



INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE



**WINTER COLLEGE ON "MULTILEVEL TECHNIQUES IN
COMPUTATIONAL PHYSICS"**

**Physics and Computations with Multiple Scales of Lengths
(21 January - 1 February 1991)**

H4.SMR 539/15

***Introduction to (Some) Modern Methods
for Electronic-Structure Calculations***

**S. Baroni
SISSI
Trieste. Italy**

INTRODUCTION TO (SOME) MODERN METHODS
FOR ELECTRONIC-STRUCTURE CALCULATIONS

Stefano Baroni
SISSA - TRIESTE

Purpose: Predict measurable properties of real materials using microscopic ingredients only (i.e. electrons, ions, and their interactions).

Systems:

- o Atoms
- o Molecules
- o Clusters & Polymers
- o Solids

Tools:

- o Density-Functional Theory
- o Pseudopotentials
- o Iterative methods applied to Quantum Mechanics.

First-Principles Study of Real Materials

Theoretical tools:

- **DFT** Density-Functional Theory.
- **LDA** Local-Density Approximation.
- **MBPT** Many-Body Perturbation Theory.
- **CP** Car-Parrinello method.
- **LRT** Linear-Response Theory.

Accessible Properties:

- **DFT + LDA:** Electronic ground-state properties.
 - Electron-density distribution.
 - Microscopic atomic geometries.
 - Cohesive energy.
 - Structural phase transitions.
 - ...
- **CP:** Dynamical properties.
 - Liquid and amorphous semiconductors.
 - Clusters.
 - Impurities.
 - Surfaces.
 - ...
- **LRT:** Electronic response to static perturbations.
 - Phonon dispersions.
 - Elastic properties.
 - Dielectric constants.
 - Piezoelectric properties.
 - ...
- **MBPT:** Electronic excited-state properties.
 - Electron and hole quasi-particle bands.
 - Optical properties.
 - ...

summing the individual band charge densities

$$(3) \quad \rho_{\text{tot}}(\mathbf{r}) = \sum_n \rho_n(\mathbf{r}).$$

In fig. 6, the individual charge densities for the four valence bands of Si (spin-orbit interactions are ignored) are given. Figure 7 contains the total charge density and a comparison with the subsequent analysis based on the measured density obtained using X-ray scattering. The agreement is excellent, and these plots illustrate the pile-up of charge in the covalent bond of Si.

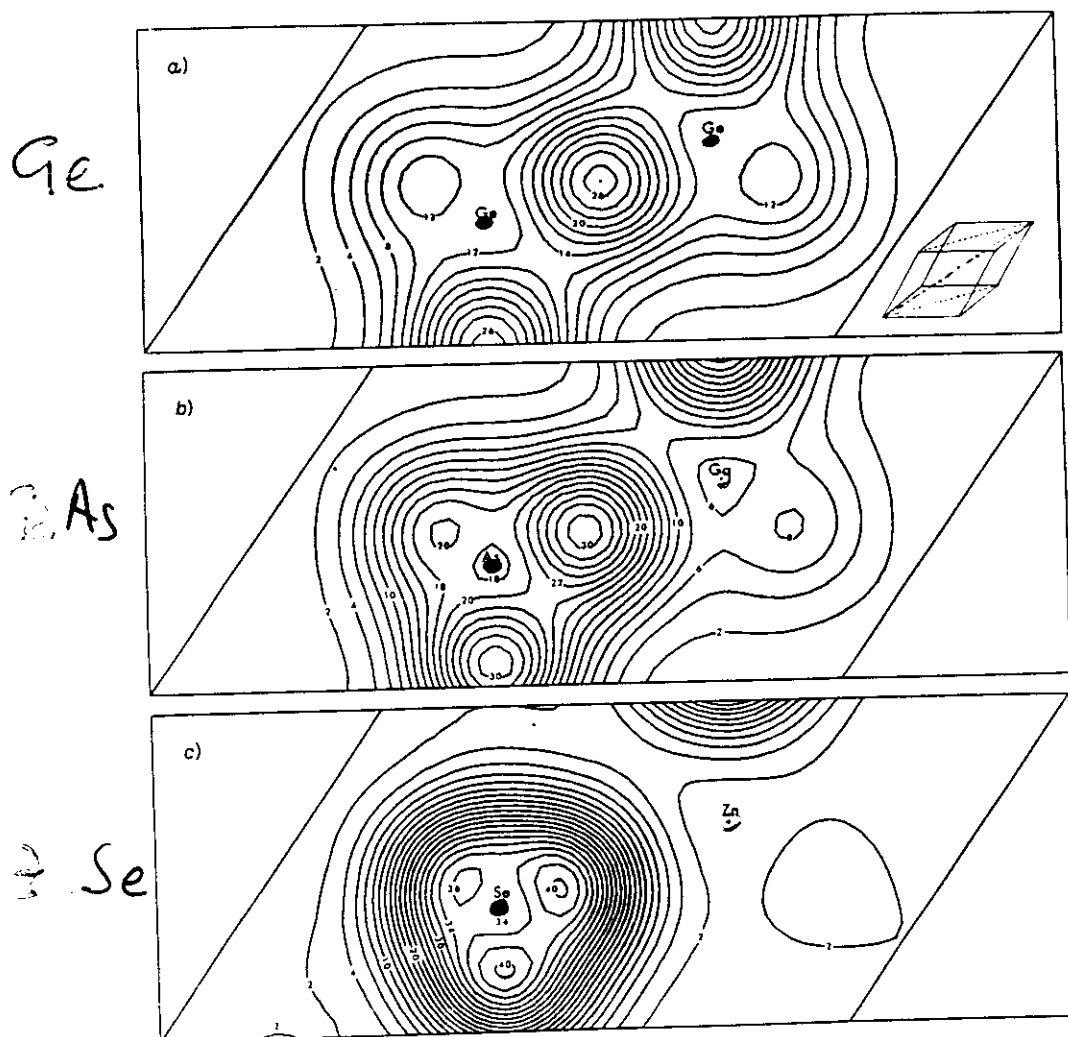


Fig. 8. - Total calculated valence charge density for a) Ge, b) GaAs and c) ZnSe. The contours are in units of e/Ω_c , where Ω_c is the unit-cell volume.

entials are
through
nonlocal
resents the
arly illus-

energy, which is evaluated by using Ewald-type summations. Explicit forms for these terms are given in ref. [28].

