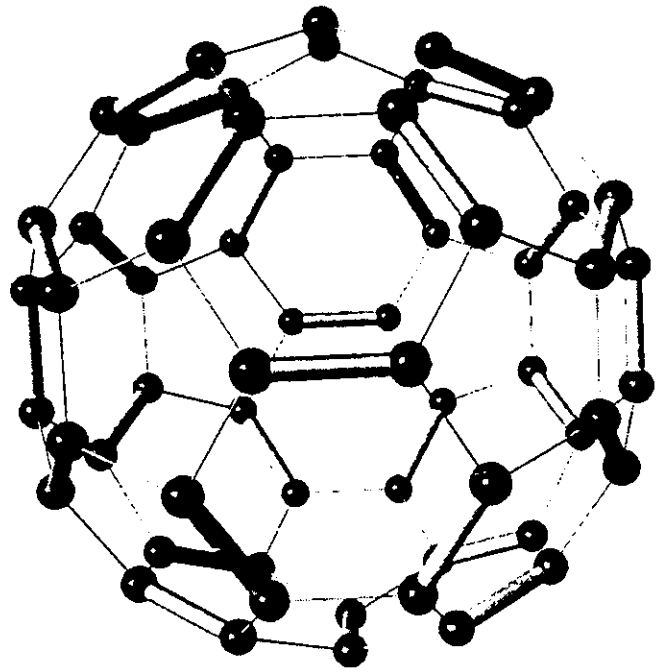
Linear Chain, 100 atoms.



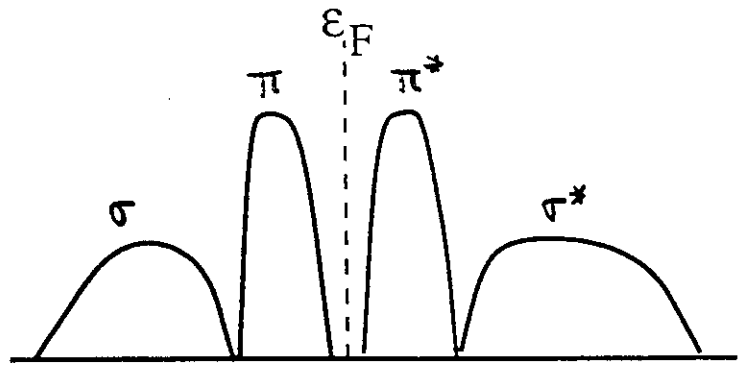
$\epsilon_A = \epsilon_B \Rightarrow$ METAL

$\chi(r) \sim \frac{1}{r} \quad r \to \infty$

C_{60}



R_c (Å)	# atoms	Single bond (Å)	Double bond (Å)	Energy (eV/atom)
inf	60	1.458	1.396	-8.008
4.8	32	1.458	1.396	-8.003
4.0	22	1.461	1.393	-7.981
3.0	14	1.466	1.387	-7.942



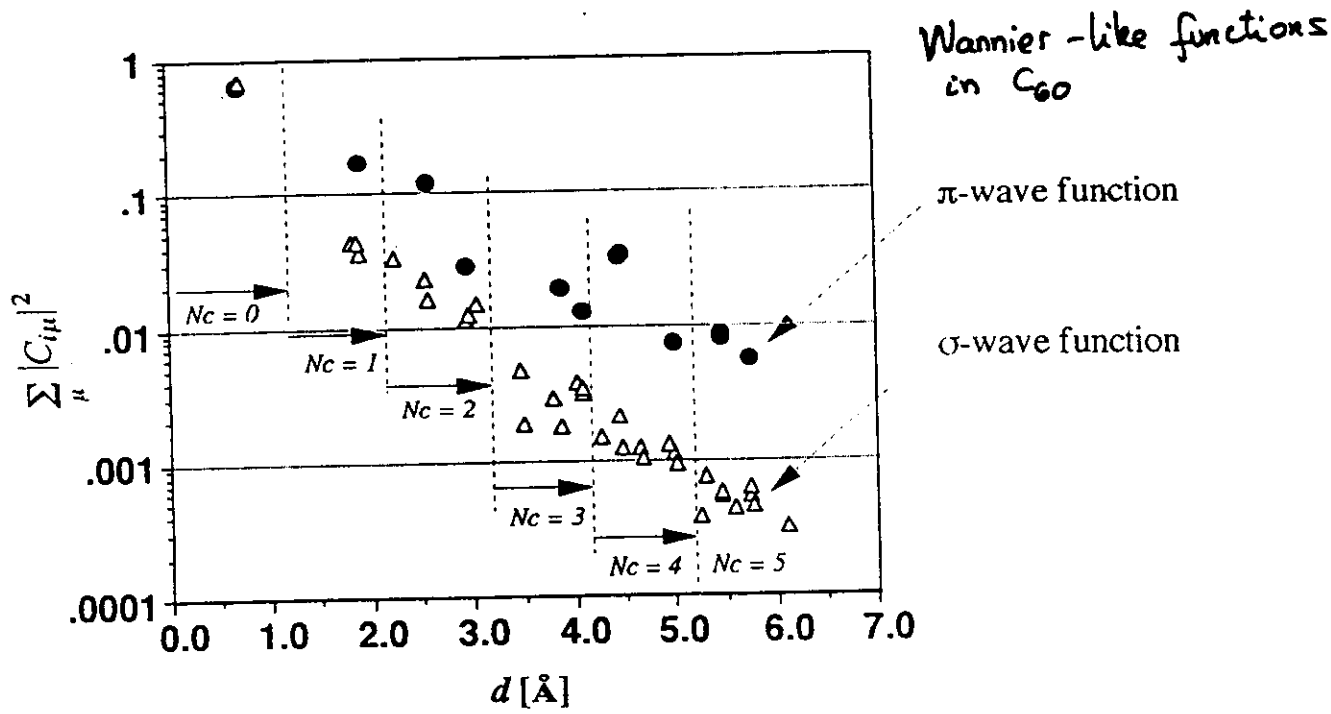

Wannier-like functions in C60
π-wave function
σ-wave function
1
.1
.01
.001
.0001
Nc = 0
Nc = 1
Nc = 2
Nc = 3
Nc = 4
Nc = 5
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
d [Å]

Fig. 2

LOCALISATION OF THE DENSITY MATRIX

(T=0)

$$\hat{\rho} = 2 \sum_{i=1}^{occ} |\psi_i\rangle\langle\psi_i|$$

We can also write $\hat{\rho}$ in terms of Wannier functions $|\chi_i\rangle$ (these are also a basis of the occupied space).

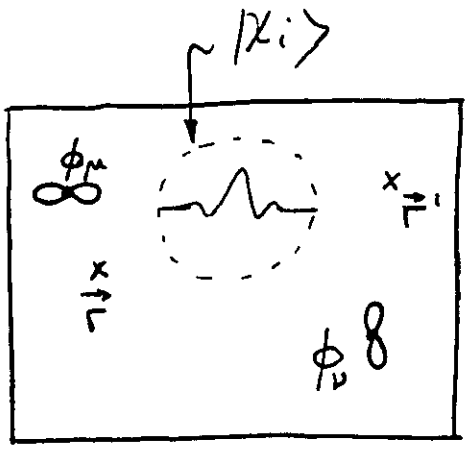
$$\hat{\rho} = 2 \sum_{i=1}^{occ} |\chi_i\rangle\langle\chi_i|.$$

- D.M. IN REAL SPACE
- D.M. IN ATOMIC ORBITALS REPRES.

$$\left(|\chi_i\rangle = \sum_{\mu=1}^{M} c_{i\mu} |\phi_\mu\rangle \right)$$

$$\rho(\vec{r},\vec{r}') = 2 \sum_{i=1}^{M/2} \chi_i(\vec{r})\,\chi_i^*(\vec{r}')$$

$$\rho_{\mu\nu} = 2 \sum_{i=1}^{M/2} c_{i\mu}^* c_{i\nu}$$



$\Rightarrow$

$$\rho(\vec{r},\vec{r}') \xrightarrow[|\vec{r}-\vec{r}'|\to\infty]{} 0$$

$$\rho_{\mu\nu} \xrightarrow[|R_\mu - R_\nu|\to\infty]{} 0$$

(Exponentially in insulators; Power-law in metals)

BASIS SETS FOR O(N)

- Best choice: LOCALIZED basis sets

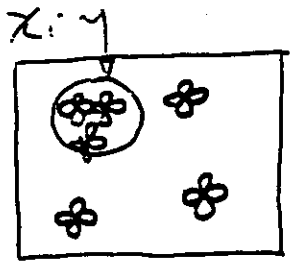
  * Atomic orbitals (Tight-Binding, LCAO)

$\phi_\mu(\vec{r} - \vec{R}_\mu)$ localized in space.

$$\chi_i(\vec{r}) = \sum_{\mu=1}^{M} c_{i\mu}\, \phi_\mu(\vec{r} - \vec{R}_\mu)$$

$$\rho_{\mu\nu} = \sum_{i=1}^{N/2} c_{i\mu}\, c_{i\nu}$$

EASY TO LOCALIZE !! Expand ONLY in terms of orbitals within R_c. Other $c_{i\mu} = 0$



  * REAL SPACE GRIDS $\chi_i(\vec{r}) = 0$ outside R_c

$\rho(\vec{r}, \vec{r}') = 0$ for $|\vec{r} - \vec{r}'| > R_c$

(Baroni, Giannozzi, Europhys. Lett. 17, 547 (92))

- "Difficult" choice: PLANE WAVES.

(But possible: G. Galli & M. Parrinello, PRL 69, 3547 (1992))

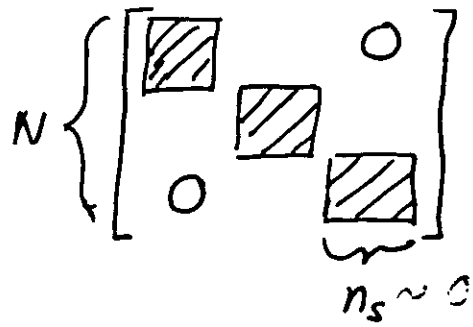
SPARSE MATRICES (few non-zero elements)

Like $H_{\mu\nu} = \langle \phi_\mu | \hat{H} | \phi_\nu \rangle$

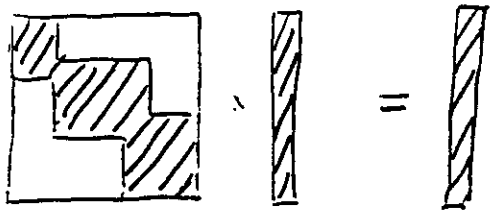
$S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$

$C_{i\mu}$

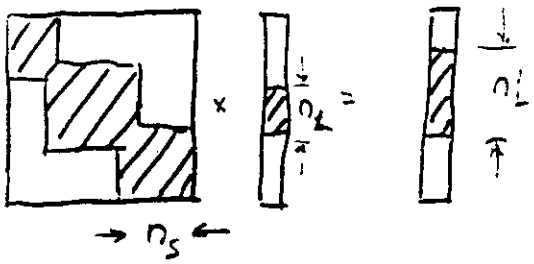
⋮



- MATRIX - VECTOR MULTIPLICATIONS :

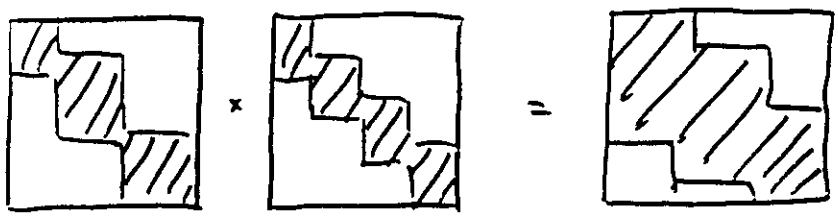


$O(N \times n_s) \sim O(N)$



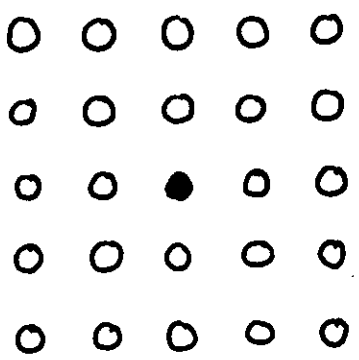
$O(n_s n_L) \sim O(1)$

- MATRIX - MATRIX MULTIPLICATIONS :

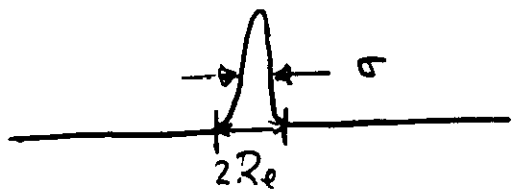


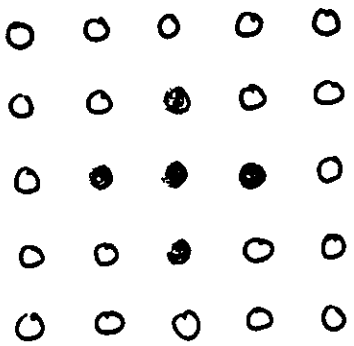
$O(N n_s n_{s'}) \sim N$

- RESULTING VECTOR OR MATRIX : LESS SPARSE

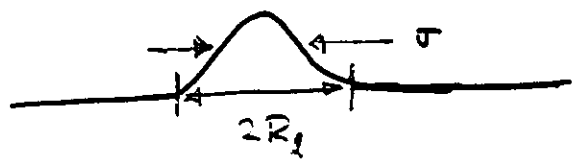


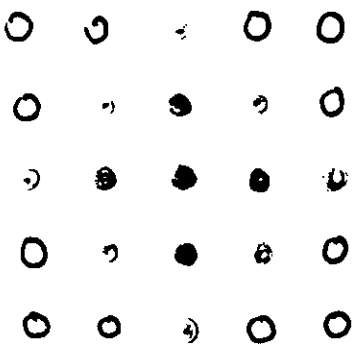
$|\phi_\mu\rangle$



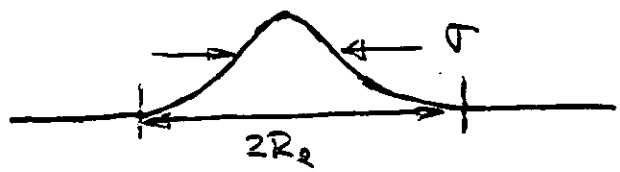


$H|\phi_\mu\rangle$





$H^2|\phi_\mu\rangle$



R_e increases with n

$H^n|\phi_\mu\rangle$: ~~~~ σ does not with large enough n

ENERGY FUNCTIONALS :

TOTAL ENERGY : DFT: $E = E_{BS} + E_{DC}[n(\vec{r})]$

$$E_{DC} = \int d\vec{r}\, n(\vec{r}) \left[V_{xc}(n(\vec{r})) - \epsilon_{xc}(n(\vec{r})) + \frac{1}{2} V_H(\vec{r}) \right]$$

E- TB $E = E_{BS} + \sum_{ij} V_R(\vec{R}_i - \vec{R}_j)$

BAND STRUCTURE ENERGY : (N electrons) $E_{BS}^0 = 2 \sum_{i=1}^{N/2} \epsilon_i$

$$E_{BS} = 2 \sum_{i=1}^{N/2} \langle \psi_i | \hat{H} | \psi_i \rangle$$ ORBITAL REPRESENTATION

$$= 2\,\mathrm{Tr}\,(\hat{\rho}\cdot\hat{H})$$ DENSITY MATRIX REPRESENTATION

$$\rho(\vec{r}, \vec{r}')$$

1ST ALTERNATIVE :

- DIAGONALIZE $\hat{H}$: ϵ_i, ψ_i ; $i = 1, \ldots, M$
- SELECT THE $\frac{N}{2}$ LOWEST
- CALCULATE $E_{BS} = 2 \sum_{i=1}^{N/2} \epsilon_i$
- ITERATE (SCF) : $\hat{H}(n)$

$O(N^3)$

(M^3)

2nd ALTERNATIVE : (CP ; CG)

- MINIMIZE E_{BS} W.R.T. :
  - $|\psi_i\rangle$
  - $\rho(\vec{r}, \vec{r}')$
- IMPOSE CONSTRAINTS
  - $\langle \psi_i | \psi_j \rangle = S_{ij} = \delta_{ij}$
  - $\hat{n}\,\hat{\rho} = \hat{\rho}$; $\int \rho(\vec{r}, \vec{r})\, d\vec{r} = N$

$O(N^3)$

$(N^2 M)$

3rd ALTERNATIVE : NEW UNCONSTRAINED FUNCTIONALS

BUILD FUNCTIONALS FOR WHICH THE CONSTRAINTS ARE NOT IMPOSED, BUT ARE REACHED DURING THE MINIMIZATION

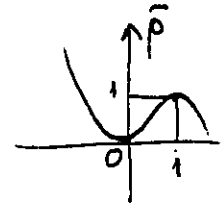
FUNCTIONALS WHICH :

- HAVE CORRECT MINIMUM (GROUND STATE ENERGY)
- CONSTRAINTS ARE SATISFIED AT THE MINIMUM.

- DENSITY MATRIX : PURIFICATION TRANSFORMATION (Li, Nunes, Vanderbilt ; Daw).

- Trial density matrix $\rho(r, r')$ NOT IDEMPOTENT
- construct $\tilde{\rho}$ from ρ, such that eigenvalues $\in [0, 1]$ → more idempotent.

  "McWeeny transformation" : $\tilde{\rho} = 3\rho^2 - 2\rho^3$.



- Minimise $E_{BS}[\tilde{\rho}]$.

- ORBITAL APPROACH : UNCONSTRAINED FUNCTIONAL (Mauri et al. ; Ordejón et al.).

$$E_{BS} = 2 \sum_{ij}^{N/2} Q_{ij} \langle \chi_i | \hat{H} | \chi_j \rangle$$

$$Q_{ij} = \sum_{n=0}^{n_r} (\mathbb{1} - S)^n \qquad S_{ij} = \langle \chi_i | \chi_j \rangle$$

— LAGRANGE MULTIPLIERS (Ordejón et al)

(GENERALIZED) RAYLEIGH-RITZ VARIATIONAL PRINCIPLE

(basis of iterative minimization procedures).

Let $E^{\circ}_{BS} = 2 \sum_{i=1}^{N/2} \epsilon_i$ be the GROUND-STATE B.S. energy

Let $|\varphi_i\rangle$, $i = 1, \ldots, N/2$ be an { ARBITRARY / ORTHONORMAL } set.

Def: $E_{BS}[\{|\varphi_i\rangle\}] = 2 \sum_{i=1}^{N/2} \langle \varphi_i | \hat{H} | \varphi_i \rangle$

THEN: (1) $E_{BS}[\{|\varphi_i\rangle\}] \geq E^{\circ}_{BS}$

(2) IFF $\{|\varphi_i\rangle\}$ ARE A UNITARY TRANSF OF THE $\frac{N}{2}$ LOWEST EIGENVECTORS

THEN

$$E_{BS}[\{|\varphi_i\rangle\}] = E^{\circ}_{BS}$$

(Trace of $\hat{H}$ in the occupied space)

DENSITY MATRIX APPROACHES

Hamiltonian $\hat{H}$

Eigenstates $|\psi_i\rangle$

DENSITY OPERATOR (Projection onto occupied subspace)

($T=0$)

$$\hat{\rho} = \sum_{i=1}^{occ} |\psi_i\rangle\langle\psi_i|$$

- REPRESENTATIONS:
  - Real space:

$$\rightarrow \rho(\vec{r},\vec{r}') = \langle \vec{r}|\hat{\rho}|\vec{r}'\rangle = \sum_{i=1}^{occ} \psi_i(\vec{r})\,\psi_i^*(\vec{r}')$$

$$n(\vec{r}) = \rho(\vec{r},\vec{r}') \leftarrow \text{Particle density}$$

  - Orbitals basis $\{|\phi_\mu\rangle,\ \mu = 1,\dots,M\}$

$$|\psi_i\rangle = \sum_{i=1}^{M} c_{i\mu}\,|\phi_\mu\rangle$$

ORTHOGONAL BASIS $\rightarrow$ $\rho_{\mu\nu} = \langle\phi_\mu|\hat{\rho}|\phi_\nu\rangle = \sum_{i=1}^{occ} c_{i\mu}^* c_{i\nu}$

- ENERGY: $E_{BS} = 2\sum_{i=1}^{occ} \epsilon_i = 2\,Tr\left[\hat{\rho}\cdot\hat{H}\right] = 2\sum_{\mu,\nu=1}^{M} \rho_{\mu\nu} H_{\nu\mu}$

- NUMBER OF ELECTRONS: $N_e = 2\,Tr[\hat{\rho}] = 2\sum_{\mu=1}^{M} \rho_{\mu\mu} = 2\int \rho(\vec{r},\vec{r})\,d\vec{r}$

- IDEMPOTENCY: $\hat{\rho}$ is a projector $\Rightarrow$ $\hat{\rho}^2 = \hat{\rho}$

DENSITY MATRIX ENERGY FUNCTIONALS

Li, Nunes, Vanderbilt, PRB 47, 10891 (93)

M. Daw, PRB 47, 10895 (93)

W. Kohn, PRL 76, 3168 (96)

$$E_{BS}[\rho] = 2\, Tr\left[\hat{\rho}\cdot\hat{H}\right] = 2\sum_{\mu,\nu=1}^{M} \rho_{\mu\nu}\, H_{\nu\mu}$$

- CONSIDER $\rho_{\mu\nu}$ AS VARIATIONAL PARAMETERS
- MINIMIZE E_{BS} W.R.T. $\rho_{\mu\nu}$
- BUT CONSTRAINTS : (1) $N = 2\, Tr[\hat{\rho}] = 2\sum_{\mu=1}^{M} \rho_{\mu\mu}$

  (2) $\hat{\rho}^2 = \hat{\rho} \Rightarrow \sum_{\alpha=1}^{M} \rho_{\mu\alpha}\rho_{\alpha\nu} = \rho_{\mu\nu}$

(1) IS EASY : GRAND POTENTIAL :

$$\ldots \quad \mu \quad \ldots$$

μ = chemical potential (Fermi energy)

(2) IS MORE DIFFICULT (BUT ESSENTIAL !!)

IDEMPOTENCY MEANS EIGENVALUES

$$\hat{\rho}^2 = \hat{\rho} \quad \Leftrightarrow \quad \lambda_i = \begin{cases} 1 & \text{occ. states} \\ 0 & \text{empty states} \end{cases}$$

$$\Omega = 2\,\mathrm{Tr}\left[\hat{\rho}\,(\hat{H} - \mu\hat{I})\right] = 2\sum_{\mu,\nu=1}^{M} \rho_{\mu\nu}\,(H_{\mu\nu} - \mu\,\delta_{\mu\nu})$$

ILUSTRATION OF NEED OF IDEMPOT. CONSTRAINTS :

Let's evaluate Ω in the basis that diagonalizes $\hat{H}$: $|\psi_i\rangle$

$$\Omega = 2\sum_{i=1}^{M} \lambda_i\,(\epsilon_i - \mu) \qquad (\lambda_i \equiv \rho_{ii})$$

NOTE THAT :

(1) $\epsilon_i < \mu \Rightarrow \Omega \longrightarrow -\infty$ ($\lambda_i \to \infty$)

(2) $\epsilon_i > \mu \Rightarrow \Omega \longrightarrow -\infty$ ($\lambda_i \to -\infty$)

$\Rightarrow$ NO MINIMUM !!

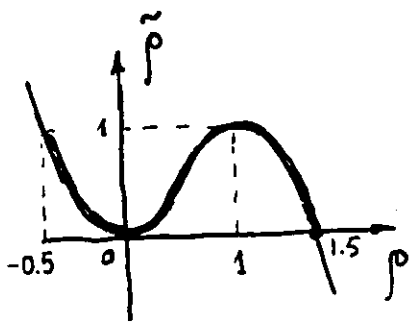
$\Rightarrow$ IDEMPOTENCY CONSTRAINTS ($\lambda_i = 0, 1$) ESSENTIAL.

BUT : WOULD BE SUFFICIENT TO IMPOSE $\lambda_i \in [0, 1]$

(minimization would drive $\lambda_i \to 1$ $(\epsilon_i < \mu)$)

$\lambda_i \to 0$ $(\epsilon_i > \mu)$

PURIFICATION TRANSFORMATION (McWeeny, Rev. Mod. Phys. 32, 335



$$\tilde{\rho} = 3\rho^2 - 2\rho^3$$

ρ TRIAL, nearly idem

$\lambda_i = \begin{cases} 1+\delta \\ \delta \end{cases}$

$\downarrow !$

$\tilde{\rho}$ MORE idempot.

$\tilde{\lambda}_i = \begin{cases} 1 - O(\delta^2) \\ O(\delta^2) \end{cases}$

$\lambda_i \in [-0.5, 1.5] \Rightarrow \tilde{\lambda}_i \in [0, 1]$

Li - Nunes - Vanderbilt Functional

PRB 47, 10891 (93)

USE ρ AS TRIAL DENSITY, $\tilde{\rho}$ AS PHYSICAL DENSITY

$$\Omega = 2\,Tr\left[\tilde{\rho}\,(\hat{H}-\mu\hat{I})\right] =$$

$$= 2\,Tr\left[(3\rho^2-2\rho^3)(\hat{H}-\mu\hat{I})\right]$$

- CHOOSE FERMI LEVEL μ
- MINIMIZE Ω W.R.T. $\rho_{\mu\nu}$
- CHECK NUMBER OF ELECTRONS

$$N_e = 2\sum_{\mu=1}^{M}\rho_{\mu\mu}$$

AND CHANGE μ IF NECESSARY. $\left\{\begin{array}{l}\text{FIXED } \mu\\ \text{FIXED } N\end{array}\right\}$

MINIMIZATION: $\dfrac{\partial\Omega}{\partial\rho_{\mu\nu}}$ easy to obtain

$\Rightarrow$ Conj. Gradients.

Steepest descents (M. Daw, PRB 47; 10895, '93)

FORMULATION WITH NON-ORTHOGONAL BASIS SETS

(Nunes, Vanderbilt ; PRB 50, 17611 (94))
(Ordejón, Drabold, Martin, Grumbach ; PRB 51, 1456 (95))

Non-orthogonal basis $\{|\phi_\mu\rangle\}$

$$S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle = \int \phi_\mu(\vec{r})\, \phi_\nu(\vec{r})\, d\vec{r}$$

PURIFIED D.M. $\hat{\rho} = 3\rho S \rho - 2\rho S \rho S \rho$

$$\Omega = 2\,Tr\left[\tilde{\rho}\,(\hat{H} - \mu \hat{I})\right] = 2 \sum_{\mu,\nu=1}^{M} \tilde{\rho}_{\mu\nu}\,(H_{\mu\nu} - \mu S_{\mu\nu})$$

$$N_e = 2\,Tr\left[\tilde{\rho}\, S\right] = 2 \sum_{\mu,\nu=1}^{M} \tilde{\rho}_{\mu\nu}\, S_{\nu\mu}$$

NOTE!!

- $\tilde{\rho}$ is much less sparse than in orthogonal
- Same localization properties $\tilde{\rho}_{\mu\nu} \longrightarrow 0$ $|R_\mu - R_\nu| \longrightarrow \infty$

$\Rightarrow$ OVERHEAD for non-orthogonal bases!!

APPROXIMATION : D.M. Truncation

$$\rho(\vec{r},\vec{r}') = 0 \qquad |\vec{r}-\vec{r}'| > R_c$$

$$\rho_{\mu\nu} = 0 \qquad |R_\mu - R_\nu| > R_c .$$

In this case : $$\Omega = 2 \sum_{\mu,\nu=1}^{M} (3\rho^2 - 2\rho^3)(H-\mu I)$$

reduces to products of sparse matrices $\Rightarrow$ $\mathcal{O}(N)$

- **PROPERTIES** :

1) Solution is a local minimum (not global)

runaway solutions $\rho \longrightarrow \infty$ states bellow μ

$\rho \longrightarrow -\infty$ " above μ

2) Energy is VARIATIONAL (as long as $\tilde{\lambda} \in [0,1]$)

$$\Omega \geq \Omega_{exact} = 2 \sum_{i=1}^{occ} \epsilon_i - \mu N$$

3) $\Omega \longrightarrow \Omega_{exact}$ as $R_c \longrightarrow \infty$

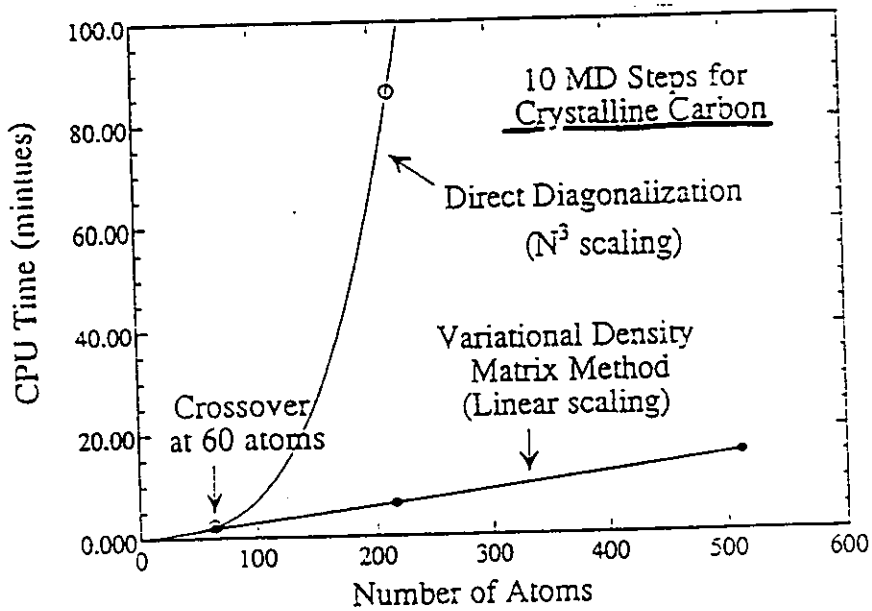
$(\Omega - \Omega_{exact} \propto O(\delta\rho^2)$

4) Variational $\Rightarrow$ accurate FORCES ! $\Rightarrow$ M.D.

$$\frac{d\Omega}{\cdot\cdot} = 2\,Tr\left[\tilde{\rho}\,\frac{dH}{\cdot\cdot}\right] \qquad (22)$$

Li-Nunes-Vanderbilt D.M. formulation

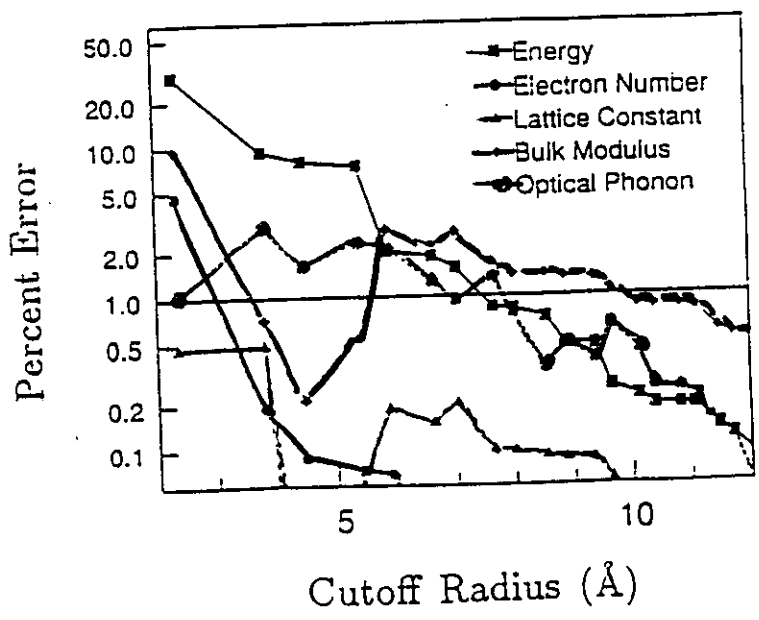
O(N) scaling



Qiu et al.
J. Phys. Cond. Matt.
6, 4153 (94)

(TB model)

Accuracy



Li, Nunes, Vanderbilt
PRB 47, 10893 (93

Cristalline Silicon
(diamond structure)

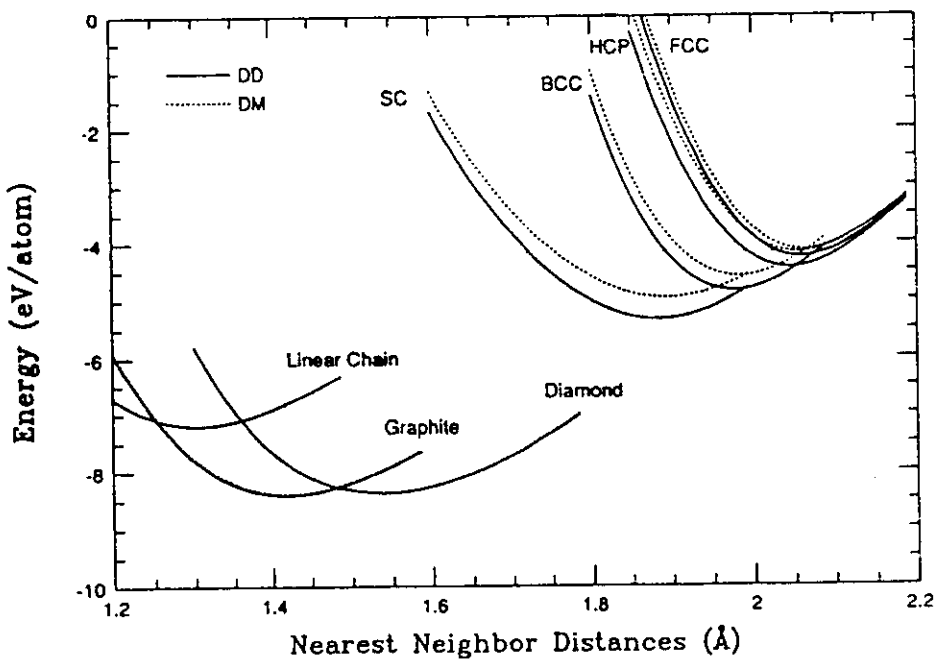
(TB Model

DENSITY MATRIX METHOD (Li, Nunes, Vanderbilt / Dow)

Results from Sui, Wang, Ho, Chen (J. Phys. C, 6, 9153 (94

Carbon Phases

(Empirical, orthogonal TB)



OTHER D.M. FUNCTIONAL METHODS :

(1) W. Kohn : PRL 76, 3168 (96)

PENALTY FUNCTION FOR IDEMPOTENCY CONSTRAINTS.

$$Q_{\mu\alpha}[\rho(\vec{r},\vec{r}')] = \underbrace{E[\tilde{\rho}] - \mu N[\tilde{\rho}]}_{\Omega \text{ (as in LNV)}} + \alpha P[\rho]$$

$(\tilde{\rho} \equiv \rho^2)$

$$P[\rho] = \left[\int \left[\rho^2 (1-\rho)^2\right]_{r'=r} dr\right]^{1/2}$$ Penalty Func

$P = 0$ iff $\hat{\rho}^2 = \hat{\rho}$

otherwise $P > 0$.

← unconstrained!

- $\boxed{\min_{\{\rho\}} Q[\rho] = \Xi_0 - \mu N = \Omega_0}$ (Ground state).
- At the minimum, $\rho^2 = \rho$.

(2) HERNANDEZ, GILLAN & GORINGE PRB 51, 10157 (95) PRB 53, 7147 (96)

GENERALIZATION OF LNV FUNCTIONAL (DFT calculati

ORBITAL-BASED ENERGY FUNCTIONALS :

$$E_{BS}[\{\chi_i\}] = 2 \sum_{i=1}^{occ = N/2} \langle \chi_i | \hat{H} | \chi_i \rangle = 2 \sum_{i=1}^{N/2} H_{ii}$$

- CONSIDER $|\chi_i\rangle$ AS VARIATIONAL PARAMETERS
- MINIMIZE E_{BS} W.R.T. $|\chi_i\rangle$: $E^0_{BS} = \min_{\{|\chi_i\rangle\}} E_{BS}[\chi_i]$
- BUT CONSTRAINTS : ORTHONORMALIZATION :

$$S_{ij} \equiv \langle \chi_i | \chi_j \rangle = \delta_{ij}$$

(NOTE : NUMBER OF ELECTRONS INSURER BY SUM OVER $\frac{N}{2}$ STATES)

ORTHONORMALIZATION $\longrightarrow$ $O(N^3)$.

ALTERNATIVE : UNCONSTRAINED FUNCTIONALS

EASIEST ONE : $$E_{BS}[\chi_i] = \sum_{i,j=1}^{occ} S_{ij}^{-1} H_{ji}$$

Used in PW calculations : Stich et al; PRB 39, 4997 (8
Arias et al.; PRL 69, 1077 (9
Galli-Parrinello; PRL 69, 3547

BUT STILL $O(N^3)$ (calculation of S^{-1})

(GENERALIZED) RAYLEIGH - RITZ VARIATIONAL PRINCIPLE

FOR NON-ORTHONORMAL STATES :

Let $E^0_{BS} = 2\sum_{i=1}^{N/2} \epsilon_i$ be the GROUND-STATE B.S. ENERGY

Let $|\varphi_i\rangle$, $i = 1, \ldots, N/2$ be an ARBITRARY SET.

(non-orthogonal, maybe!)

Def. $E_{BS}\left[\{|\varphi_i\rangle\}\right] = 2\sum_{i,j=1}^{N/2} S^{-1}_{ij} H_{ji}$

$S_{ij} = \langle \varphi_i | \varphi_j \rangle$

$H_{ij} = \langle \varphi_i | \hat{H} | \varphi_j \rangle$

TRACE EVALUATED FOR NON-ORTHOGONAL SET!!

THEN : (1) $E_{BS}\left[\{|\varphi_i\rangle\}\right] \geq E^0_{BS}$

(2) IFF $\{|\varphi_i\rangle\}$ ARE A LINEAR COMBINATION

[(non-linearly-dependent with each other!!)] OF THE LOWEST $N/2$ EIGENSTATES

THEN

$$E_{BS}\left[\{|\varphi_i\rangle\}\right] = E^0_{BS}$$

(Trace of $\hat{H}$ in occupied space)

NEW ENERGY FUNCTIONALS :

ONE DERIVATION : LAGRANGE MULTIPLIERS.

P. Ordejón et al. PRB 48, 14646 (93)
PRB 51, 1456 (95)

WE WANT

- MINIMIZE $E_{BS} = 2\sum_{i=1}^{occ} H_{ii}$
- OBTAIN ORTHOGONAL STATES

$$S_{ij} \equiv \langle \chi_i | \chi_j \rangle = \delta_{ij}$$

- Avoid orthogonalization

SOLUTION $\longrightarrow$ LAGRANGE MULTIPLIERS :

$$\tilde{E}_{BS} = 2\sum_{i=1}^{N/2} H_{ii} - 2\sum_{i,j=1}^{N/2} \Lambda_{ij} (S_{ij} - \delta_{ij})$$

$$\left.\begin{aligned} \frac{\partial \tilde{E}_{BS}}{\partial \chi_i} &= 0 \\ \frac{\partial E_{BS}}{\partial \Lambda_{ij}} &= 0 \end{aligned}\right\} \Rightarrow \quad \Lambda_{ij} = H_{ij}$$

(At the solution)

$$\tilde{E}_{BS} = 2\sum_{i=1}^{N/2} H_{ii} - 2\sum_{i,j=1}^{N/2} (S_{ij} - \delta_{ij}) H_{ij}$$

$$\tilde{\tilde{E}} = 2 \sum_{i,j=1}^{N/2} (2\delta_{ij} - S_{ij}) H_{ji}$$

$$= 2 \, Tr^{occ} \left[(2 \cdot \mathbb{1} - S) H \right]$$

FURTHER (BETTER) APPROXIMATIONS TO Λ_{ij}

n^{th} approx: $\Lambda^{(n)} = \sum_{m=0}^{n} (\mathbb{1} - S)^m H$

$\Rightarrow$ Family of Functionals:

$$\tilde{\tilde{E}}^{(n)} = 2 \, Tr^{occ} \left[\sum_{m=0}^{n} (\mathbb{1} - S)^m H \right]$$

ANOTHER DERIVATION OF THE SAME FUNCTIONALS FAMILY

F. Mauri, G. Galli & R. Car, PRB 47, 9973 (93)

TAYLOR SERIES EXPANSION OF S^{-1}: $E_{BS} = 2 \, Tr^{occ} [S^{-1} H]$

$$S^{-1} = \left[\mathbb{1} - (\mathbb{1} - S) \right]^{-1} \approx \sum_{i=0}^{n} (\mathbb{1} - S)^i$$

$\Downarrow$

$\sim$ [illegible]

PROPERTIES OF THE FUNCTIONALS $\tilde{E}^{(N)}$

Mauri, Galli; PRB 50, 4316 (94)
Ordejón, Drabold, Martin, Grumbach; PRB 51, 1456 (95)

FOR ODD N

(1) $\tilde{E}[\chi_i] \geq E[\chi_i] = 2 \sum_j S^{-1}_{ij} H_{ji}$

(2) $\tilde{E}[\chi_i] = E[\chi_i] \iff \{\chi_i\}$ is ORTHONORMAL set

UNCONSTRAINED MINIMIZATION OF $\tilde{E}$ YIELDS:

- EXACT E^0_{BS}
- ORTHONORMAL STATES χ_i

(NOTE): (1) IS ONLY TRUE IF $\hat{H}$ IS NEGATIVE DEFINITE
(i.e., all its eigenvalues are $\epsilon_i < 0$)

GLOBAL MINIMUM if $\hat{H}$ is neg. def.