The total energy must be calculated very precisely if it is to be used to compute structural and vibrational properties. An estimate of the precision requirements for the total energy are $0.01 \text{ Ryd} \cdot \text{atom}^{-1}$ for the cohesive energy, $0.001 \text{ Ryd} \cdot \text{atom}^{-1}$ for the lattice constant or bulk moduli and $0.0001 \text{ Ryd} \cdot \text{atom}^{-1}$ for phonon frequencies. These requirements can be satisfied using pseudopotentials. One advantage of this method is the fact that the energies of core electrons which are of the order of $-10^3 \text{ Ryd} \cdot \text{atom}^{-1}$ are not carried along and then subtracted out in structural calculations. In the pseudopotential model when the core and valence electrons are far apart, the crystal energy is approximately $-10 \text{ Ryd} \cdot \text{atom}^{-1}$.

In fig. 12, the total energy $E(v)$ for Si is given as a function of volume (or lattice constant) assuming seven different crystal structures. The diamond structure lies lowest in energy. The minimum volume and curvature of $E(v)$ near the minimum determine the lattice constant and bulk modulus for each structure. The cohesive energy can be evaluated by comparing the energy for the solid at the volume corresponding to the $E(v)$ minimum and at a volume

momentum
on potential.

cal-density
possible to
functional
of the total
computing
accurately

momentum
g the total
band struc-
which stand-

omic kinetic
the electron-
potential, the
is computed
re Coulomb

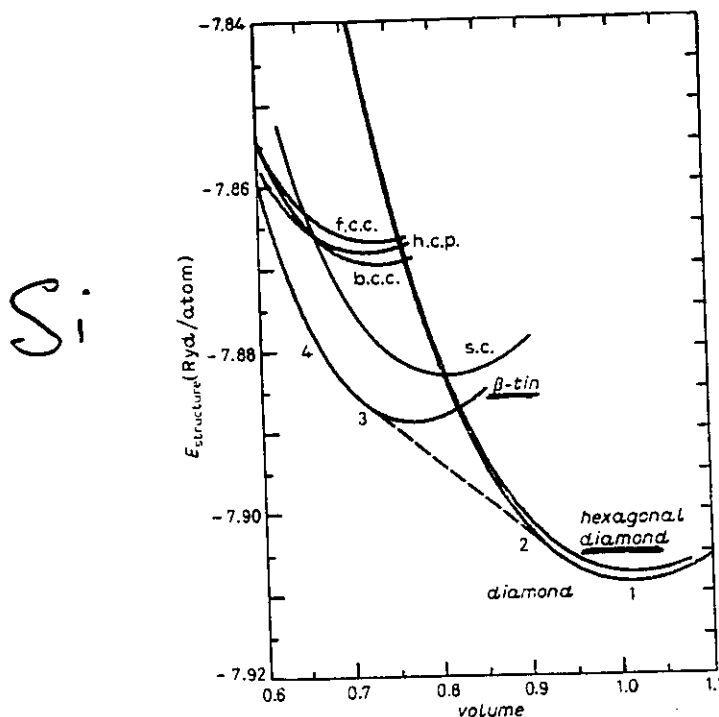
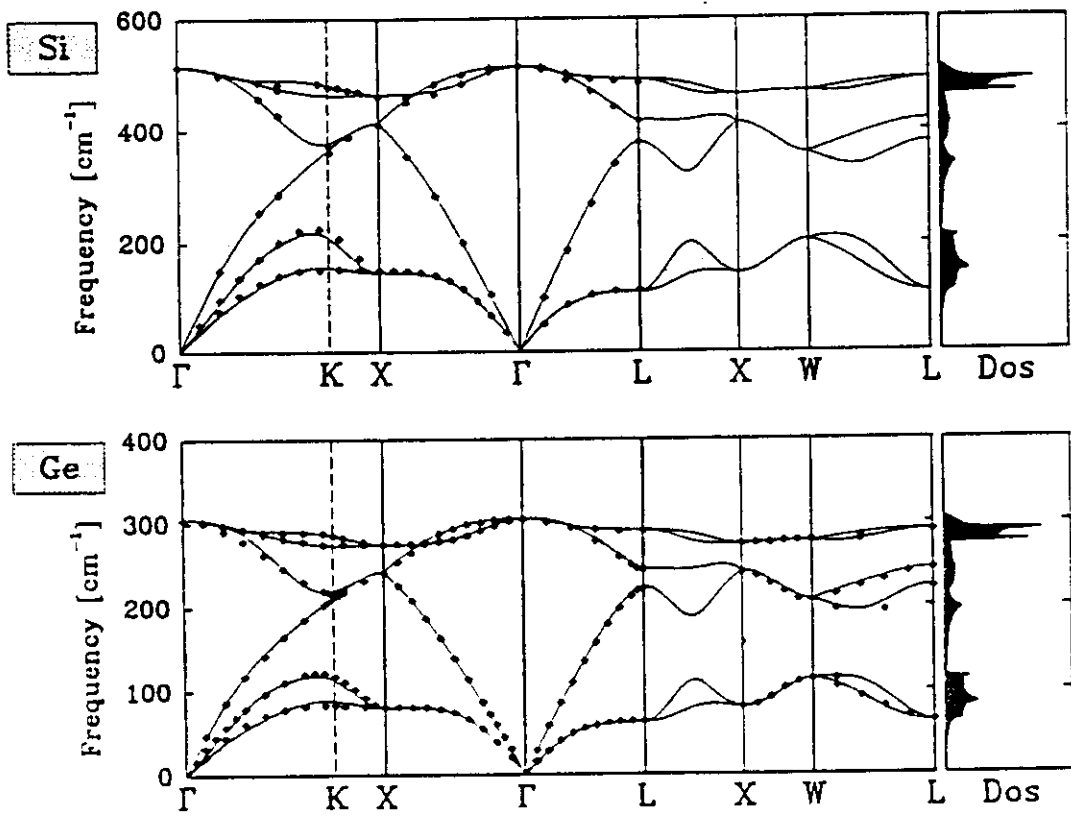