BUT Local minimum if occupied $\epsilon_i < 0$

... ON ALL ENERGY SHIFT: $E \to E - n$

LOCALISATION APPROXIMATION

WAVE FUNCTIONS TRUNCATION : $\chi(\vec{r}) = 0$ $\quad \vec{r} > R_c$

Imposing truncation yields <u>Wannier-like</u> functions

MINIMIZE $\tilde{E} = 2 \sum_{i,j=1}^{N/2} (2\delta_{ij} - S_{ij}) H_{ji}$

W.R.T. <u>TRUNCATED</u> χ_i

$\Rightarrow$ PRODUCTS OF SPARSE MATRICES $\Rightarrow$ $O(N)$

localize around R_c

In practice : $|\chi_i\rangle = \sum_{\mu=1}^{M} c_{i\mu} |\phi_\mu\rangle$

$$\tilde{E}[\{c_{i\mu}\}] = 2 \sum_{i,j=1}^{N/2} \left[2 S_{ij} - \sum_{\mu,\nu=1}^{M} c_{i\mu} c_{j\nu} S_{\mu\nu} \right] \left[\sum_{\mu,\nu=1}^{M} c_{i\mu} c_{j\nu} H_{\mu\nu} \right]$$

minimize $\tilde{E}$ W.R.T. $c_{i\mu}$.

PROPERTIES (LIKE IN D.M. APPROACH) :

1) VARIATIONAL $\tilde{E} \geq E_{exact}$, for given R_c

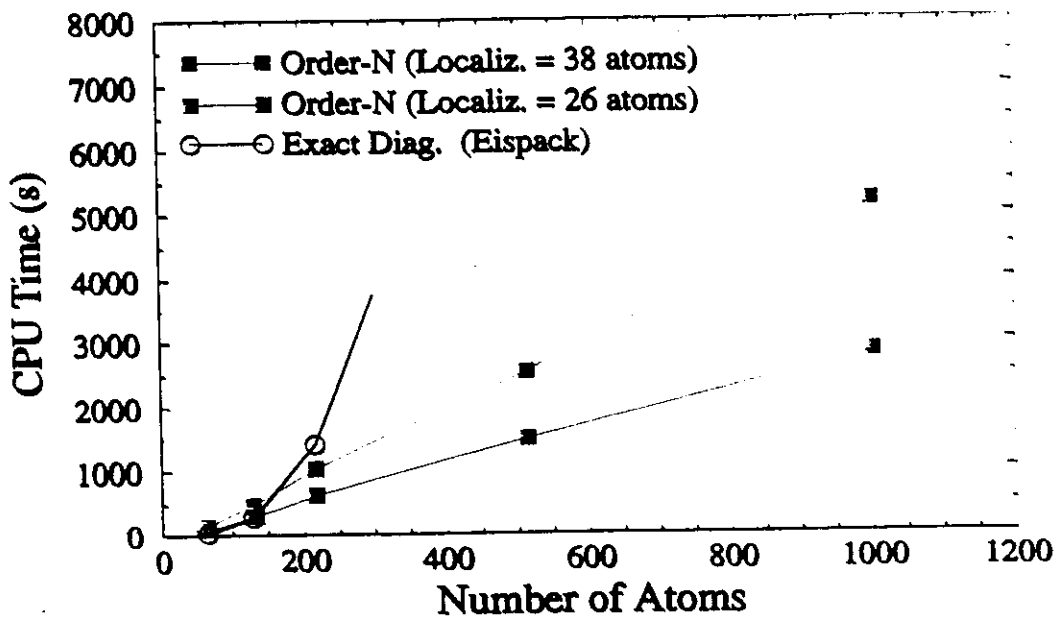
2) $\tilde{E} \longrightarrow E_{exact}$ when $R_c \longrightarrow \infty$

$\Rightarrow$ [illegible] $\Rightarrow$ M.D (37)

LINEAR SCALING

c-Si (Diamond structure)

(Supercells with different number of atoms)

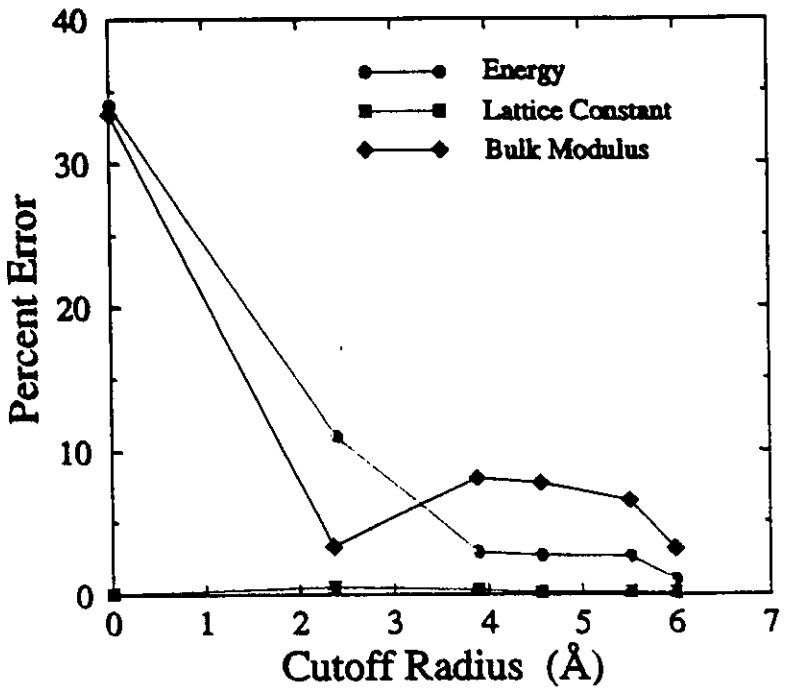


First Neighbors Tight-Binding Hamiltonian

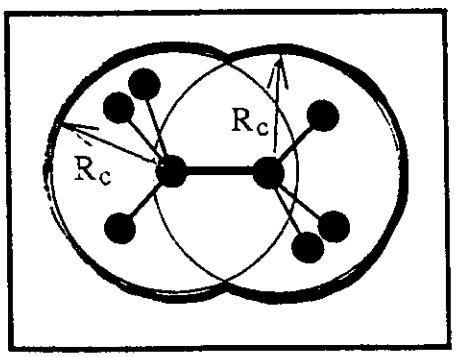
(J. Chadi, Phys. Rev. B 29, 785 (1984))

Crystalline Silicon (Diamond Structure)

512 Atoms Supercell (Γ Point)



Localized Wave Functions centered on the bonds



ab initio Tight-Binding Calculation

(Sankey-Drabold Method: Tight-Binding form of LDA Harris Functional)

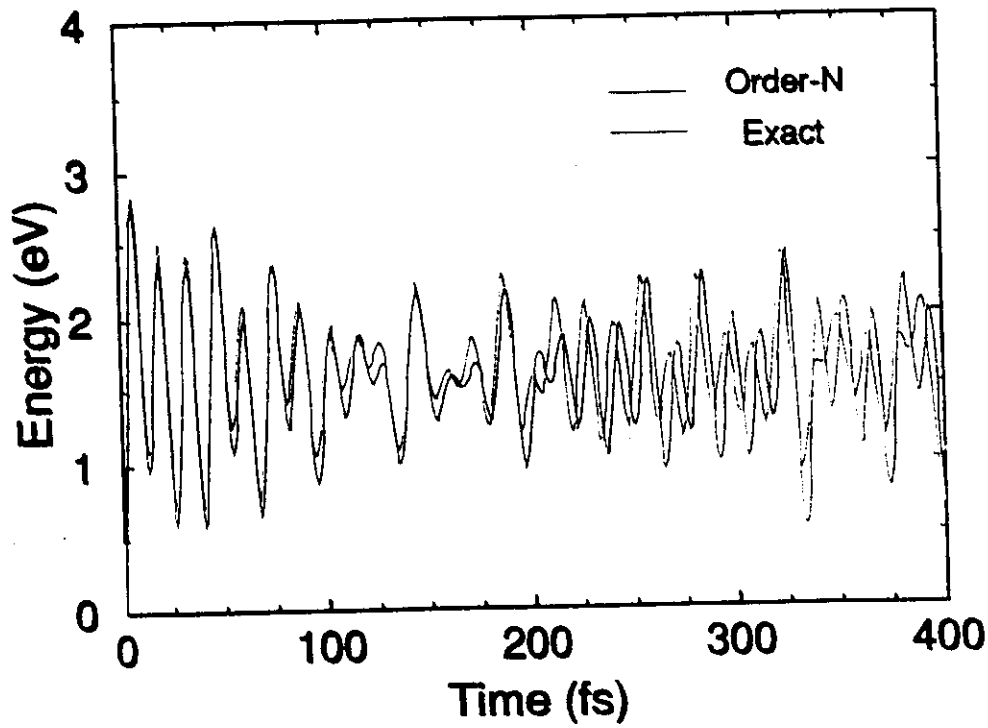
MOLECULAR DYNAMICS

(Thermal Simulations)

c-C (Diamond structure)
64 atoms Supercell
T_0 = 400 K; <T> ~ 200K

Order-N: R_c = 2.8 Å

(26 atoms)



PROBLEMS OF THE $\tilde{E}$ FUNCTIONAL:

WHEN LOCALISATION IS IMPOSED:

EXISTENCE OF LOCAL MINIMA (BESIDES THE PHYSICAL ONES)

$\Rightarrow$ • UNPHYSICAL CHARGES, INCORRECT FORCES, ETC.

• DEPENDS ON INITIAL STATE FOR MINIMIZATION.

SOLUTION Kim, Mauri, Galli; PRB 52, 1640 (95)

• Increase the number of W.F. in the functional

$M > N/2$ ($M \leq M$ = basis set size)

• Introduce global variable (Fermi Level)

μ (to ensure correct N)

$$\tilde{\tilde{E}} = 2 \sum_{i,j=1}^{m} (2\delta_{ij} - S_{ij})(H_{ji} - \mu S_{ji}) + \mu N$$

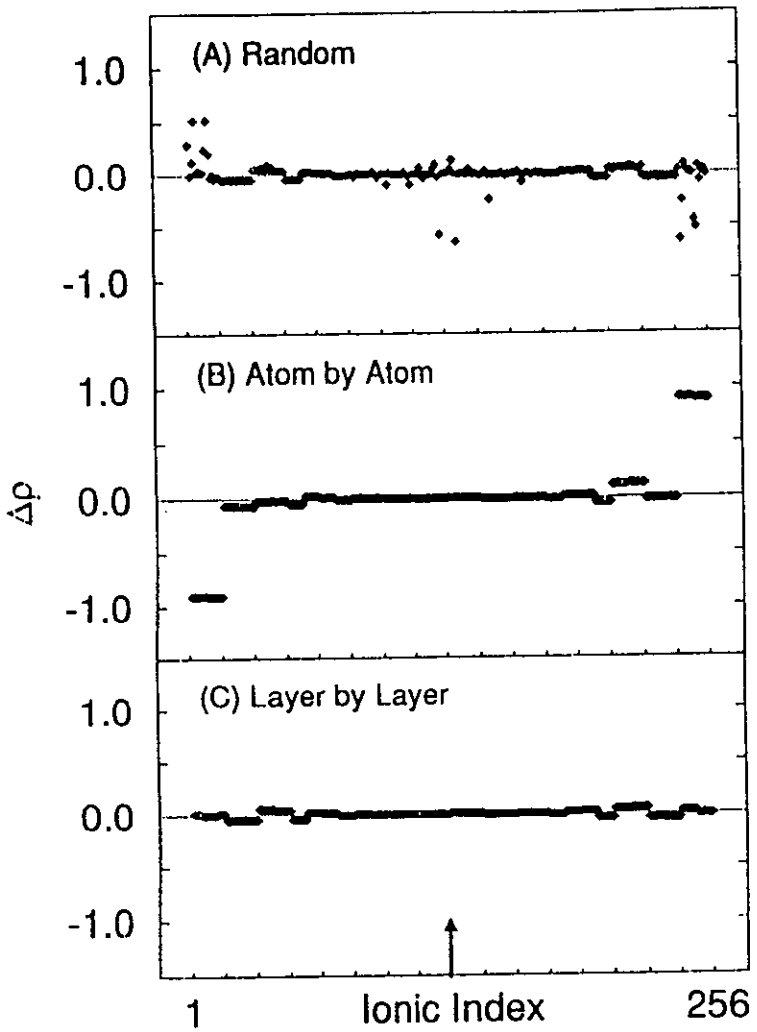
• Fixes the problem of local minima.

• Increases variational freedom (more orbitals $\{\chi_i\}$)

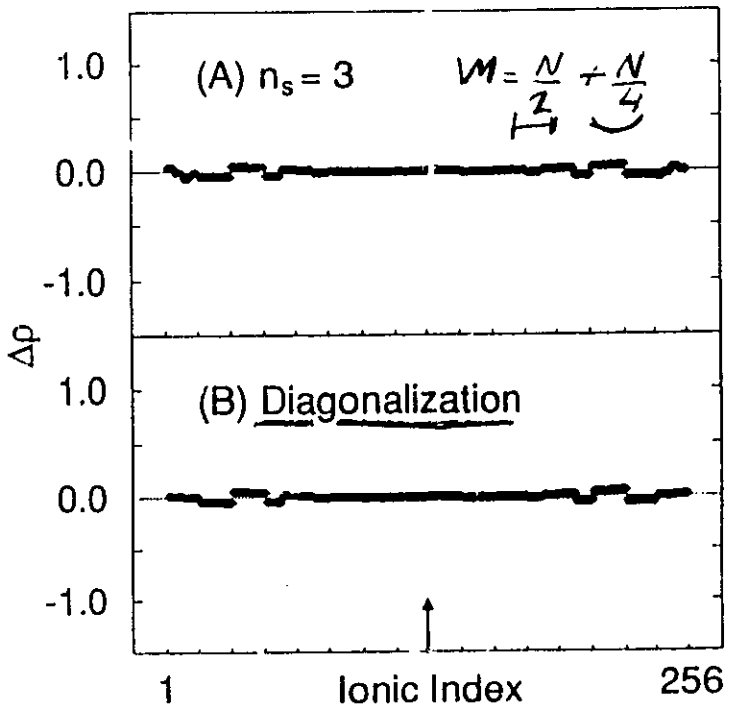
$\Rightarrow$ BETTER ENERGIES, FORCES ...

FOR SAME R_c.

$$\tilde{E} = 2 \sum_{i,j=1}^{N/2} (2\delta_{ij} - S_{ij}) H_{ji}$$



$$\tilde{E} = 2 \sum_{i,j=1}^{M} (2\delta_{ij} - S_{ij}) \cdot (H_{ji} - \mu S_{ji}) + \mu N$$



Mauri et al
Ordejón et al Hierse-Stechel Kim et al Li-Nunes-Vanderbilt
Dav Hernandez et al.

	MGC/ODGM	HS	KMG	LNV/D/NV	HGG
$\{\phi\}_i$	var. par.	var. par.	var. par.	basis fncts.	var. par.
L	I	var. par.	I	var. par.	var. par.
K	2I -S	2L -LSL	2I -S	3LsL-2LsLsL	3LSL-2LSLSL
$\tilde{\rho}$	$2\rho - \rho^2$	$2\rho - \rho^2$	$2\rho - \rho^2$	$3\rho^2 - 2\rho^3$	$3\rho^2 - 2\rho^3$
M	$= N/2$	$= N/2$	$> N/2$	= # of basis fncts.	$> N/2$
η	= const.	= const.	$= \mu$	$= \mu$	$= \mu$
S_0	$\approx$ I	$\neq$ I	$\neq$ I	$\equiv$ s	$\neq$ I

Table from G. Galli (to be published)

Hernandez, Gillan & Goringe. PRB 53, 7147 (96):

$$\rho(\vec{r},\vec{r}') = \sum_{ij}^{M} L_{ij}\, \phi_i(\vec{r})\, \phi_j(\vec{r}')$$

$$\check{\rho}(\vec{r},\vec{r}') = \sum_{ij}^{M} K_{ij}\, \phi_i(\vec{r})\, \phi_j(\vec{r}')$$

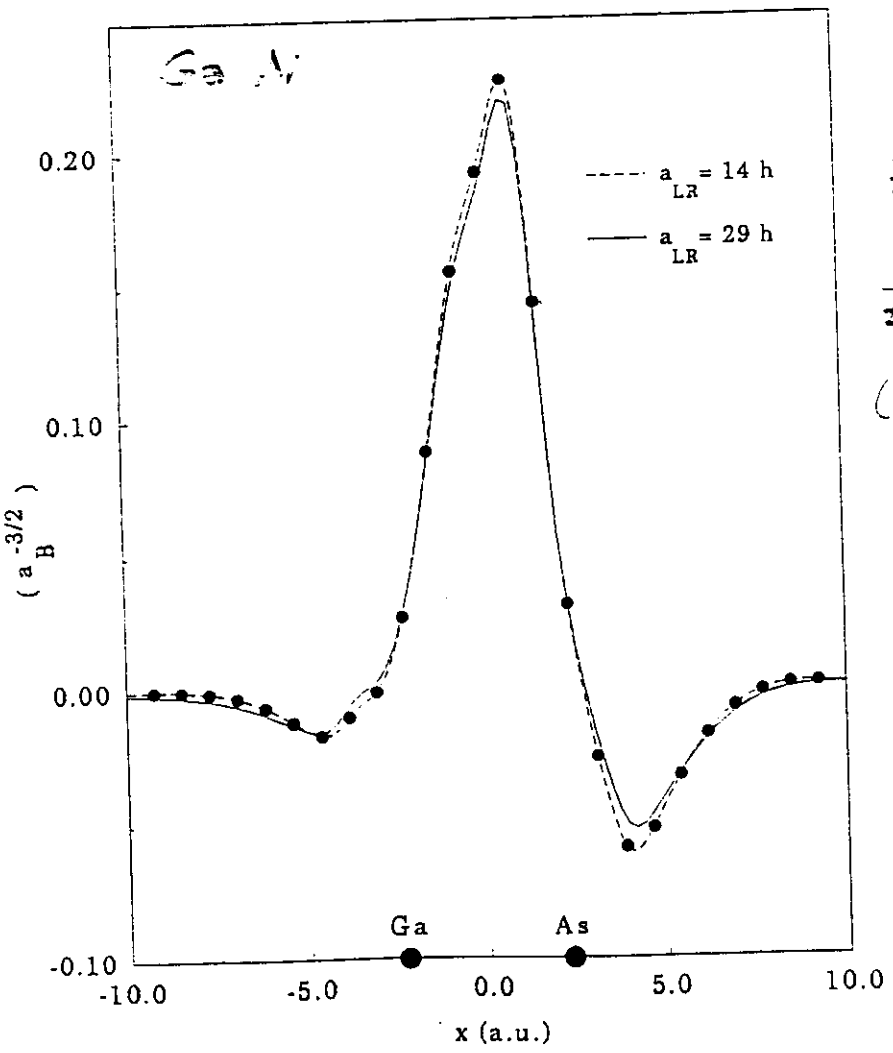
$$E = 2 \sum_{ij}^{M} K_{ij} \langle \phi_i | \hat{H} - \eta | \phi_j \rangle - E_{DC}[\check{\rho}] + \eta N$$

WANNIER FUNCTIONS :

USEFUL FOR OTHER THINGS (BESIDES OCW)

- Polarization in Solids
  King-Smith and Vanderbilt ; PRB 47 , 1651 (93)
  Resta , Rev. Mod. Phys. 66 , 899 (94)
- Effective Charges Z^*
- Dielectric Constants
  Nunes and Vanderbilt , PRL 73 , 712 (94)

⋮



(W.F.)

$Z^*_{As} = 2.02$

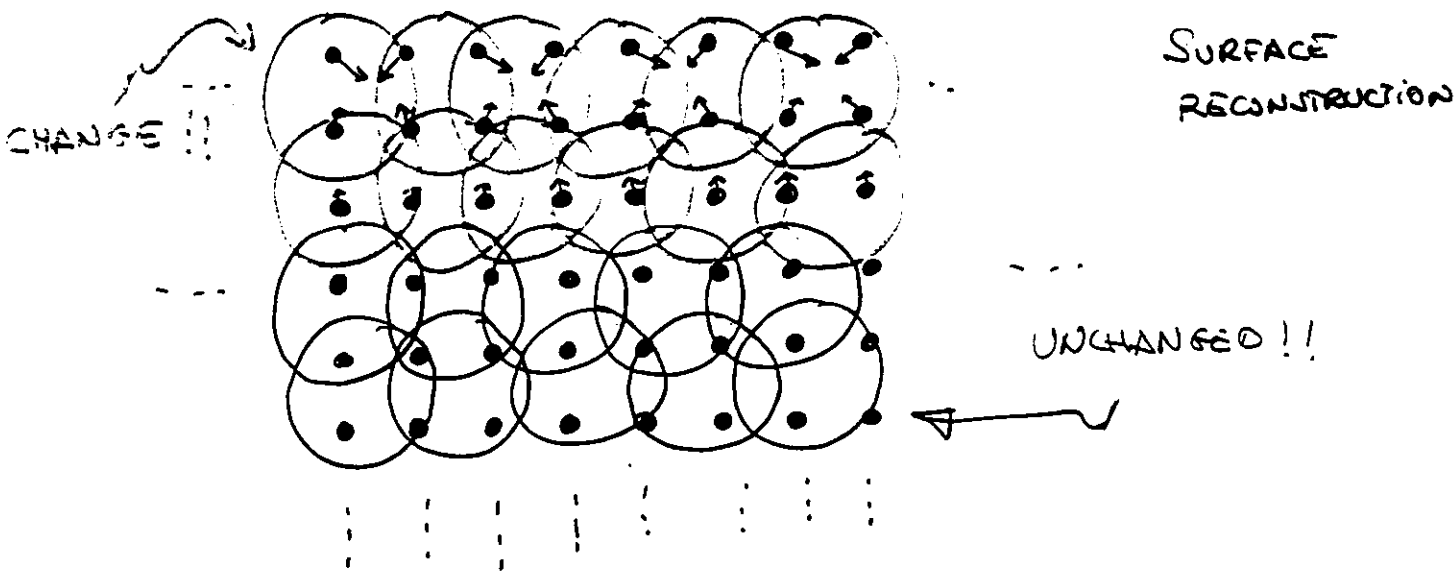
$Z^*_{As} = 2.17$

(P.W. + Linear Response)

P. Fernandez et al, PRB 55, R1909 (97)

FOCUSING ON LOCAL PARTS OF LARGE SYSTEMS

FOR INSTANCE : <u>LOCAL RELAXATIONS</u>



⇒ IN <u>LOCAL</u> PROCESSES ⟶ OPTIMIZE { W.F. / D.M. } <u>ONLY</u> LOCALLY !

THE REST OF THE <u>(UNCHANGED)</u> SYSTEM IS THE

<u>(BEST)</u> <u>CONTOUR CONDITION</u>

<u>EXAMPLES</u> :

- SURFACE RECONSTRUCTIONS
- DEFECTS
- CHEMICAL REACTIONS (SURFACES ; LARGE MOLECU
- ⋮

PHONON CALCULATIONS WITH LINEAR SCALING

Calculation of phonon spectra:

- Compute Dynamical Matrix:

$$D_{ij}^{\alpha\beta} = \frac{\partial^2 E}{\partial x_i^\alpha \partial x_j^\beta} \times \frac{1}{\sqrt{m_i m_j}}$$

  - Move atom i in the α direction by Δx (small)
  - Solve electrons and compute forces on all the atoms

$$F_j^\beta = \frac{dE}{dx_j^\beta}$$

$$D_{ij}^{\alpha\beta} \approx \frac{F_j^\beta}{\Delta x} \times \frac{1}{\sqrt{m_i m_j}}$$

  - Repeat for each atom on each direction $\Longrightarrow 3N$ computations
  - If standard diagonalization is used for the electronic problem, the overal computation scales as N^4
  - If Order-N is used for the electronic problem, the overal computation scales as N^2

- Diagonalize the Dynamical matrix to obtain the phonon eigenmodes. This step scales as N^3.

- Another possibility: Finite-T MD simulation → [illegible] → vibr. spectrum
  (J. Kohanoff et al.)

"Advantages" of DM approach: (1) Dynamical matrix
(2) low-frequency modes (expensive in MD
(3) T=0 spectrum

Order-N Approach for Phonon Calculations

Ordejón et al. PRL, 75, 1324 (95)

- We use three basic approximations to obtain an O(N) scaling in the calculation of the Dynamical matrix:

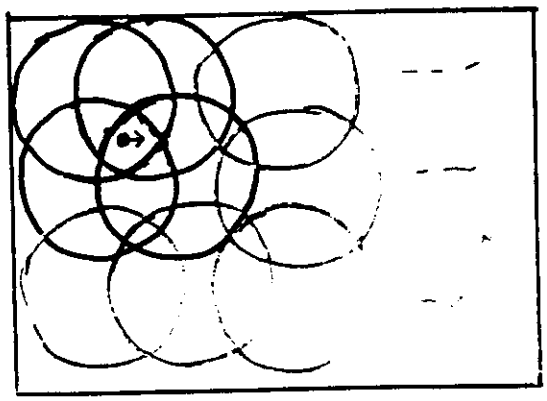
  1. **Description of the electronic states by means of truncated Localized Wave Functions.** We use our Order-N electronic structure method to compute the energy and forces.

  2. **Restricted minimization of the electronic energy**. For each atomic displacement, we only allow to change those LWF's which contain the atom that is moving. All the rest of LWF are unchanged. Therefore, the cost of the calculation of the electronic wave functions and the total energy for each atomic displacement is constant (independent of the size of the system), or **O(1)**.

  3. **Truncation of the dynamical matrix.** We assume that the elements of the dynamical matrix connecting two atoms which are further away than a cutoff R_f are zero. Therefore, when atom i is displaced, only the forces on those atoms closer than R_f to atom i must be computed. Besides, the resulting dynamical matrix is **sparse.** O(N)

- Once the dynamical matrix is obtained, the phonon spectrum can be computed by direct diagonalization, which cost is small compared to the obtention of $D_{ij}^{\alpha\beta}$. An O(N) scaling can also be obtained in this step if the phonon spectrum is computed using the Maxent method proposed by Drabold and Sankey, Phys. Rev. Lett. **70**, 3631 (1993), since the dynamical matrix is sparse.

1) LOCALIZED WAVE FUNCTIONS



2) $$S_I \equiv \{ \psi_j \mid |\vec{R}_j - R_I| < R_c \}$$ $\vec{R}_I \equiv$ position of moving atom I

$$\tilde{E} = 2 \sum_{i \text{or} j \in S_I} H_{ij} (2\delta_{ij} - S_{ij}) + 2 \sum_{i,j \notin S_I} H_{ij} (2\delta_{ij} - S_{ij}) \equiv \tilde{E}_1^I + \tilde{E}_2^I$$

$\tilde{E}_2^I$ constant !

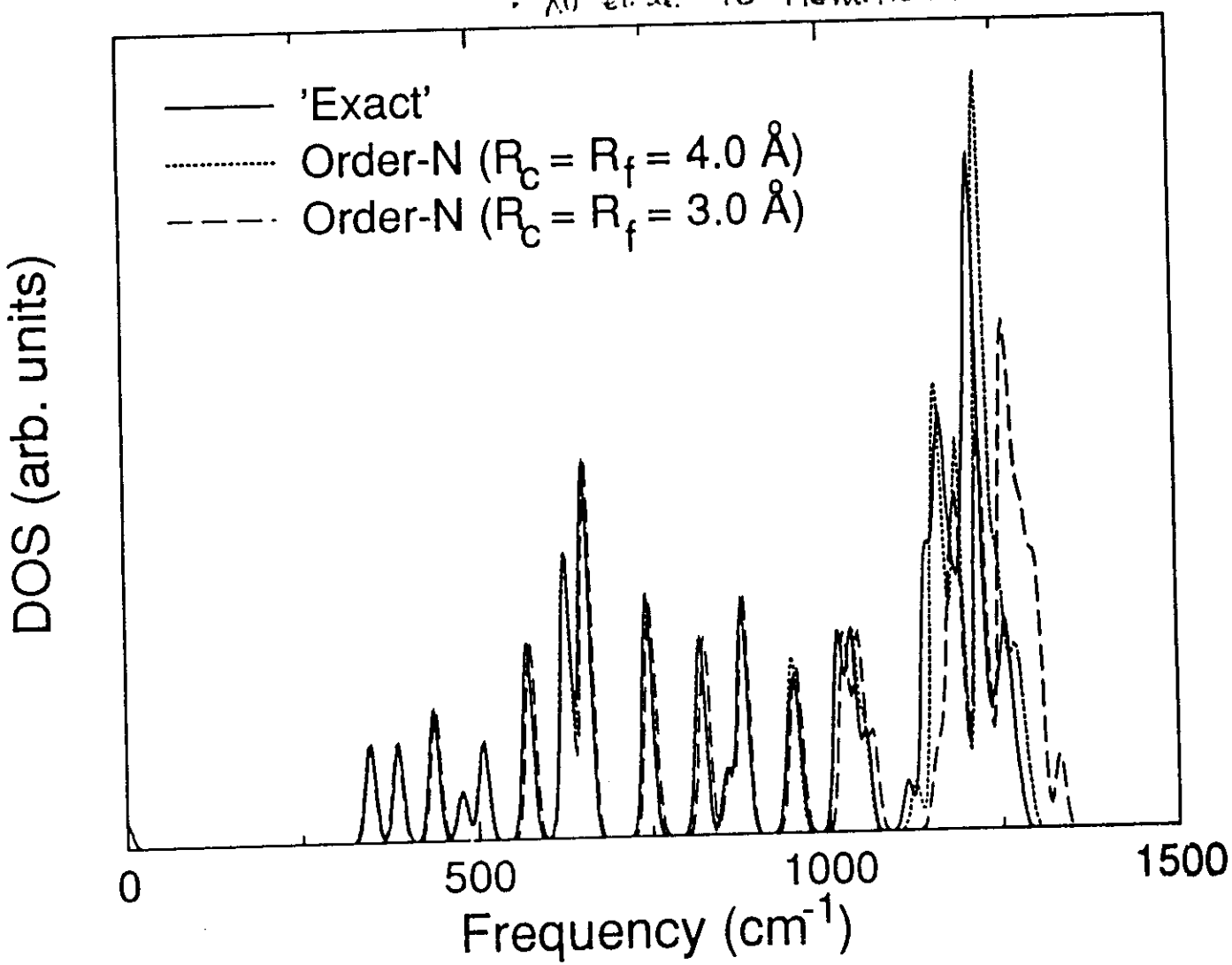
$\rightarrow \psi_j \in S_I$ obtained minimizing $\tilde{E}_1^I \Rightarrow O(1)$

$\rightarrow \psi_j \notin S_I$ solutions of system in equilibrium.

3) TRUNCATE DYNAMICAL MATRIX

$$D_{ij} = 0 \qquad |R_i - R_j| > R_f$$

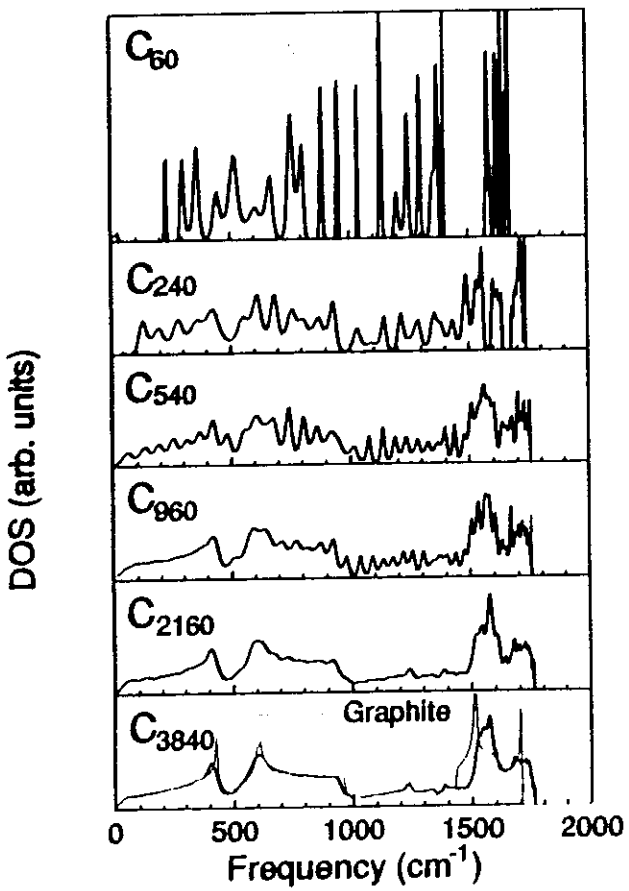
TEST SYSTEM : • C_{216} (diamond) supercell (Γ point BZ sampling)
• $\vec{q}=0$ phonons
• Xu et al. TB Hamiltonian



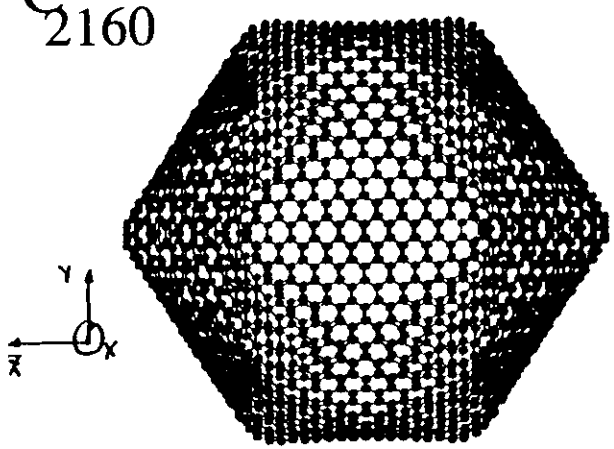
$R_c^{\sigma} = 1.0\,\text{Å}$ $R_c^{\pi} = 5.0\,\text{Å}$

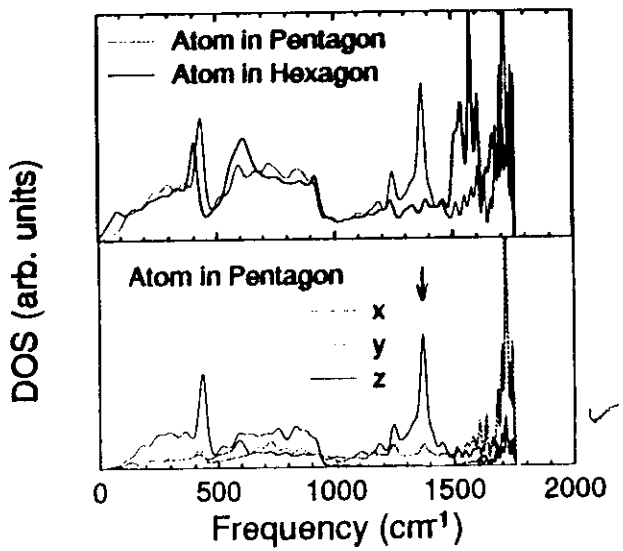
$R_g = 50\,\text{Å}$

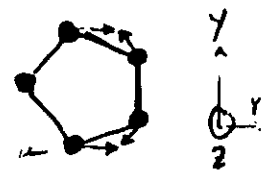
(3) Phonon Spectra



C_{2160}







PROJECTION METHODS

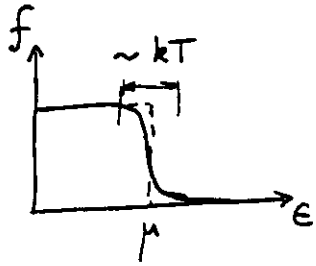
Let $|\varphi\rangle$ be an <u>arbitrary</u> state

<u>FERMI MATRIX</u> (DENSITY OPERATOR)

$(T \neq 0)$ $\qquad \hat{F}_{\mu,T} = f\left[\frac{\hat{H}-\mu}{kT}\right] \qquad f(x) = \frac{1}{e^x+1}$

$$\hat{F}_{\mu,T}\,|\psi_i\rangle = f\left[\frac{\epsilon_i-\mu}{kT}\right]\cdot|\psi_i\rangle$$

thermal occupation



What is $\hat{F}_{\mu,T}\,|\varphi\rangle$??

$$|\varphi\rangle = \sum_i c_i\,|\psi_i\rangle \Rightarrow \hat{F}_{\mu,T}|\varphi\rangle = \sum_i c_i\, f\left[\frac{\epsilon_i-\mu}{kT}\right]|\psi_i\rangle$$

$\Rightarrow$ $\hat{F}_{\mu,T}$ <u>Projects out</u> the unoccupied states

TOTAL ENERGY :

$$E_{B.S.} = 2\,Tr\left[\hat{H}\,\hat{\rho}\right] = 2\,Tr\left[\hat{H}\,\hat{F}_{\mu,T}\right] =$$

$$= 2\sum_{\mu=1}^{M} \langle \phi_\mu | \hat{H}\,\hat{F}_{\mu,T} | \phi_\mu \rangle .$$

Def.: $|f_\mu\rangle \equiv \hat{F}_{\mu,T}\,|\phi_\mu\rangle .$

↑ LOCALISED !! (column of the density matrix)

How to exploit these properties ?? (Goedecker)

(TCHEBYSHEV) POLYNOMIAL REPRESENTATION OF $\hat{F}_{\mu,T}$

$$\hat{F}_{\mu,T} \simeq \frac{c_0}{2} + \sum_{j=1}^{n_p} c_j\, T_j(\hat{H}) .$$

RECURRENCE

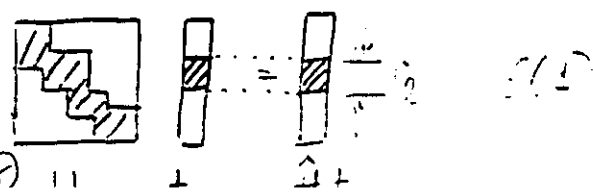
$$|t_\mu^0\rangle = |$$

$$|f_\mu\rangle = \frac{c_0}{2}|t_\mu^0\rangle + \sum_{j=1}^{n_p} c_j\,|t_\mu^j\rangle . \qquad |t_\mu^1\rangle = H|$$

$$|t_\mu^{j+1}\rangle = 2\hat{H}|t_\mu^j\rangle - |t_\mu^{j-1}\rangle$$

+ PRODUCT TRANSFORMATION

(final result IS localized)



ISSUES :

(1) ELECTRONIC TEMPERATURE ⟶ FINITE !!

Insulators : NOT A PROBLEM :-

$kT < E_g$

Chebyshev. representation : $n_p \simeq 4 \dfrac{\epsilon_{max} - \epsilon_{min}}{E_g} \simeq 0(5$

Metals : Lower T ⇒ more terms in Tcheb. series.
AND larger r_c

(2) FERMI LEVEL

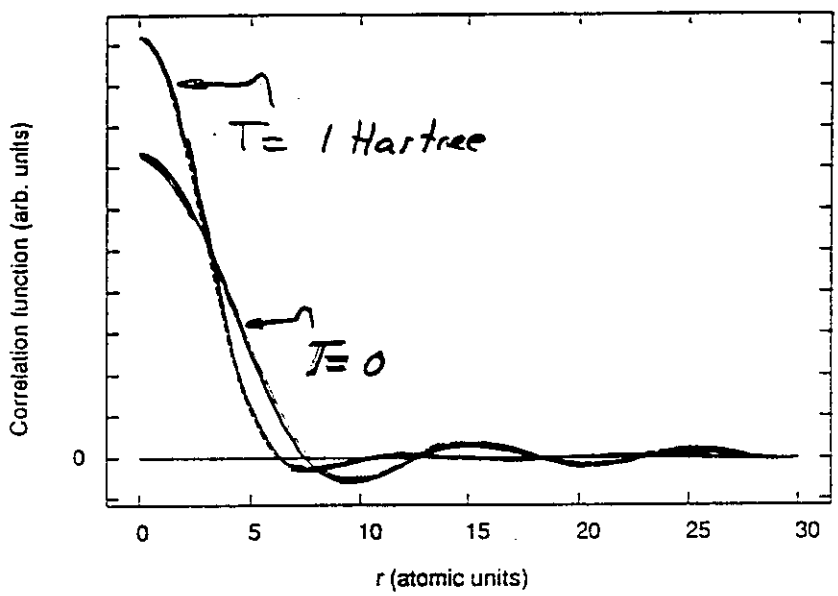
FIXED ⇒ N NOT CONSERVED

VARIABLE ⇒ MORE COMPUTATIONS
& LESS ACCURATE FORCES.

(3) POSSIBLE EFFICIENT WAY TO COMPUTE NON-ORTHOGONAL
[illegible] FUNCTIONS. (Stephen & Drabold, unpublished
[illegible] Goedecker ... unpublished)

JELLIUM. $r_s = 2$.

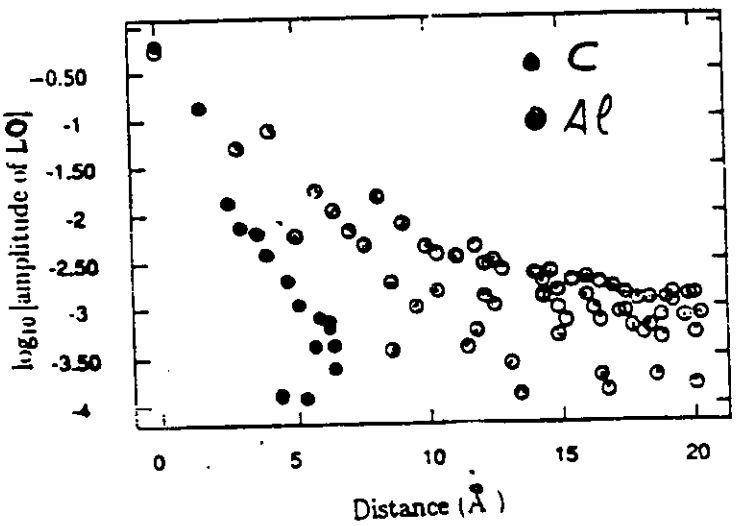
$\rho(r,r')$



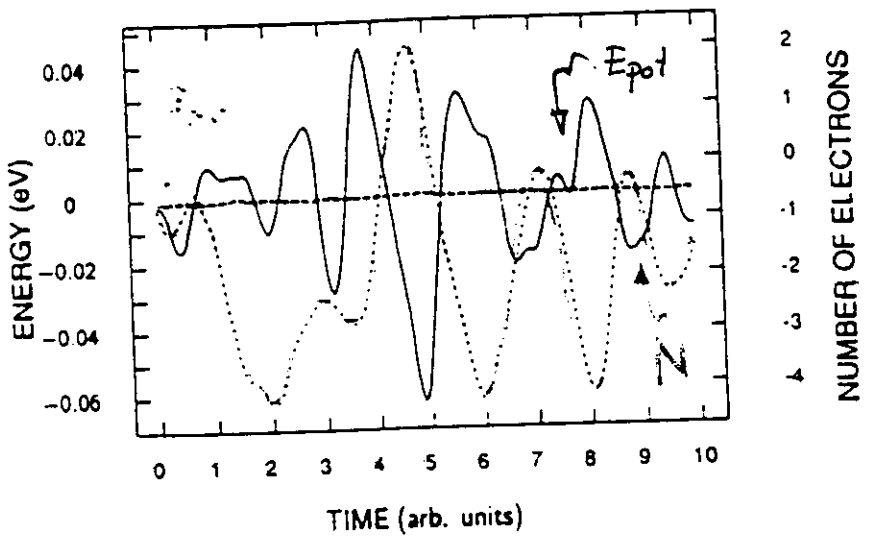
METALS: $\rho(r,r')$ VERY LOCALIZED ...