Fig. 12. - Total-energy curves for various assumed crystal structures of Si as a function of volume normalized to the observed volume. The dashed line is the common tangent between the diamond and white-tin phases.

TABLE I. Equilibrium lattice parameter (a , [a.u.]) used in the present calculations, and calculated Born effective charges (Z^*), and static dielectric constants (ϵ_∞).

	Si	Ge	GaAs	AlAs	GaSb	AlSb
a	10.20 (10.26)	10.60 (10.68)	10.60 _s (10.68)	10.60 _s (10.69)	11.40 (11.49)	11.51 (11.58)
Z^*	- (-)	- (-)	2.07 (2.07)	2.17 (2.18)	1.73 (1.88)	1.91 (2.18)
ϵ_∞	13.6 (12.1)	18.7 (16.5)	12.3 (10.9)	9.2 (8.2)	18.1 (14.4)	12.2 (10.2)

a few %
} $\approx 10\%$



a few %

Figure 1. Calculated phonon dispersions and density of states of elemental semiconductors, Si and Ge. Experimental data are denoted by diamonds (from Reis. 28 and 29).

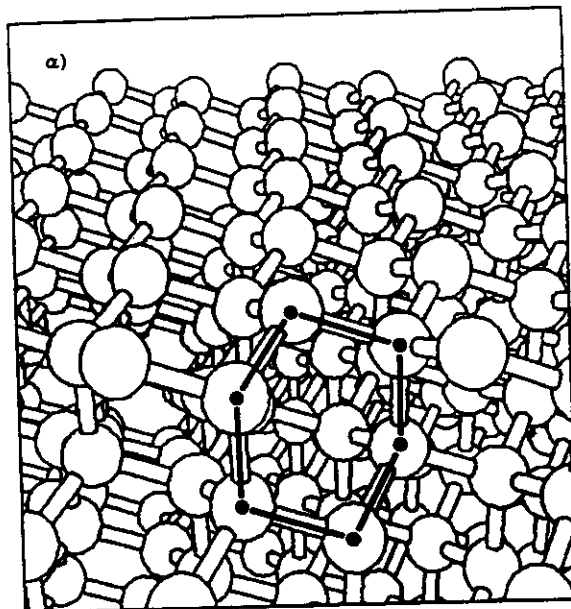
Similar agreement for other semiconductors

COHEN

surface
displace-
surface
al side,
that it
energy
model,
instead

curve in agreement with experiment? A proposal [40] which appears to have many of the desired properties is the π -bonded chain model. The major objection to this model when it was first introduced was that several bonds needed to be broken to produce the chain geometry, and this would be ener-

Si (111)
Ideal



buckling
n atomic

istence of
orists to
i surface
h-quality
on which
uld be a
remained
1) was a
simplest
electron
mic units
itions are
structures
dering on
e a stable
uestion of
attice con-

Si (111)
Reconstructed

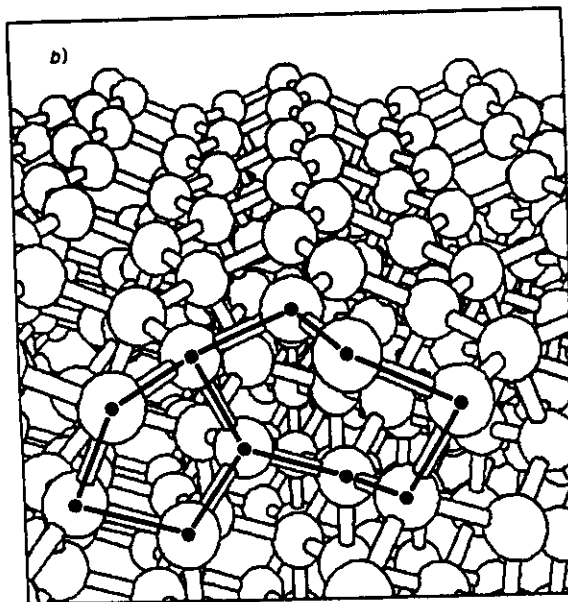


Fig. 22. - a) represents the ideal geometry for Si(111), b) represents the π -bonded chain model for Si(111).

(1) lattice
dispersion

QUANTUM MECHANICS & DFT

SCHRÖDINGER EQUATION:

$$\left(\sum_i \left(-\Delta + V_{\text{ext}}(r_i) \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \right) \psi_{\alpha}(r_1, \dots, r_n) = E_{\alpha} \psi_{\alpha}(r_1, \dots, r_n)$$

$V_{\text{ext}} \rightarrow \psi_{\alpha} \rightarrow$ Physical Properties: $\theta_{\alpha} = \langle \psi_{\alpha} | \theta | \psi_{\alpha} \rangle$

$$\theta = \theta[V_{\text{ext}}]$$

$$n(r) = n[V_{\text{ext}}](r)$$

DENSITY-FUNCTIONAL THEORY

$n(r) \rightarrow V_{\text{ext}}(r) \rightarrow$ Physical Properties

$$E[V_{\text{ext}}] = \min_{\int n(r) = N} \left(F[n] + \int n(r) V_{\text{ext}}(r) dr \right)$$

DENSITY-FUNCTIONAL THEORY

Purpose: prove that:

- $n(r) \rightarrow V(r)$
- $E[V] = \min_{\int n(r) = N} \left(F[n] + \int V(r) n(r) dr \right)$

Proof:

$$\text{Let } H = T + V + W \rightarrow \psi$$

$$H' = T + V' + W \rightarrow \psi'$$

Suppose $\exists V' \rightarrow \psi' \rightarrow n'(r) \neq n(r)$

$$E' = \langle \psi' | H' | \psi' \rangle < \langle \psi | H | \psi \rangle$$

||

$$\langle \psi | H | \psi \rangle + \int (V'(r) - V(r)) n(r) dr$$

$$E' = E + \int (V'(r) - V(r)) n(r) dr$$

$$E = E' + \int (V(r) - V'(r)) n(r) dr$$

$$E + E' < E + E' \quad !!!$$

DENSITY-FUNCTIONAL THEORY - II

$$n(r) \rightarrow V \rightarrow \psi \rightarrow \Theta = \langle \psi | \Theta | \psi \rangle$$

In particular:

$$\langle T + W \rangle \equiv F[n(r)]$$

Define:

$$E[n] = F[n] + \int V_0(r) n(r) dr$$

Clearly,

$$E[n_0] = E_0$$

$$\text{If } n \neq n_0 \rightarrow V \neq V_0 \rightarrow \psi \neq \psi_0$$

$$\begin{aligned} E[n] &= \int n V_0 dr + \langle \psi | T + W | \psi \rangle \\ &= \langle \psi | H_0 | \psi \rangle \\ &> E[n_0] \end{aligned}$$

DENSITY-FUNCTIONAL THEORY

$$E_0 = \min_{\int n(r) = N} \left(F[n] + \int n(r) V(r) dr \right)$$

$$\delta \left(E[n] - \mu \int n(r) dr \right) = 0$$

\Downarrow

$$\frac{\delta F}{\delta n(r)} + V(r) = \mu$$

$$F[n] = T_0[n] + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' + E_{xc}[n]$$

$$\frac{\delta T_0}{\delta n} + \underbrace{\int \frac{n(r')}{|r-r'|} dr'}_{V_{scf}(r)} + \frac{\delta E_{xc}}{\delta n(r)} + V(r) = \mu$$

$$n(r) = \sum_i |\psi_i(r)|^2 \theta(\epsilon_i - \epsilon_F)$$

$$\left(-\Delta + V_{scf}(r) \right) \psi_i(r) = \epsilon_i \psi_i(r)$$

THE LOCAL-DENSITY-APPROXIMATION

$$E_{xc}[n] \approx \int \epsilon_{xc}(n(r)) n(r) dr$$

$$\frac{\delta E_{xc}}{\delta n(r)} \approx \epsilon_{xc}(n(r)) + n(r) \frac{d\epsilon_{xc}}{dn} \equiv v_{xc}(r)$$

KOHN-SHAM EQUATIONS

$$\left(-\Delta + V_{\text{EXT}}(r) + \int \frac{n(r')}{|r-r'|} dr' + v_{xc}(r) \right) \psi_i(r) = \epsilon_i \psi_i(r)$$

$$n(r) = \sum_i |\psi_i(r)|^2 \vartheta(\epsilon_i - \epsilon_F)$$

$$E[n] \equiv E[\{\psi_i\}] =$$

$$-\sum_i \vartheta(\epsilon_i - \epsilon_F) \int \psi_i^* \Delta \psi_i + \int n(r) V(r) dr$$

$$\sim \sim + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' + \int \epsilon_{xc}(n(r)) n(r) dr$$

FORCES

Suppose

$$V(r) = V_\lambda(r)$$

where

$$\frac{dE}{d\lambda} \quad ???$$

$$\lambda \rightarrow \lambda + \Delta\lambda$$

$$\left\{ \begin{array}{l} V_\lambda \rightarrow V_\lambda + \Delta\lambda V'_\lambda \\ n_\lambda \rightarrow n'_\lambda + \Delta\lambda n''_\lambda \end{array} \right.$$