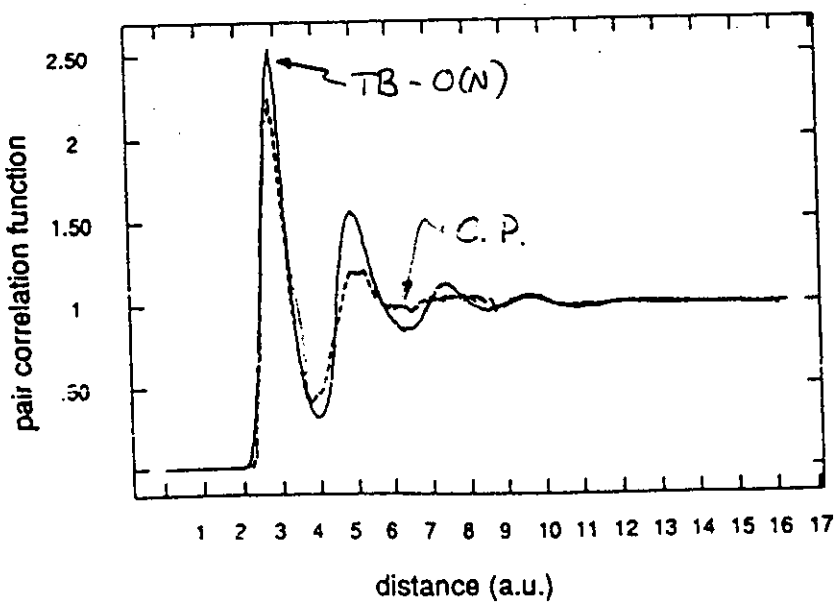
AT UNPHYSICAL TEMPERATURES.

Goedecker & Teter, PRB 51, 9455 (95)



C-C
512 atoms
5000 K
Fixed ρ



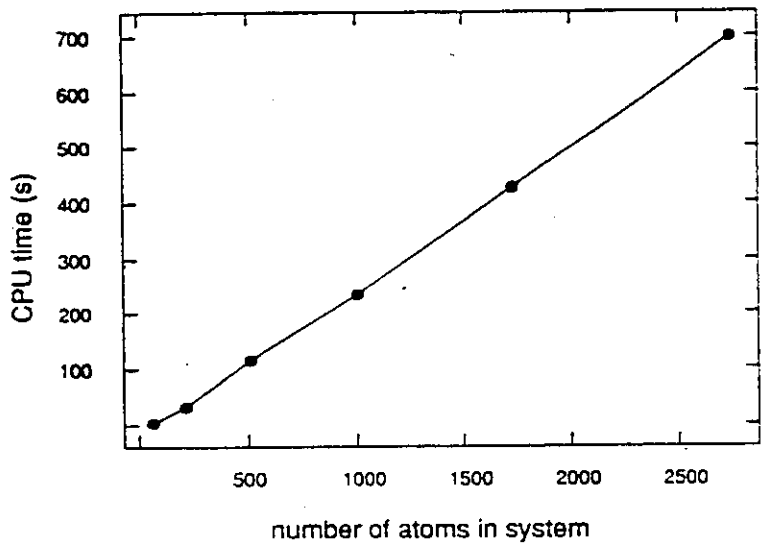


Goedecker & Colombo, PRL 73, 122 (94)

CPU VS. SYSTEM SIZE

(CARBON CELLS) ETB

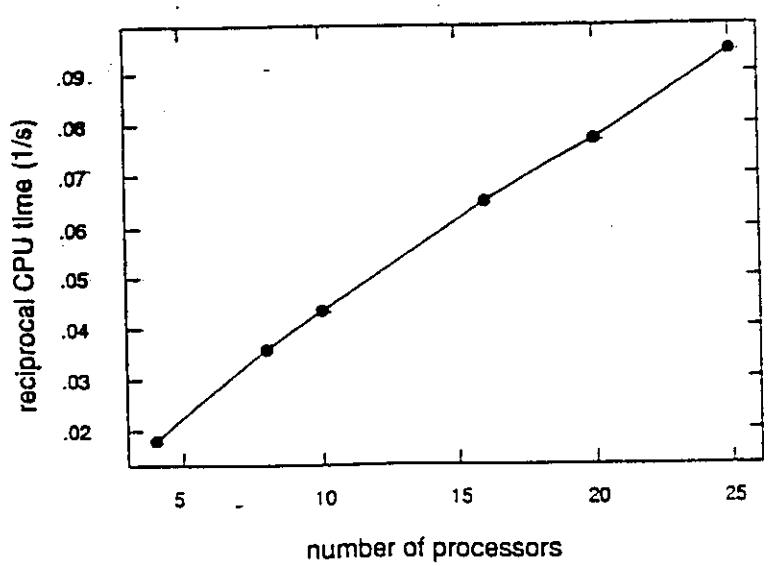
DIAMOND.



PARALLELIZATION*

CPU VS. # OF PROCESSORS

C_{1000} cell



* ... (SUTTON et al. CPC 97, 123.

MOMENTS METHODS

- MOMENTS AND D.O.S.

$$H\psi_i = \epsilon_i \psi_i \quad (i = 1, N)$$

Def: D.O.S. associated with H:

$$n(E) = \frac{1}{N} \sum_{i=1}^{N} \delta(E - \epsilon_i)$$

Moments of $n(E)$:

$$\mu_n \equiv \int_{-\infty}^{\infty} dE\, E^n n(E) = \frac{1}{N} \sum_{i=1}^{N} \epsilon_i^n = \frac{1}{N} Tr(H^n)$$

- PROBLEM (philosophy):

1) OBTAIN APPROXIMATE MOMENTS μ_n

2) ESTIMATE D.O.S. FROM μ_n

3) COMPUTE PHYSICAL PROPERTIES

$n(E)$

$$E_{B.S.} = 2 \int_{-\infty}^{\epsilon_F} E \cdot n(E)\, dE$$

$$\left(N = 2 \int_{-\infty}^{\epsilon_F} n(E)\, dE \right)$$

...

(2) RECONSTRUCT $n(E)$ FROM MOMENTS

(SEVERAL APPROACHES).

- **KERNEL POLYNOMIAL METHOD**

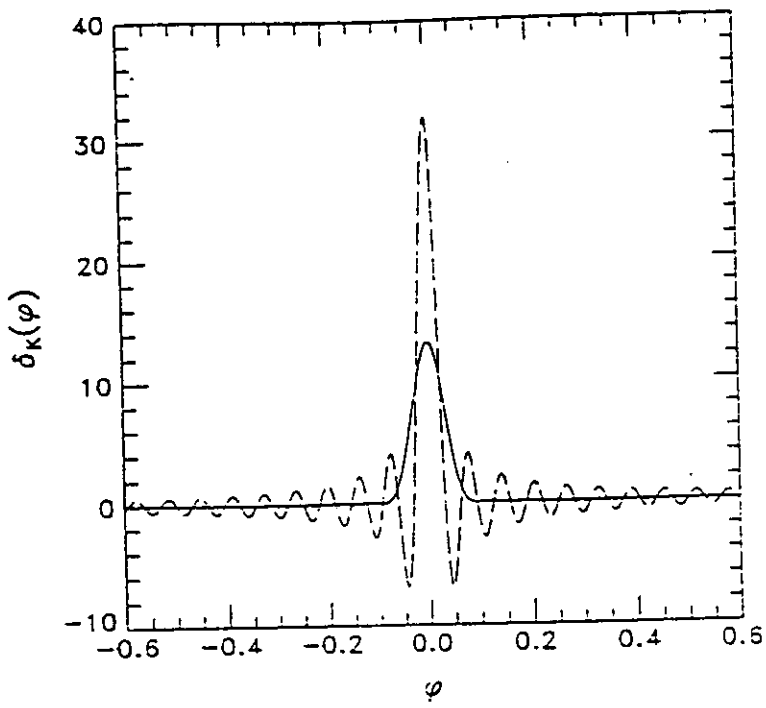
  (Silver, Roeder, Voter & Kress) PRB 53, 12733 (96)

  J. Comp. Phys. 124, 115 (96)

$$n(x) \approx \frac{1}{\pi\sqrt{1-x^2}}\left[\mu_0 g_0 + 2\sum_{m=1}^{M} \mu_m g_m T_m(x)\right]$$

(g_m = Gibbs damping factors)

Can be shown to be a convolution of the exact D.O.S. with a (kernel) polynomial



kernel polynomial

$$\delta_K(\phi) = \sum_{m=0}^{M} \frac{1}{2\, g_m}\, g_m \cos(m\phi) \qquad x = \cos(\phi)$$

$$n^{KP}(\phi) = \int_0^{2\pi} \delta_K(\phi - \phi')\, n^{exact}(\phi')\, d\phi'$$

More moments $\Rightarrow$ [illegible]

- **MAXIMUM ENTROPY METHOD**

(Drabold & Sankey, PRL 70, 3631 (93))

Information theory: Reconstruct original data from incomplete information (image reconstruction).

Moments problem: find $n(\epsilon)$ so that:

- Satisfy data (constraints):

$$\mu_n = \int_{-\infty}^{\infty} d\epsilon \; \epsilon^n \; n(\epsilon) \equiv \langle r_n(x) \rangle .$$

- Maximize "ENTROPY"

$$S^* \equiv -\int_{-\infty}^{\infty} d\epsilon \; n(\epsilon) \; \ln [n(\epsilon)]$$

[See Turek, J. Phys. C 21, 3251 (88)]

I) OBTAINING MOMENTS (APPROXIMATE)

(SEVERAL APPROACHES)

- **STATISTICAL APPROACH** (Drabold & Sankey, PRL 70, 3631 (9

Let $x \in \mathbb{R}^N$ $\qquad x = \sum_i \alpha_i |\psi_i\rangle$

Def $\nu_n(x) \equiv x^\dagger H^n x$ (computed in $O(N)$ if H sparse)

$= \sum_i |\alpha_i|^2 \epsilon_i^n$

$$\nu_n(x) = \mu_n \iff |\alpha_i|^2 = \frac{1}{N} \quad \forall i$$

"Impartial" vector $x = \frac{1}{N} \sum_i |\psi_i\rangle$ yields exact μ_n

STATISTICAL APPROACH:

x as a random variable. Let $\langle \cdot \rangle$ denote average over randomly picked x:

$$\langle \nu_n(x) \rangle = \sum_{i,j=1}^{N} \langle x_i^* H_{ij}^n x_j \rangle = \sum_{i,j=1}^{N} (H^n)_{ij} \langle x_i x_j \rangle$$

Random process $\Rightarrow$ $\langle x_i x_j \rangle = \delta_{ij}$

$$\langle \nu_n(x) \rangle = \sum_{i=1}^{N} H_{ii}^n = \mathrm{Tr}(H^n) = \mu_n$$

END

TECHNICAL ISSUES:

1) USE MOMENTS OF <u>TCHEBYSHEV</u> POLYNOMIALS

(more stable than power moments)

- Shift and scale H: $\bar{H} = \frac{H-b}{a}$

$$\epsilon \in [a,b] \longrightarrow \bar{\epsilon} \in [-1;1].$$

- Tchebyshev moments: $\mu_n = \int_{-1}^{1} d\bar{\epsilon}\; n(\bar{\epsilon})\, T_n(\bar{\epsilon})$

- Use recursion relations: $\mu_n \simeq \left\langle \langle x | T_n(\bar{H}) | x \rangle \right\rangle$

$$T_n(\bar{H}) = 2\bar{H}\, T_{n-1}(\bar{H}) - T_{n-2}(\bar{H})$$

2) COST OF CALCULATION:

$$O(N m n_r)$$

$N \equiv$ # electrons

$m \equiv$ # moments

$n_r \equiv$ # random vectors

m, n_r <u>independent</u> of N ?

(for given accuracy).

- MORE n_r $\Rightarrow$ MORE ACCURACY (FEW ARE ENOUGH)
- MORE m $\Rightarrow$ SHARPER D.O.S. (ABOUT 100)

(1) OBTAINING MOMENTS (APPROXIMATE)

(SEVERAL APPROACHES)

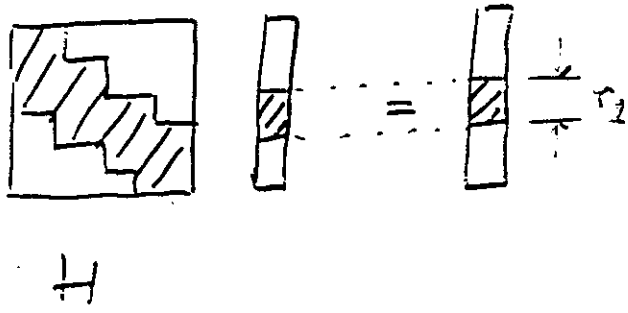
- TRUNCATED MOMENTS APPROACH

(Voter, Kress and Silver, PRB 53, 12733 (96))

$$\mu_n = \frac{1}{N} Tr(H^n)$$

$$= \frac{1}{N} \sum_{\mu=1}^{M} \langle \phi_\mu | \underbrace{H^n | \phi_\mu \rangle}_{H|\phi^{n-1}\rangle}$$

TRUNCATE PRODUCTS (like in the projection method of Goedecker)



H

$\Rightarrow$ SCALING: $O(M \cdot m \cdot n_z) \sim O(N)$

M = # of basis orbitals $\propto N$

m = # of moments

n_z = # of non-zero elements in box region

RANDOM VECTOR MOMENTS

+

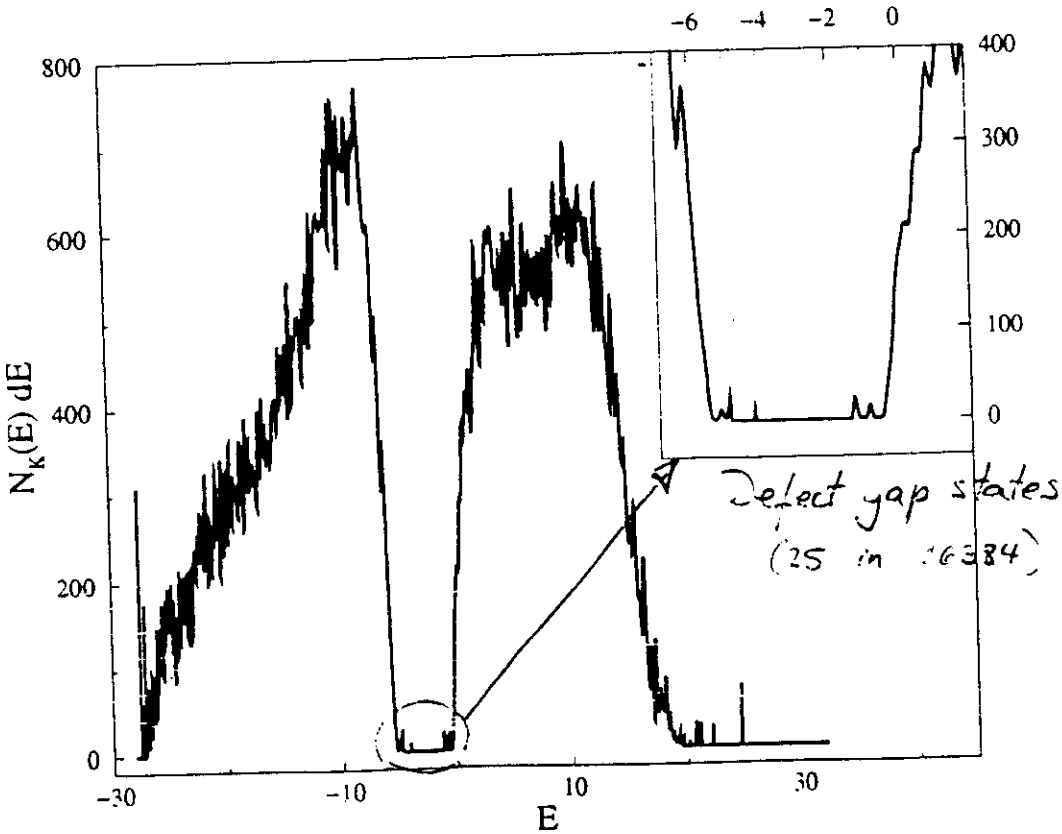
MAXIMUM ENTROPY * RESULTS *

(Röder, Silver, Kress, Landrum, Drabold & Dong)
Simulations Multiconference '96 Proceedings
High Performance Computing '96

ta-C (amorphous carbon, sp^3)

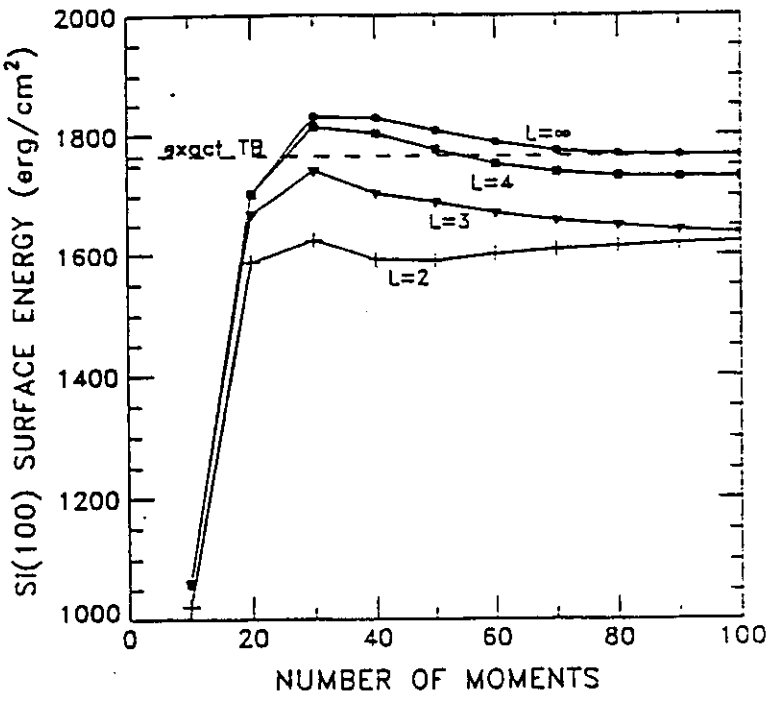
Röder et al.
Simul. Multiconf. '96 Pro

- [illegible]
- [illegible] moments
- [illegible] random vectors



Select gap states
(25 in 16384)

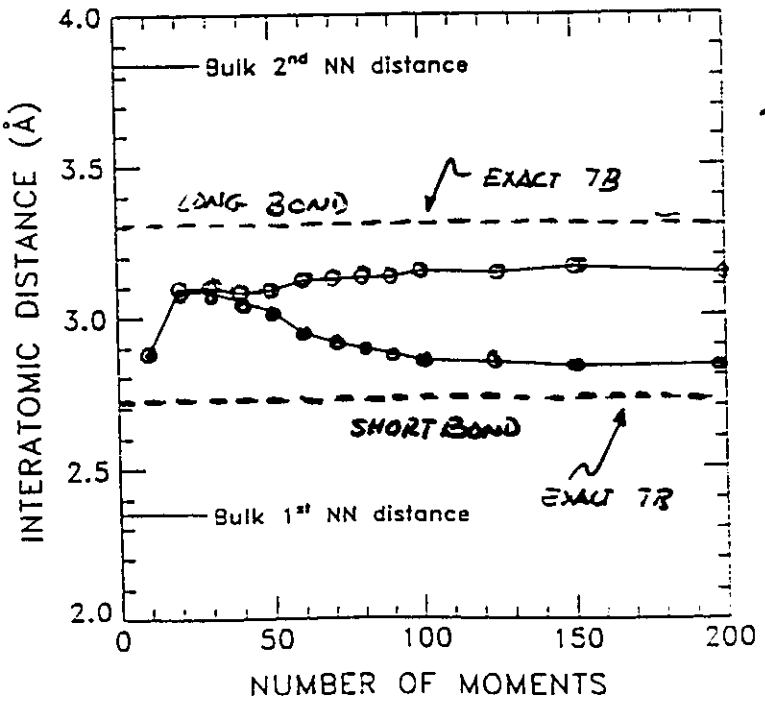
TRUNCATED MOMENTS + K.P.M.