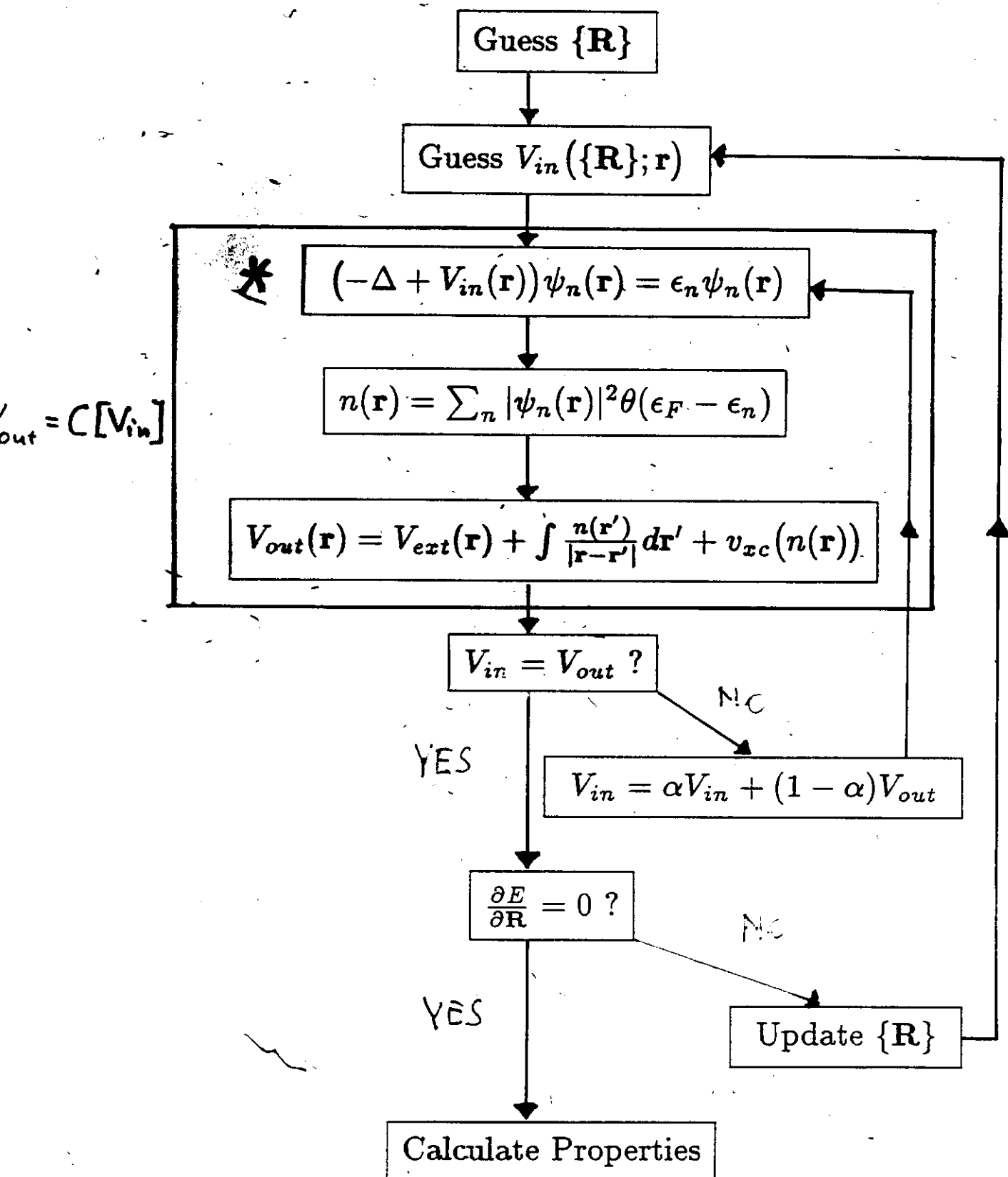
$$\int n'_\lambda(r) dr = 0$$

$$E_{\lambda+\Delta\lambda} = \min_{\int n'_\lambda dr = 0} \left(\overbrace{F[n_\lambda]}^{E_\lambda} + \int V_\lambda n_\lambda \right)$$

$$+ \Delta\lambda \left[\int n'_\lambda \left(\frac{\delta F}{\delta n_\lambda} + V'_\lambda \right) + \int V'_\lambda n_\lambda \right] + \mathcal{O}(\Delta\lambda^2)$$

$$\frac{dE}{d\lambda} = \int dr \frac{dV_\lambda(r)}{d\lambda} n_\lambda(r)$$

How does one do in practice?



Operation Count: \$\$\$ $\approx N_R \times N_{it} \times \C

THE PLANE-WAVE PSEUDOPOTENTIAL METHOD

- Use PSEUDOPOTENTIALS to get rid of core electrons which are chemically inactive.