UNRELAXED Si (100) SURFACE ENERGY, VS # OF MOMENTS / TRUNCATION RANK

JAHN-TELLER DISTORSION OF VACANCY IN SILICON

(216 atoms cell)



(L = 3)

TRUNCATION RANK

HOMO-LUMO GAP

SELECTED EIGENVECTORS

"EXACT"

'Folded Spectrum' method.

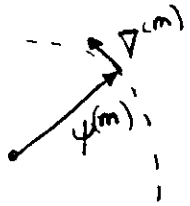
- C.G. Minimization of $\langle\psi|(\hat{H}-E_{ref})^2|\psi\rangle$ (w.r.t. $\psi=\sum_\mu c_\mu \phi_\mu$)

$\phi_\mu \equiv$ atomic orbitals $\Rightarrow$ $\hat{H}$ sparse $\Rightarrow$ $O(N)$.

(Another possibility: Lanczos $(\hat{H}-E_{ref})^2|\psi\rangle = \lambda|\psi\rangle$)

- Programing is trivial !

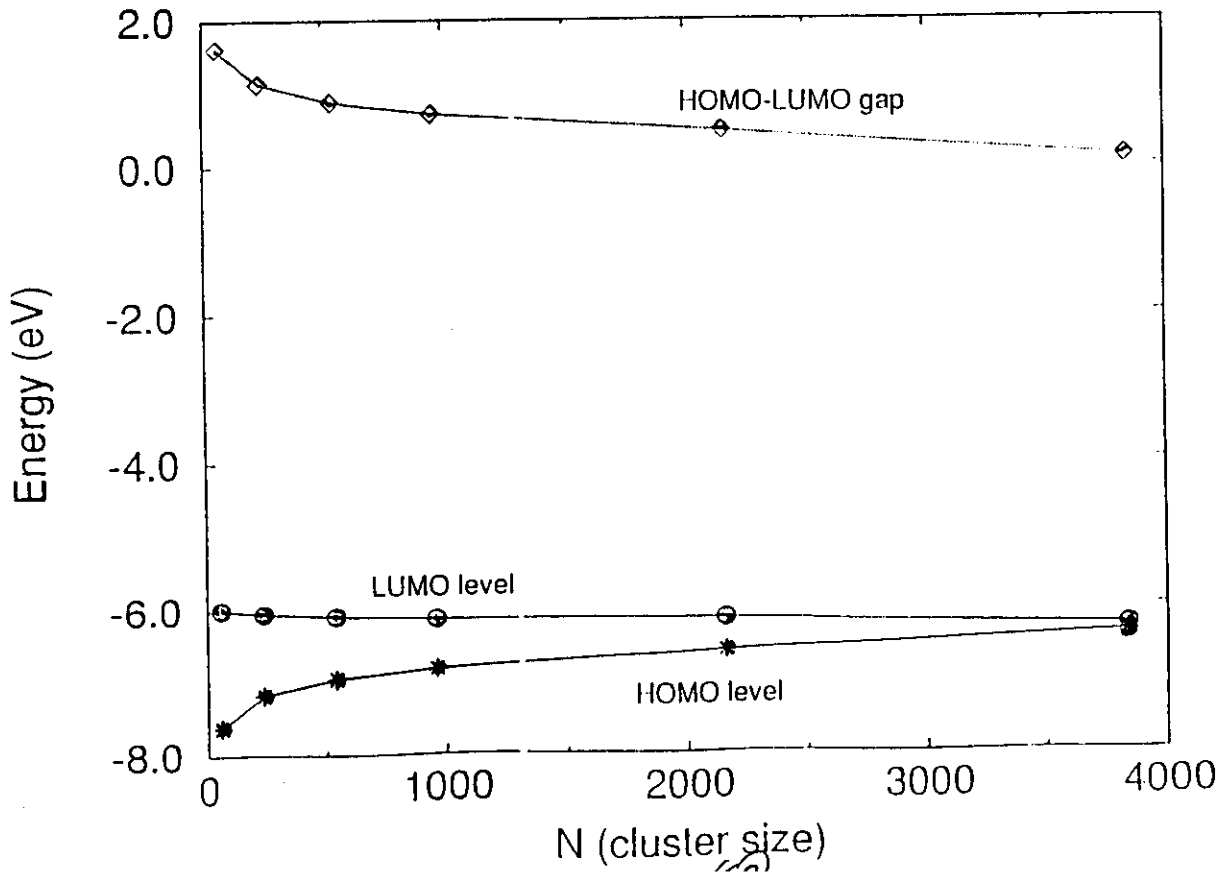
$|\psi| = 1$ $\Rightarrow$



$$\psi^{(m+1)} = \cos\theta \cdot \psi^{(m)} + \sin\theta \cdot \frac{\nabla^{(m)}}{|\nabla^{(m)}|}$$

- Extremely fast ; (C_{3840} : 5 min / eigenvalue in HP workstation).

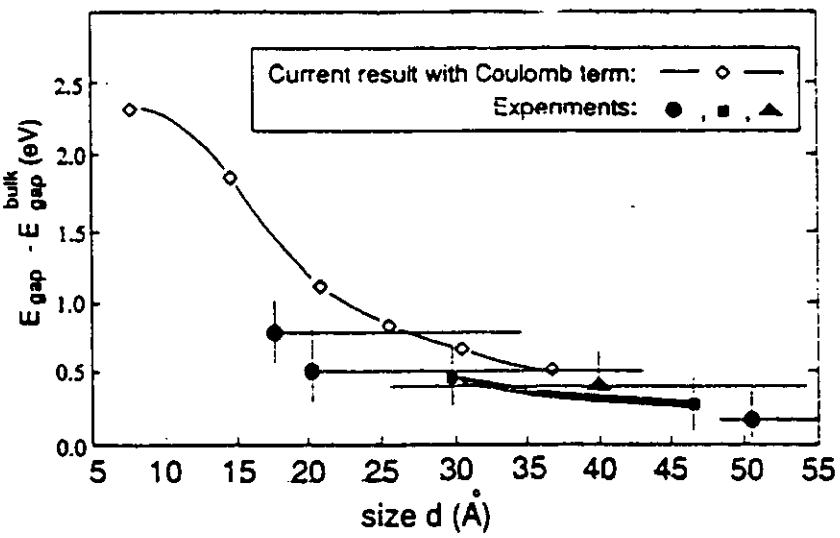
Large Fullerenes (TB model)

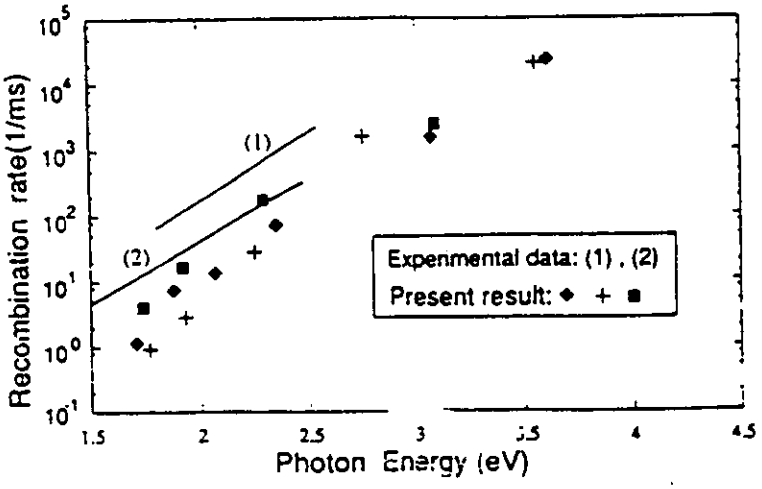


Wang - Zunger

Quantum Dots : (thousands of atoms)

- Empirical Pseudopotentials
- Plane waves





$$\frac{1}{\tau} = \frac{4}{3} \frac{\chi \omega n}{m^2 c^2} \langle i | \hat{p} | f \rangle^2$$

AB-INITIO ORDER-N METHODS

THE DENSITY MATRIX APPROACH.

E. Hernandez & M. Gillan; PRB 51, 10157 (95)
E. Hernandez, M. Gillan & C. Goringe; PRB 53, 7147 (96)

main characteristics:

(1) formulation in terms of the DENSITY MATRIX in REAL SPACE. $\rho(\vec{r}, \vec{r}')$

(2) USE of REAL SPACE GRID TO REPRESENT THE D.M.

(3) LDA Approximation, with LOCAL PSEUDO.
(ONLY VALENCE ELECTRONS)
(NON-LOCAL PSEUDOPOTENTIALS ARE UNDERWAY...)

(4) EXPENSIVE, BUT PRECISE!
(GRID SPACING SMALL → LARGE # OF VARIABLES

DENSITY MATRIX REPRESENTATION:

(Hernandez - Gillan, PRB 51, 10157 (95))
(Hierse - Stechel, PRB 50, 17811 (94))

ASSUME THAT ρ BE "SEPARABLE" (VARIATIONAL GUESS)

$$\rho(\vec{r}, \vec{r}') = \sum_{\alpha\beta=1}^{M} \phi_\alpha(\vec{r})\, K_{\alpha\beta}\, \phi_\beta(\vec{r}')$$

- $\phi_\alpha(\vec{r})$:
  - Support functions (like a basis to expand the D.M.)
  - A few per atom (tipically 4 for Si, (but no restriction)
  - BUT not fixed: variational degrees of freedom $\phi_\alpha(\vec{r})$
- $K = 3\,\underline{L}SL - 2\,LSLSL$ (like $\tilde{\rho} = 3\rho^2 - 2\rho^3$ (purification transformation $\Rightarrow$ avoid constraints)

$S_{\alpha\beta} = \langle \phi_\alpha |$

VARIATIONAL PARAMETERS: MINIMIZE $E = 2\,Tr[\hat{\rho}\hat{H}]$ w.r.t.:

- $\phi_\alpha(\vec{r})$ at the grid points

LOCALISATION APPROXIMATION :

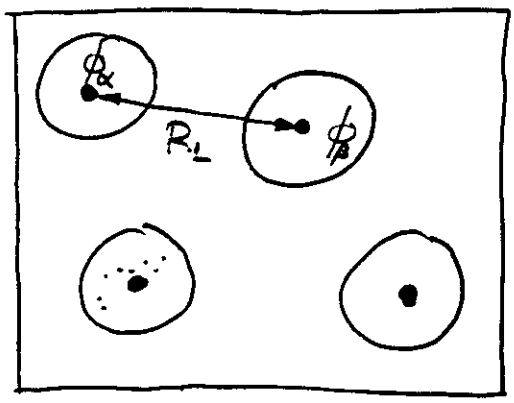
$$\rho(\vec{r},\vec{r}') = \sum_{\alpha\beta} \phi_\alpha(\vec{r})\, K_{\alpha\beta}\, \phi_\beta(\vec{r})$$

$$K = 3\,\mathcal{L}\,S\,\mathcal{L} - 2\,\mathcal{L}\,S\,\mathcal{L}\,S\,\mathcal{L}$$

$$\Downarrow !$$

(1) $\phi_\alpha(\vec{r}) = 0 \qquad |\vec{r} - \vec{R}_\alpha| > R_{cut}$

(2) $K_{\alpha\beta} = 0 \qquad |\vec{R}_\alpha - \vec{R}_\beta| > R_L$



CALCULATION OF DFT ENERGY: GRID.

$$E^{KS} = E_K + E_H + E_{xc} + E_{PS} + E_{i-i}.$$

KINETIC ENERGY: finite differences
(Chelikowsky et al, PRL 73, 712 (94))

n^{th} order:
$$\frac{\partial^2 \phi_\alpha}{\partial x^2}(n_x, n_y, n_z) \simeq \frac{1}{h^2} \sum_{m=-n}^{n} C_{|m|}\, \phi_\alpha(n_x+m, n_y, n_z)$$

[for grid point (n_x, n_y, n_z)]

$$E_K = 2 \sum_{\alpha\beta} K_{\alpha\beta}\, T_{\beta\alpha} \qquad T_{\beta\alpha} = -\frac{\hbar^2}{2m} \int d\vec{r}\, \phi_\beta \nabla^2 \phi_\alpha$$

evaluated by integration on grid

XC TERMS: $$n(\vec{r}_i) = 2 \sum_{\alpha\beta} \phi_\alpha(\vec{r}_i)\, K_{\alpha\beta}\, \phi_\beta(\vec{r}_i)$$

$$E_{xc} = \int d\vec{r}\; n(\vec{r})\, \epsilon_{xc}[n(\vec{r})] \leftarrow \text{integrate on grid}$$

HARTREE TERMS: FFT:

$$n(\vec{r}_i) \xrightarrow[\text{FFT}]{} n(\vec{G}) \longrightarrow V_H(G) \xrightarrow[\text{FFT}]{} V_H(\vec{r}_i)$$

$$V_H(G) = 4\pi\Omega e^2\, n(\vec{G})$$

SILICON

Grid spacing $h = 0.34$ Å

Hernandez et al. PRB 53 7147 (96)

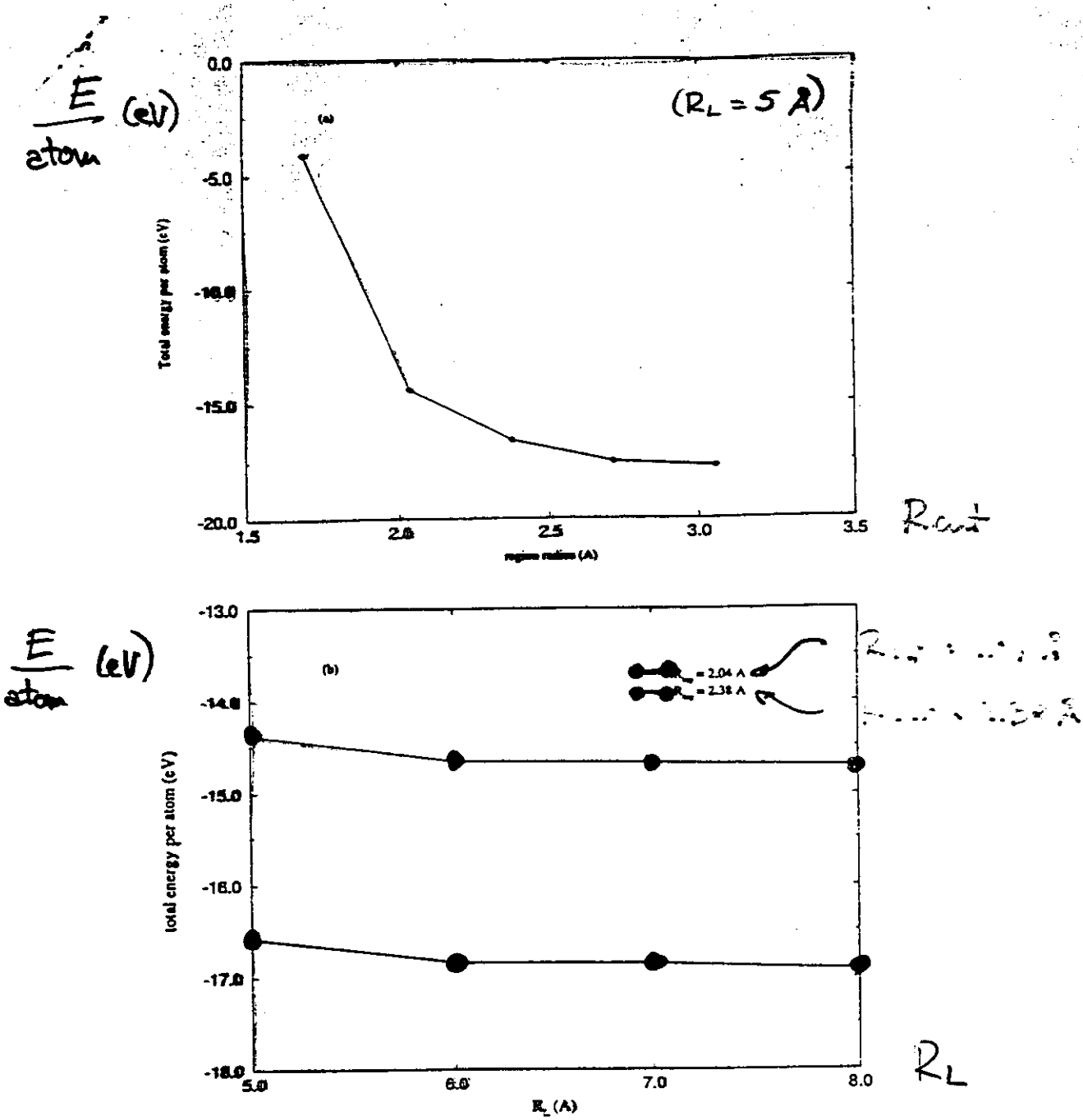


FIG. 1. (a) Total energy per atom as a function of the support region radius R_{reg} with $R_L = 5$ Å. (b) Total energy per atom as a function of the range of the L matrix, R_L, for two different support region radii, $R_{reg} = 2.04$ and 2.38 Å.

SILICON

Grid spacing $h = 0.34$ Å
Hernandez et al PRB 53, 7147 (96)

OPTIMIZED ϕ_α

S-type

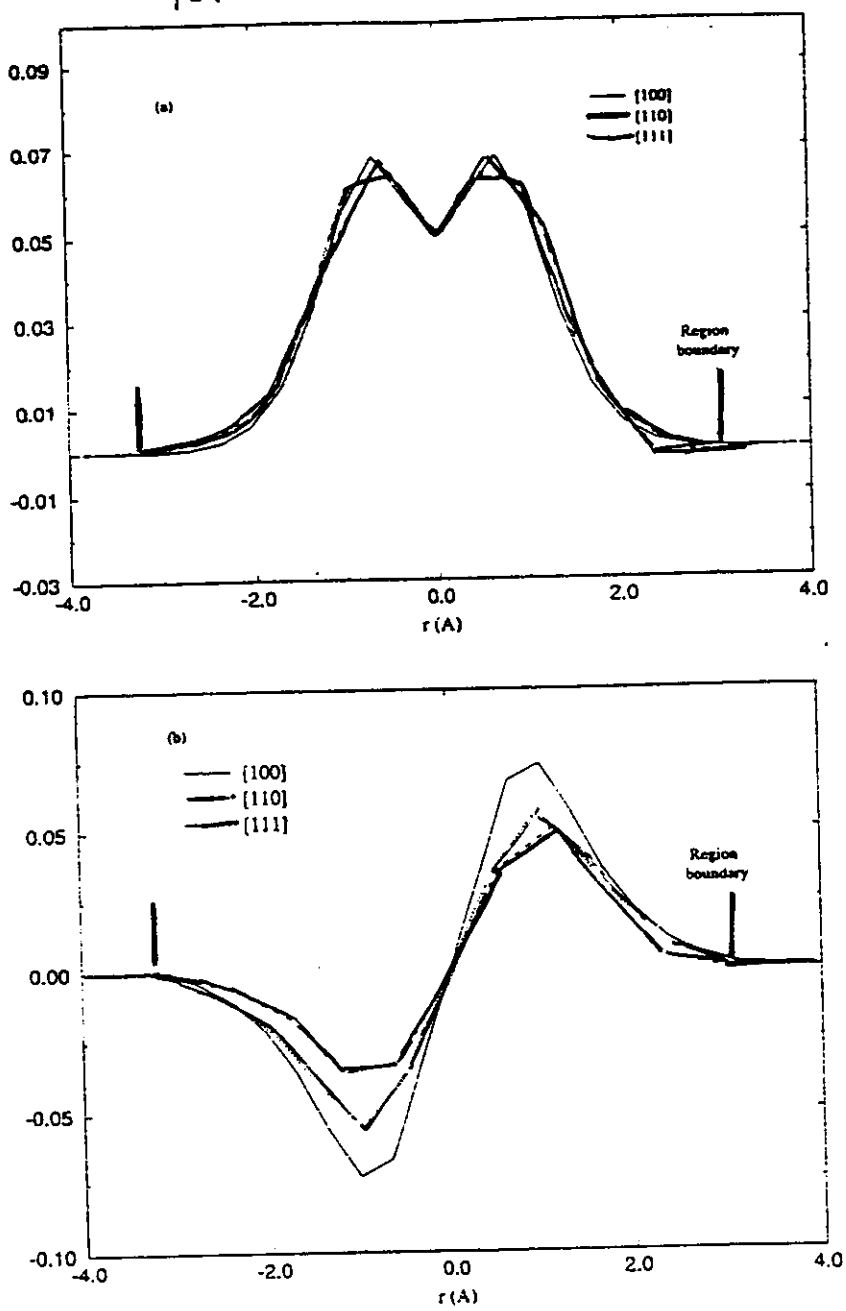


FIG. 2. Support functions after minimization of the total energy with $R_{reg} = 3.05$ and $R_L = 5.0$ Å. (a) s-like support function, and (b) p_x-like support function.

AB-INITIO ORDER-N METHODS

LCAO APPROACH

P. Ordejón, E. Artecho, J.M. Soler; PRB 53, R10441 (96
Mat. Res. Soc. Symp. Proc 408, 85 (96)

D. Sanchez-Portal, P. Ordejon, E. Artecho, JM. Soler; Int. J. Quantum C (in press)

Main characteristics:

(1) Basis of ATOMIC ORBITALS (arbitrarily large)

(2) formulation in terms of Loc. WANNIER FUNCTIONS

(orbital O(N) functional formulation).
P. Ordejón et. al; Mauri et al; Kim et al.

$$\underbrace{\psi_i(\vec{r})}_{\text{L.W.F}} = \sum_{\mu=1}^{M} a_{\mu i} \underbrace{\phi_\mu(\vec{r})}_{\text{A.O.}}$$ (like TB!!!)