$$V_{\text{ext}}(r) = \sum_R \sum_{\text{PS}} v_{\text{PS}}(r-R)$$

ionic potentials having only valence states

- Use PLANE WAVES to expand wavefunctions

$$\psi_n(r) = \sum_q e^{i q \cdot r} C_n(q)$$

$$\sum_{q'} H_{qq'} C_n(q') = \epsilon_n C_n(q)$$

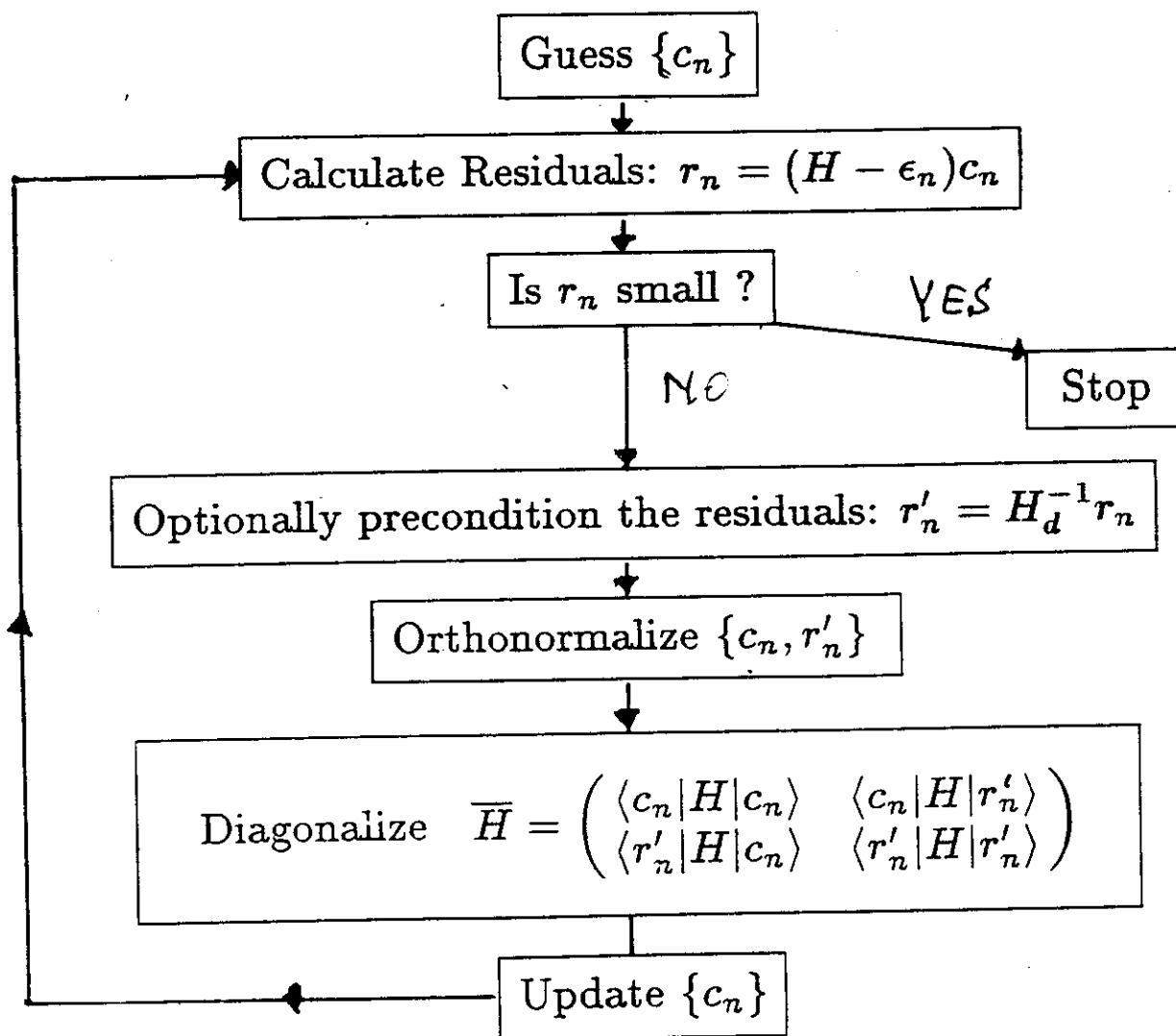
$$H_{qq'} = q^2 \delta_{qq'} + \tilde{V}_{\text{SCF}}(q-q')$$

Diagonalizing the Hamiltonian

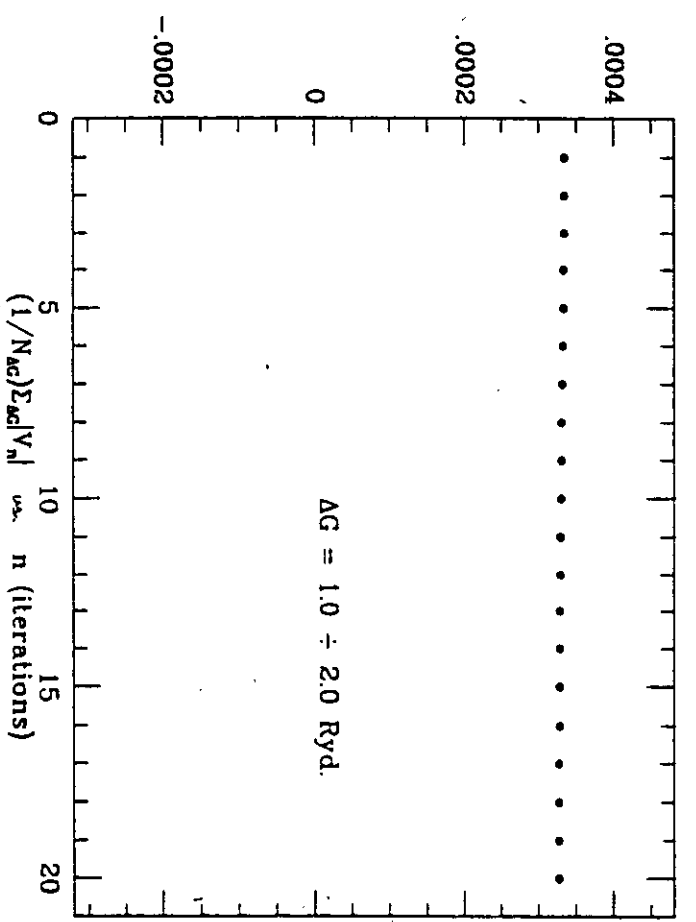
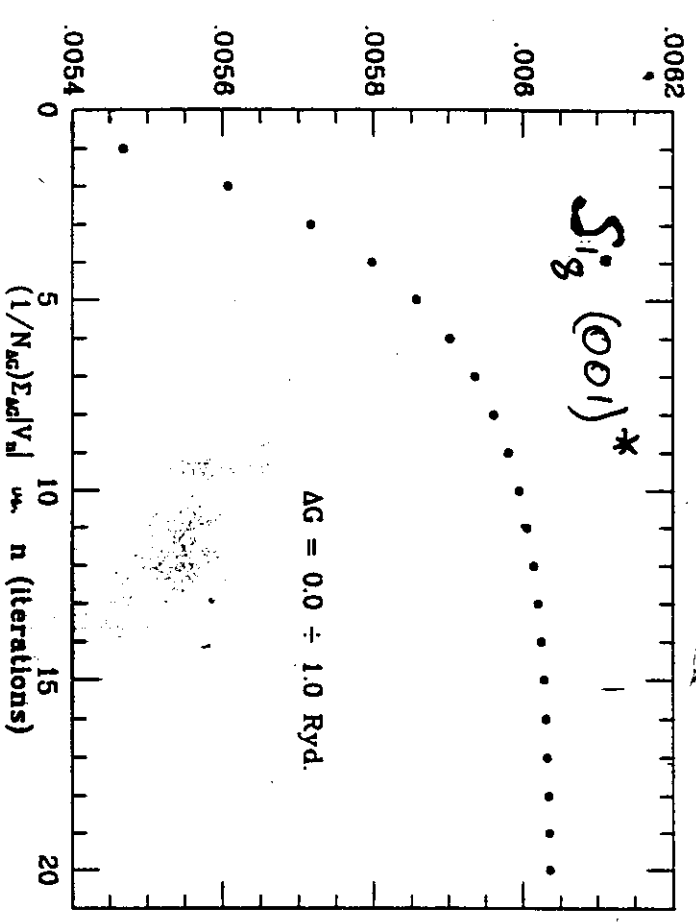
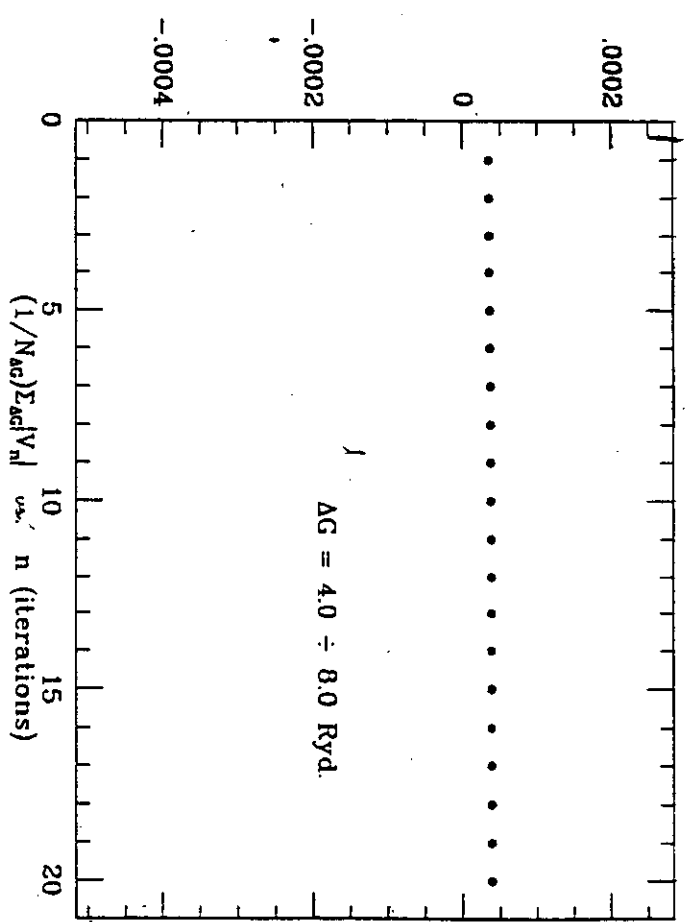
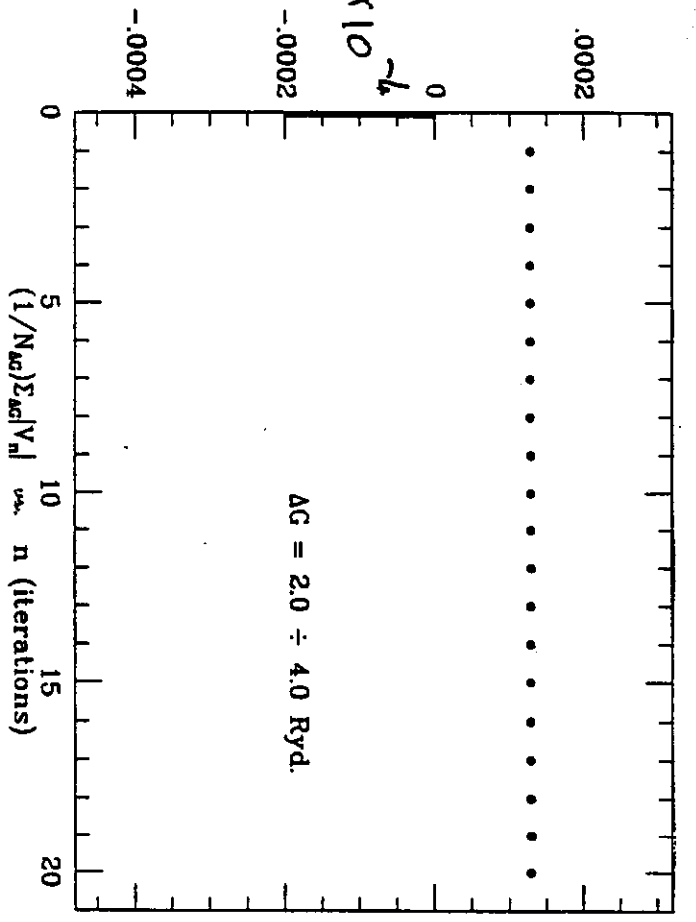
Factorization Methods