(3) LDA, GGA, LSD, approximation,
with NON-LOCAL PSEUDOPOTENTIALS

(4) CHEAP !! for small basis sets (minimal, s-z

PRECISE !! for large sets (PS)

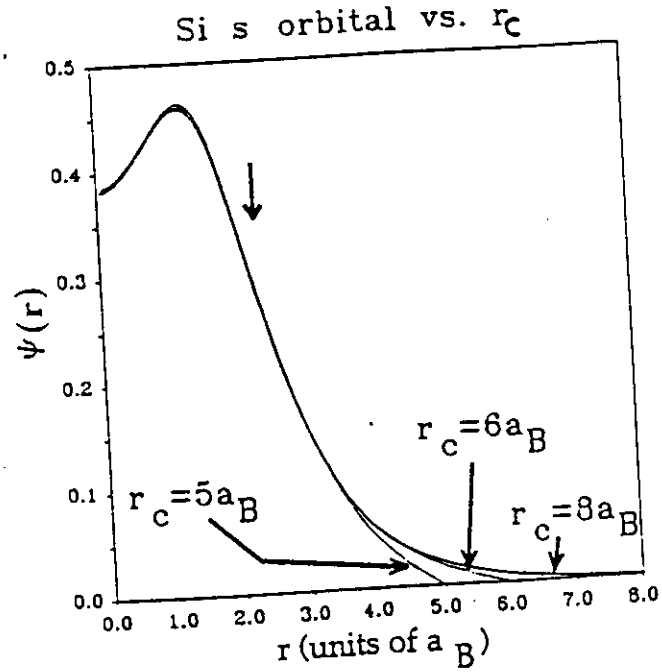
BASIS

FINITE RANGE PSEUDOATOMIC

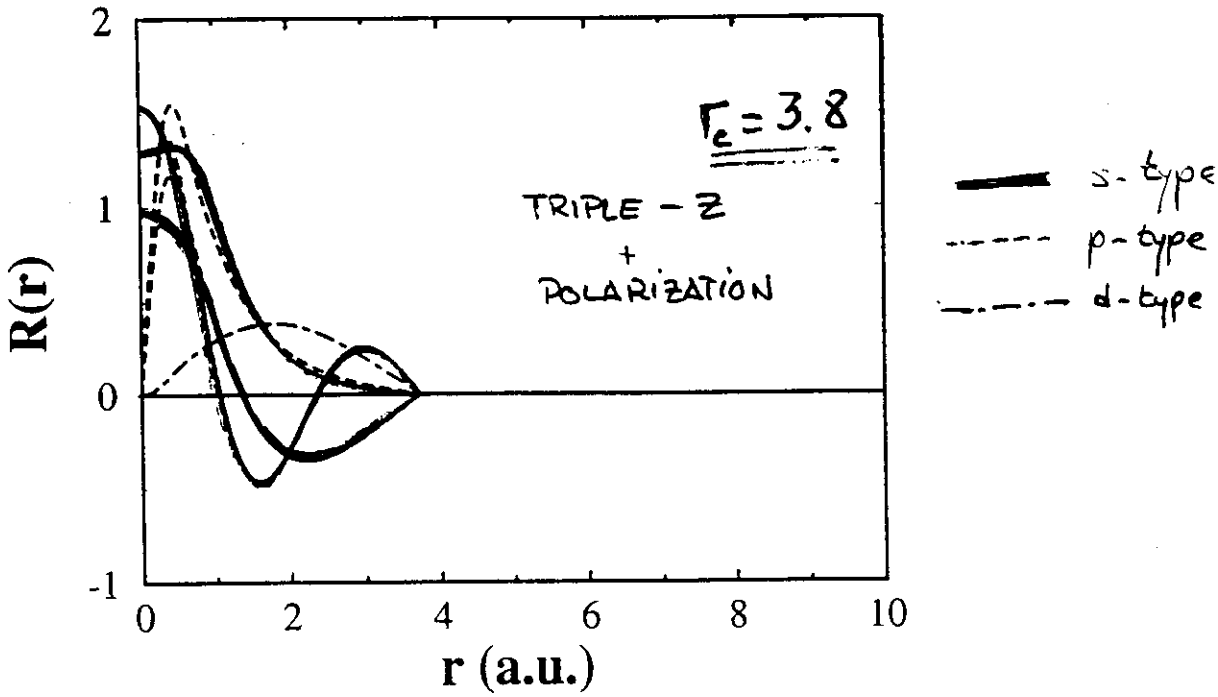
ORBITALS

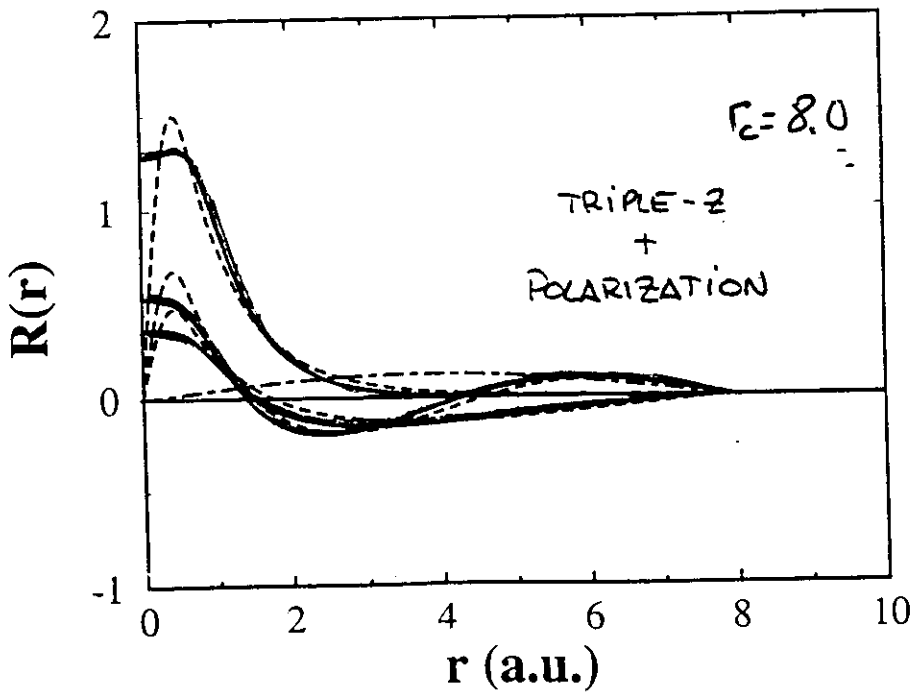
(SANKEY & NIKLEWSKI, PRB 40 3979 (1989))

SOLUTION OF THE PSEUDO-ATOM (ATOM WITH PSEUDOPOT)
WITH $\Psi(r=r_c) = 0$



OXYGEN PAO's


$r_c = 3.8$
TRIPLE − Z
+
POLARIZATION
s-type
p-type
d-type
R(r)
r (a.u.)
2
1
0
-1
0
2
4
6
8
10


$r_c = 8.0$
TRIPLE-Z
+
POLARIZATION
R(r)
r (a.u.)
2
1
0
-1
0
2
4
6
8
10

LDA HAMILTONIAN (for given $\rho(\vec{r})$).

$$H^{KS} = T + \overbrace{V_L + V_{NL}}^{P.S.} + V_H + V_{xc}$$

NEUTRAL ATOM CHARGE: $\rho^{NA}(\vec{r}) = \sum_i \rho_i^0(\vec{r})$

$$\rho(\vec{r}) = \rho^{NA}(\vec{r}) + \delta\rho(\vec{r}).$$

$$V_H(\vec{r}) = V_H^0(\vec{r}) + V_H^\delta(\vec{r}).$$

$$H^{KS} = \overbrace{T + V_{NL} + (V_L + V_H^0)}^{V_{NA}} + V_H^\delta + V_{xc}$$

(1) & S (2)

ENERGY:

$$E = E_{BS} - \frac{e^2}{2}\int V_H(r)\,\rho(r)\,dr + \frac{e^2}{2}\int V_H^0(r)\,\rho^0(r)\,dr$$

$$+ \int [\epsilon_{xc} - V_{xc}]\,\rho(r)\,dr + \underbrace{\frac{e^2}{2}\sum_{ii'}\frac{Z_i Z_{i'}}{|R_i - R_{i'}|} - \frac{e^2}{2}\int V_H^0(r)\rho_{at}}_{U_{ii-oo}}$$

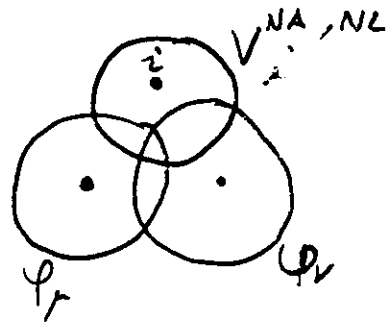
① • Short ranged $\left.\begin{aligned} V_{NL}(\vec{r}-\vec{R}_i) &= 0 \\ V_{NA}(\vec{r}-\vec{R}_i) &= 0 \end{aligned}\right\}$ $|\vec{r}-\vec{R}_i| > R_c$

• Non-SCF : Do not depend on $\delta\rho(\vec{r})$ (only on $\rho^0(\vec{r})$).

$T_{\mu\nu} = \langle \varphi_\mu | -\frac{1}{2}\nabla^2 | \varphi_\nu \rangle$; $S_{\mu\nu} = \langle \varphi_\mu | \varphi_\nu \rangle$

$V^{NA}_{\mu\nu,i} = \langle \varphi_\mu | V^i_{NL} | \varphi_\nu \rangle$

$V^{NA}_{\mu\nu,i} = \langle \varphi_\mu | V^i_{NA} | \varphi_\nu \rangle$



TWO-CENTER & [illegible] INTEGRALS

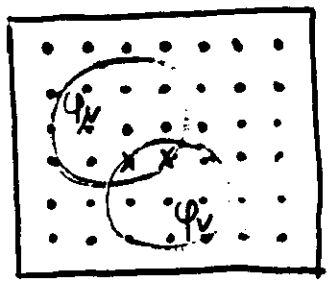
DIRECT LCAO ⟶ TABULATED

(beforehand ; stored on disk ; interpolated during MD)

PRECISE & CHEAP

(Sankey-Niklewski et al: PRB 40, 3979 (89))

② Depend on $\rho(\vec{r})$ $\Rightarrow$ COMPUTED ON A <u>GRID</u>



① $\delta\rho(\vec{r}_\lambda) = \sum_{\mu\nu} \delta\rho_{\mu\nu}\, \varphi_\mu(\vec{r}_\lambda)\, \varphi_\nu(\vec{r}_\lambda)$

$\downarrow$ FFT

$\delta\rho(\vec{G}) \rightarrow V_H^\delta(\vec{G})$

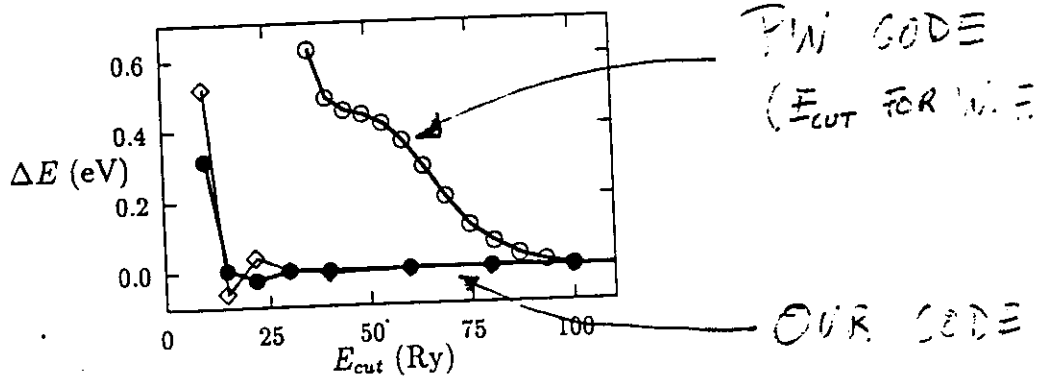
$\downarrow$ FFT

$V_H^\delta(\vec{r}_\lambda)$

② $\langle \varphi_\mu | V_H^\delta + V_{XC} | \varphi_\nu \rangle = \sum_\lambda \varphi_\mu(\vec{r}_\lambda)\, V(\vec{r}_\lambda)\, \varphi_\nu(\vec{r}_\lambda)$

<u>NOTE THAT</u>: ONLY V_H^δ, V_{XC} ARE DONE ON GRID

(<u>NOT</u> T, V_{NL}, V_{NA})



FOR <u>C</u>ARBON (DIAMOND)

$\Delta E = E(E_{CUT}) - E(100\,Ry)$

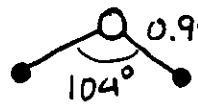
(PER UNIT CELL (2 ATOMS))

[<u>BHS</u> pseudopotentials]

GOING TO LARGER BASIS SETS

A (MODIFIED) NEW SCHEME

- H_2O MOLECULE



(Exp.)

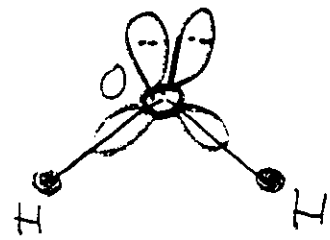
  - MINIMAL BASIS (SINGLE-ζ ; sp^3 for O
    s for H)

    BEST RESULTS : ≳ 10% ERROR IN d(H-O) and θ

  - PW : $d = 0.96 - 0.98$ Å
    $\theta = 103° - 105°$

    (Li et al PRB 47, 4
    Bernd et al PRB 48,

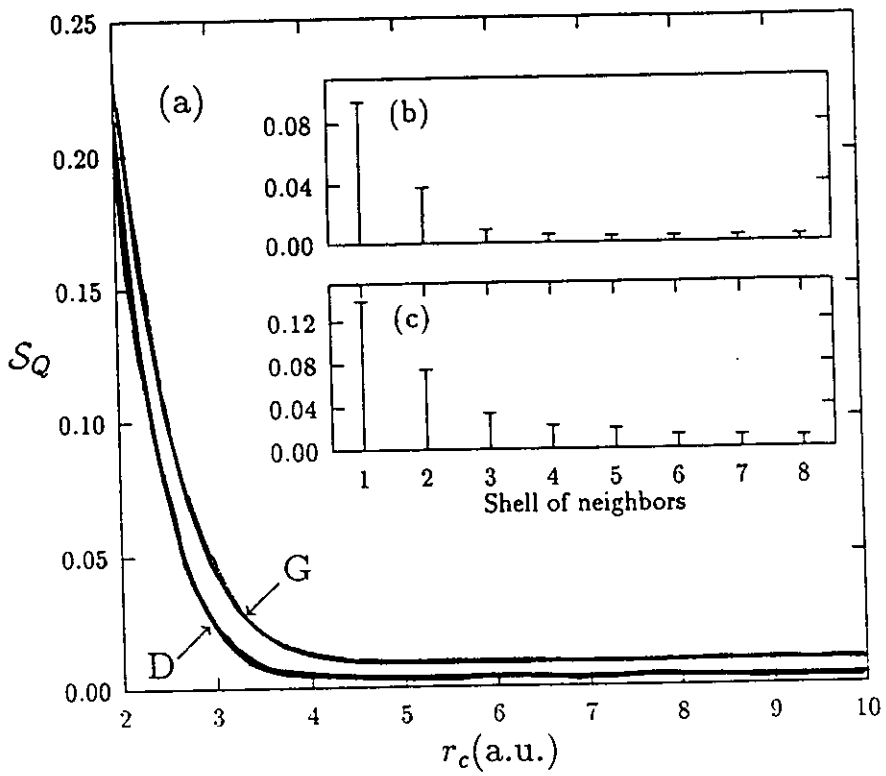
$\Rightarrow$ NEED IMPROVED LCAO BASIS



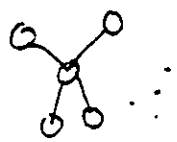
- PROBLEM : 3-center integral tables become TOO LARGE !

SOLUTION ⟶ ELIMINATE 3-CENTER TABLES.

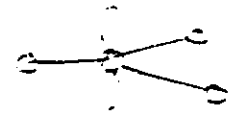
CARBON (Minimal basis)



DIAMOND:



GRAPHITE:



'SPILLAGE': J. Sanchez-Portal et al. [J. Phys: Cond. Matter 8, 3859 (96)]

$$S = \sum_{n}^{\text{eigen}} \left\langle \Psi_n^{PW} \middle| (\mathbb{1} - \hat{P}_{LCAO}) \middle| \Psi_n^{PW} \right\rangle$$

(Measure of basis set accuracy for a given system)

MODIFIED SCHEME :

① $$E_{tot} = 2\sum_i q_i \langle \psi_i | -\tfrac{1}{2}\nabla^2 + V_{NL} | \psi_i \rangle + \int V_{NA}(\vec{r})\,\delta\rho(\vec{r})\,d\vec{r} + \tfrac{1}{2}\int V_H^{\delta}(\vec{r})\,\delta\rho(\vec{r})\,d\vec{r} + \int \epsilon_{xc}(\vec{r})\,\rho(\vec{r})\,d\vec{r} - \frac{1}{8\pi}\int V_{NA}(\vec{r})\,\nabla^2 V_{NA}(\vec{r})\,d\vec{r} - E_{ions}$$

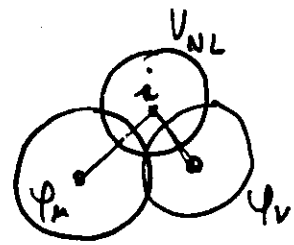
Two center integrals!

$$H^{KS}_{\mu\nu} = T_{\mu\nu} + V^{NL}_{\mu\nu} + V^{NA}_{\mu\nu} + V^{\delta}_{H\mu\nu} + V^{xc}_{\mu\nu}$$

[note that $V^{NA}_{\mu\nu}$ done on grid, but with the exact $V^{NA}(\vec{r})$; $V^{NA}_{\mu\nu} = \sum_A \varphi_\mu(\vec{r}_A)\, V_{NA}(\vec{r}_A)\, \varphi_\nu$

② NON-LOCAL PSEUDOPOTENTIALS :

KLEINMAN-BYLANDER



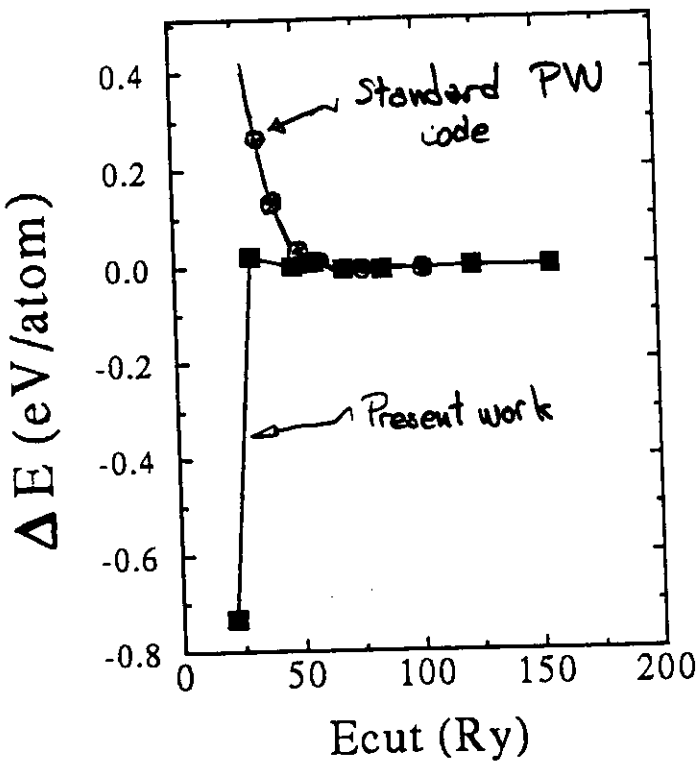
$$\langle \varphi_\mu | V_{NL}(i) | \varphi_\nu \rangle = \sum_k \langle \varphi_\mu | \chi^i_k \rangle\, \epsilon^i_k\, \langle \chi^i_k | \varphi_\nu \rangle$$

$\langle \varphi_\mu | \chi_k \rangle \longrightarrow$ TWO CENTER TABLES!

ENERGY CONVERGENCE VS. GRID SPACING

Troullier-Martins Pseudopotentials (PRB 43, 8861 (9

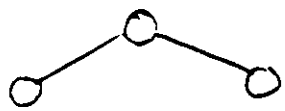
CARBON (diamond struct.)



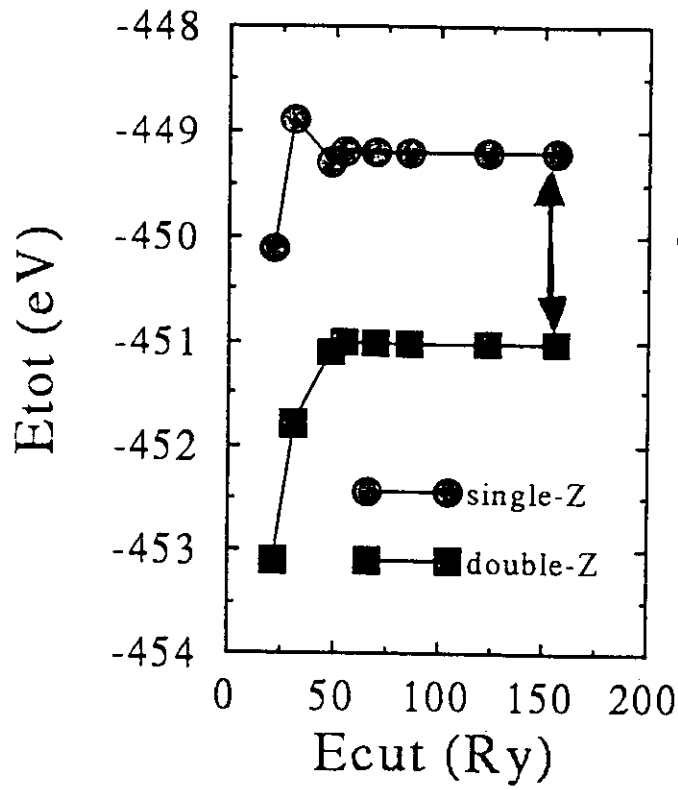
$$\Delta E = E(\epsilon_{cut}) - E(\text{converged})$$

ENERGY CONVERGENCE VS. GRID SPACING

DEPENDENCE ON BASIS SET SIZE



C_3 CLUSTER



0.6 eV/atom

s-Z: sp^3

d-Z: $s^2 p^6$

(Troullier-Martins Pseudopotentials)

A TEST CASE : THE H_2O MOLECULE

* Supercell $20 \times 20 \times 20$ a.u. ; $E_{cut} = 200$ Ry
* Troullier-Martins pseudopotentials (KB)
* PAO's

① Small R_c for PAO's $R_c = 3.8$ (Oxygen) ; 5.6 (Hydrog

GOOD GEOMETRIES , POOR ENERGIES (TOTAL E.)

Basis	d (Å)	θ (deg)	B.E. (eV)	ΔE (eV)
Single-ζ	1.082	96.1°	10.17	~ 4
Double-ζ	1.011	105.4°	11.48	~ 3
Triple-ζ + Pol	0.979	103.2°	12.63	~ 1.5
(PW)	0.96 - 0.978	103° - 105°	11.6	-

② Optimized R_c for PAO's (wrt. energy).

	Oxygen	Hydrogen
1st-ζ :	$R_c = 7.0$ Bohr	$R_c = 7.0$ Bohr
2nd-ζ :	$R_c = 5.0$	$R_c = 6.0$
Pol :	$R_c = 2.6$	$R_c = 2.1$

GOOD GEOMETRIES AND TOTAL ENERGIES.

Basis	d (Å)	θ (deg)	ΔE (eV)
Double-ζ	1.008	109.9°	~ 1
Double-ζ + Pol.	0.989	105.3°	~ 0.3
(PW)	0.96 - 0.978	103° - 105°	-

BASIS SETS — DIATOMIC MOLECULES

TABLE I. Bond lengths (in Å) calculated for some diatomic molecules using different bases. SZ: single-ζ pseudo-atomic orbitals with large cut-off radius (r_c = 6.2 a.u.); SZ(SR) same with short r_c (3.3 a.u. for H, 4.1 for C, 3.6 for N, and 3.2 for O); SZ(scaled) scales the SZ bases with scale factors determined variationally: 0.950 for C, 0.975 for N, 0.980 for O and 0.800 for H:. For CO and NO the scaling factors are found to be the same as for the dimer of each element; DZ(SV): split-valence double-ζ for long r_c orbitals; DZ(SR): Short r_c double-ζ bases.

	Experiment[22]	APW[22]	SZ	SZ(scaled)	SZ(SR)	DZ(SV)	DZ(SR)
H_2	0.741	0.767	0.928	0.772	0.789	0.773	0.727
C_2	1.244	1.249	1.425	1.348	1.332	1.279	1.262
N_2	1.098	1.098	1.283	1.255	1.194	1.123	1.125
O_2(LDA)	1.207	1.212	1.487	1.445	1.296	1.366	1.259
O_2(LSD)	1.207	—	1.406	1.388	1.284	1.293	1.241
CO	1.127	1.132	1.309	1.276	1.206	1.172	1.156
NO	1.148	1.148	1.409	1.376	1.252	1.233	1.234

TABLE II. Calculated bond lengths (in Å) for some diatomic molecules adding polarization orbitals to double-ζ (DZP) short range (SR) basis sets. r_c for the polarization orbitals minimize the total energy. In parenthesis, the relative error with respect to experiment.

	Exp.	100 Ry DZP(SR)	200Ry DZP(SR)
H_2	0.741	0.729 (1.49%)	0.726 (2.01%)
C_2	1.244	1.253 (0.74%)	1.250 (0.46%)
N_2	1.098	1.103 (0.45%)	1.092 (0.55%)
O_2(LDA)	1.207	1.215 (0.66%)	1.206 (0.08%)
O_2(LSD)	1.207	1.203 (0.32%)	1.197 (0.83%)
CO	1.127	1.117 (0.89%)	1.118 (0.75%))
NO	1.148	1.144 (0.31%)	1.142 (0.55%)

Double-ζ + Polariz^{n}

Δ = 5 %

TABLE III. Bond lenghts (in Å) for HCN using different basis sets.

	Exp.	SZ(SR)	DZ(SR)	DZ(SV)
d(HC)	1.066	1.136	1.070	1.083
d(CN)	1.153	1.211	1.159	1.174

TABLE IV. LDA results for the H_2O dimer using different basis sets. For notation see Ref. 23. Lenghts in Å and angles in degrees. PLW: plane-wave calculation. VWN: Vosko, Wilk and Nusair[25] functional for correlation. BE: Binding energy (Kcal/mol).

	SZ(SR)	DZ(SR)	DZP(SR)	SZ	DZ	DZP	PLW-VWN[23]	LCAO-VWN[24]	Exp[22]
r(O-O)	2.628	2.575	2.687	2.723	2.590	2.747	2.70	2.71	2.98±0.01
$r(O_a\text{-}H)$	1.012	0.971	0.976	1.049	0.999	0.986	0.961	0.980	
φ_a	105.6	110.1	106.1	108.7	112.2	106.7	106.2	104.7	—
$r(O_d\text{-}H_1)$	1.042	0.999	0.988	1.069	1.026	1.002	0.980	0.997	—
$r(O_d\text{-}H_2)$	1.007	0.972	0.971	1.041	1.000	0.981	0.961	0.977	—
φ_d	103.0	106.9	105.6	107.5	113.3	107.3	106.1	105.4	
θ_d	1.2	0.4	6.3	6.7	7.1	7.5	4.84	9.0	6±20
BE	19.39	20.39	19.37	14.21	15.54	11.01	9.06	9.16	5.44±0.7

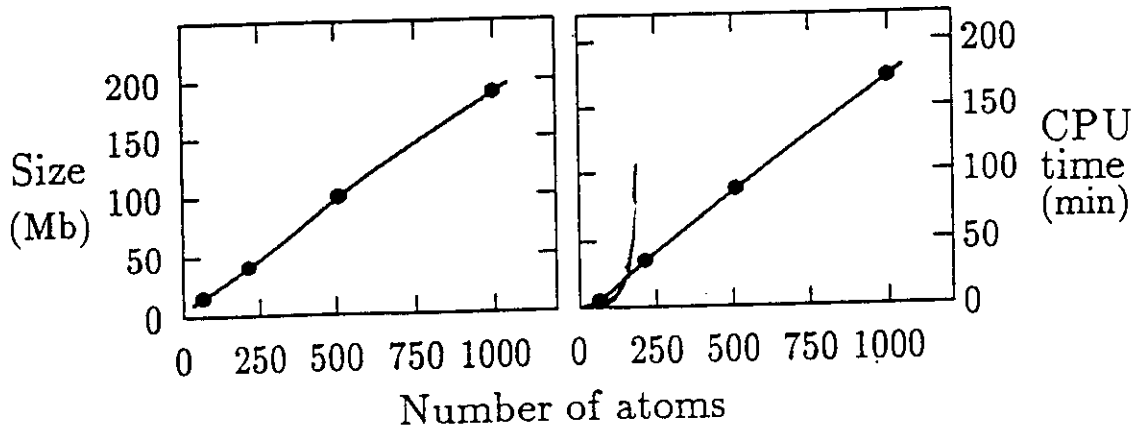
TABLE V. GGA[14] results for the H_2O dimer using different basis sets. For notation see Ref. 23. Lenghts in Å and angles in degrees. BE: Binding energy (Kcal/mol). B: Becke[26] functional for GGA. PW: Perdew-Wang91[27] functional for GGA.

	SZ(SR)	DZ(SR)	DZP(SR)	SZ	DZ	DZP	PLW-B[23]	LCAO-B[24]	LCAO-PW[24]
r(O-O)	2.663	2.641	2.715	2.837	2.752	2.902	2.98	2.886	2.877
$r(O_a\text{-}H)$	1.013	0.967	0.971	1.051	0.996	0.981	—	0.979	0.981
φ_a	105.2	109.2	105.8	107.2	111.2	106.2	—	106.2	104.4
$r(O_d\text{-}H_1)$	1.039	0.989	0.987	1.066	1.015	0.988	—	0.990	0.990
$r(O_d\text{-}H_2)$	1.008	0.967	0.967	1.045	0.997	0.980	—	0.977	0.979
ϕ_d	103.2	106.6	105.3	107.1	110.8	104.7	—	106.2	106.0
θ_d	-0.8	0.1	4.9	6.9	2.6	4.7	—	7.0	15.1
BE	15.17	15.92	15.57	10.16	11.76	7.36	4.90	4.51	5.993

ORDER-N:

PERFORMANCE

SILICON: CUBIC SUPERCELLS

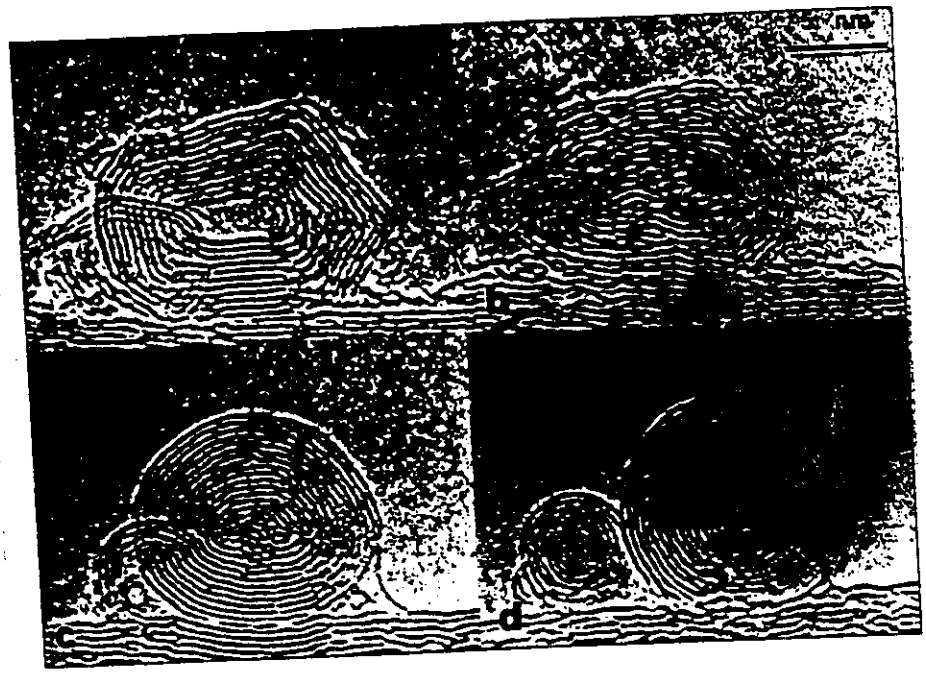


TIME: 1 SCF ITERATION

ON AN IBM POWERPC

(17 MFLOPS)

"FUCKY CANIONS"



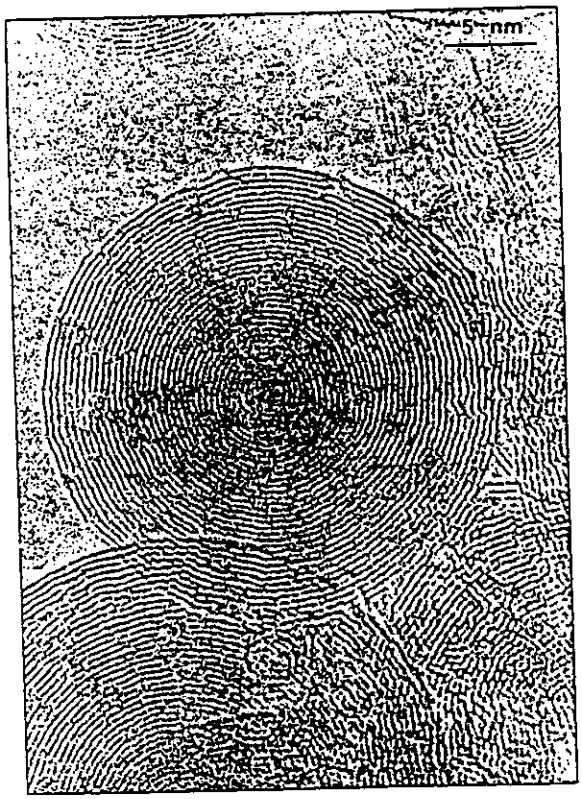


Figure 3. High-resolution electron micrograph of a quasi-spherical onionlike particle. Note the remarkable sphericity and the size of the innermost shell (≈1 nm). Graphitic layers are represented by dark lines. The distance between layers is ≈3.4 Å.[15]

W. Yang et al. PRB 49, 8526 (94
PRB 49, 11421 (94

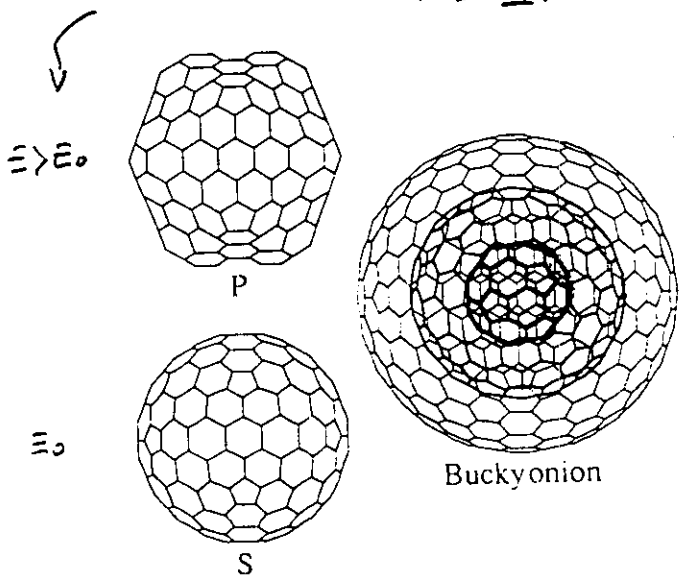


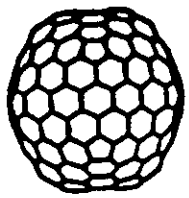
Figure 5. Geometric models of closed graphitic shells: truncated icosahedron (marked P), spherical shell (marked S), concentrical arrangement of the first three spherical fullerenes C_{60}, C_{240}, C_{540} (marked buckyonion).

D. Ugarte, MRS Bulletin Vol XIX, Nº
Nov 94.

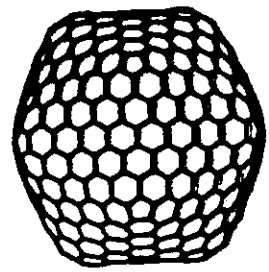
RELAXATION OF FULLERENES

* SCF - LDA *

C_{60}



C_{240}



C_{540}

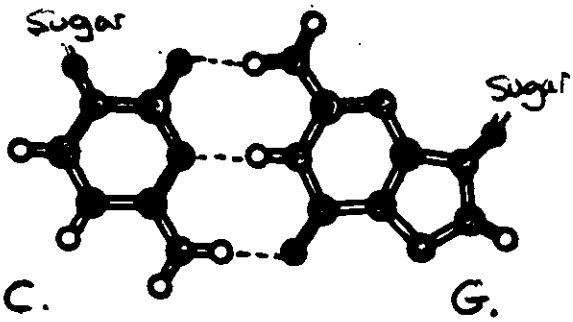
DYNAMICAL QUENCHING (STARTING FROM ITOH et al., PRB 53 (96)

C_{60} :	EXP.	THIS METHOD	OTHER LDA
SINGLE BOND	1.45 ± 0.015	1.472	1.43 - 1.45
DOUBLE BOND (Å)	1.40 ± 0.015	1.416	1.38 - 1.40

TROULLIER & MARTINS, PRB 46, 1754 (92) & REF.

↳ YANNONI et. al. J. AM. CHEM. SOC. 113, 3190 (91)

TIME STEPS:	100 - 200
SCF CYCLES / TIME STEP:	~ 5
CG ITER / SCF CYCLE:	~ 20

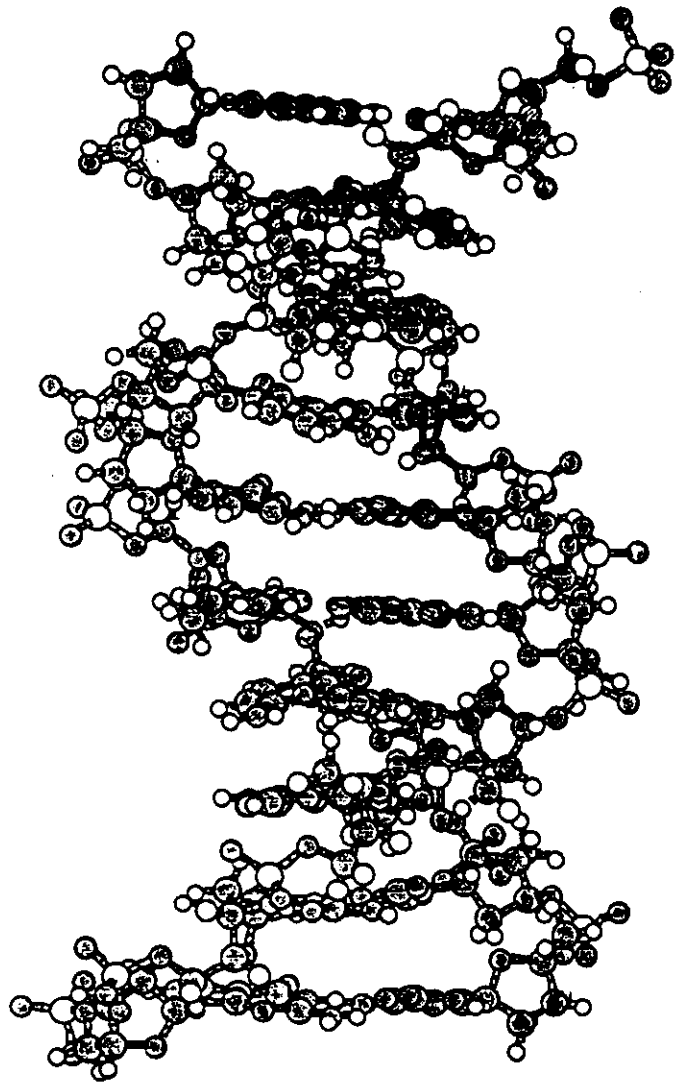


644 atoms

Length ~ 34 Å

ϕ ~ 20 Å

- Initial positions: X-ray diffraction on microcrystalline samples.
- Dry DNA.



GC10-DNA Segment

DNA GC-10 SEGMENT

- DOUBLE HELIX, 10 BASE PAIRS (GOANINE - CYTOSINE)

  ~650 ATOMS H, C, N, O, P (Periodic)

- MINIMAL (SP^3) BASIS (SINGLE-Z) 

- LDA (Perdew-Zunger) 

- Trullier-Martins Pseudo potentials.

- E_{cut} = 120 Ry (for the charge density)

  $\Delta E_{(200Ry - 100Ry)} \simeq 0.5$ meV/atom.

- LOCALIZED WANNIER FUNCTIONS: $R_c = 4.0$ Å

  $\Delta E_{(O(N)-diag)} \simeq 1$ meV/atom

  $\Delta F_{(O(N)-diag)} \simeq 0.01$ eV/Å

- MEMORY: ~500 Mb HP-C110 CPU time ~ 10 days
  (Relaxation !!) 400 MD steps

- NEAREST LOCAL MINIMUM Sugar groups in opposite sides

  $\sigma = \sqrt{\frac{\sum_i (\vec{r}_i^{th} - \vec{r}_i^{exp})^2}{N}} \approx 0.23$ Å

  $R_{exp} = 10.70$ Å $R_{th} = 10.61$ Å