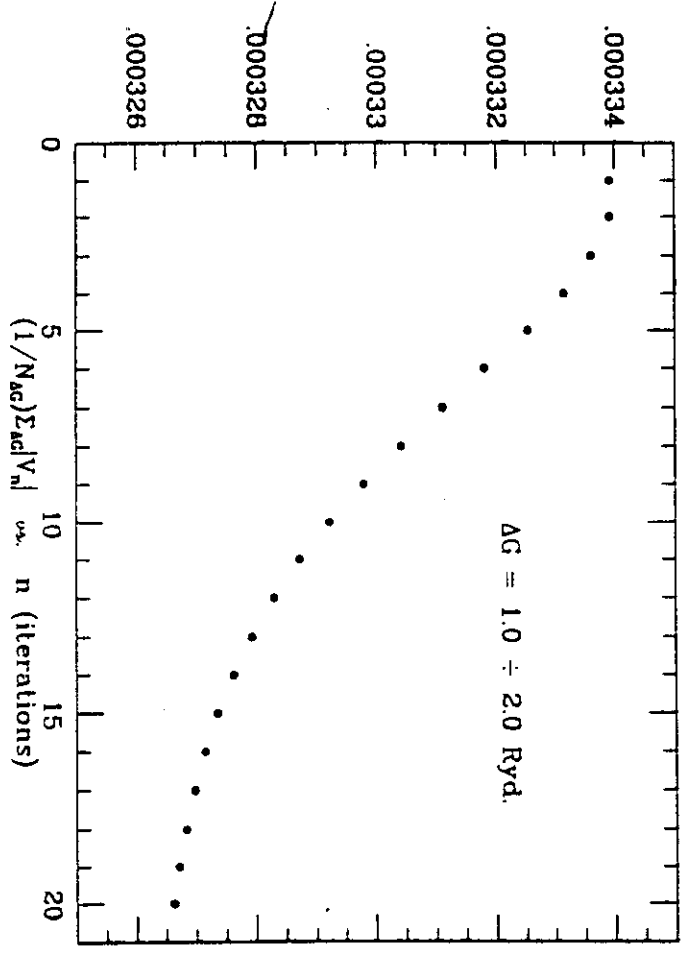
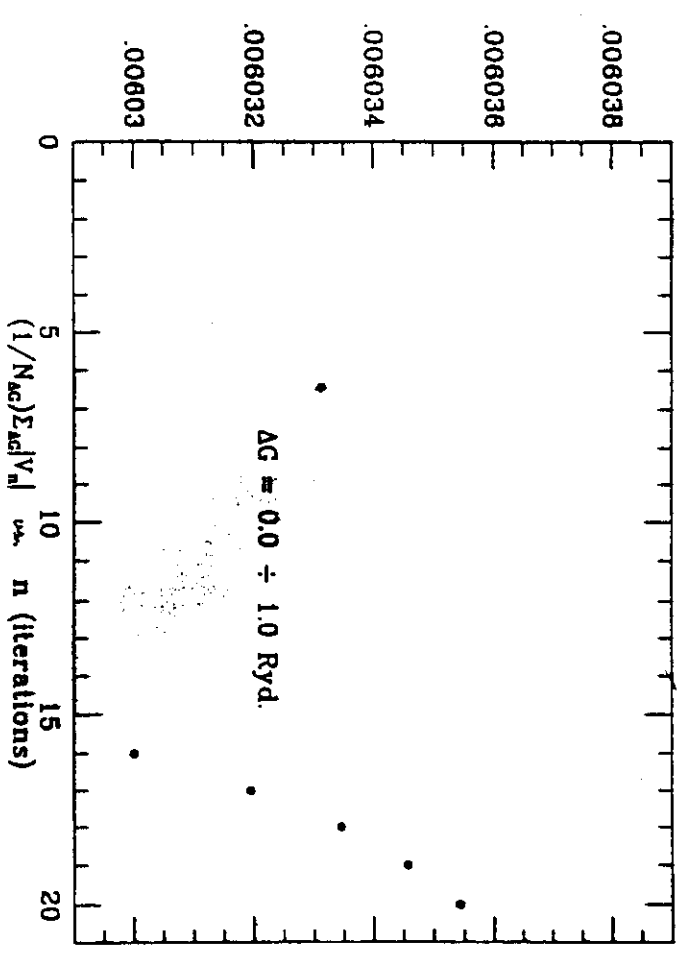
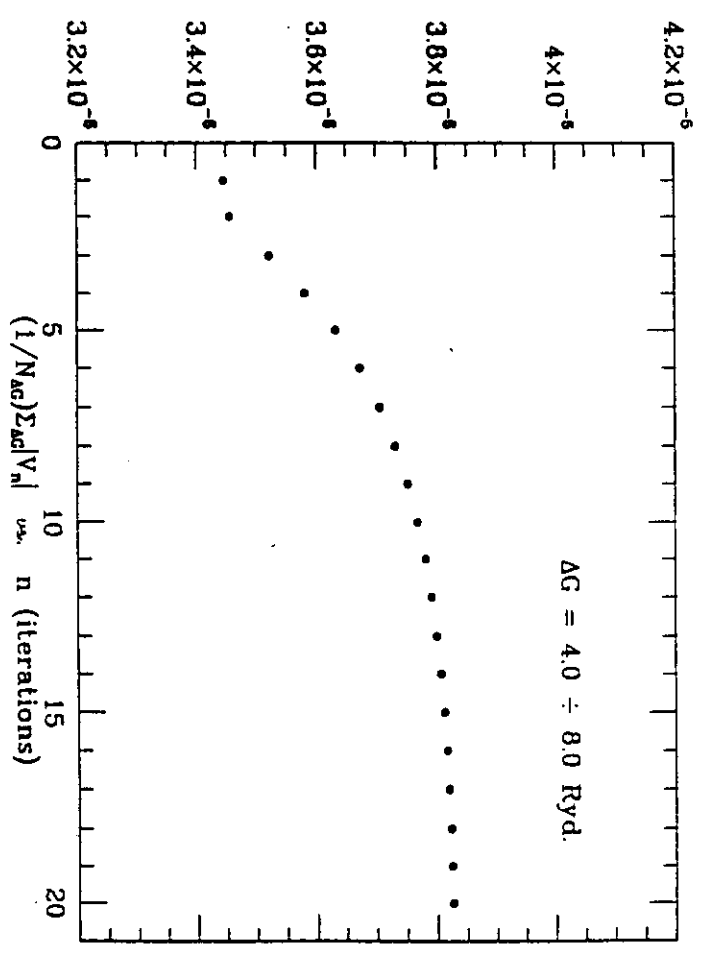
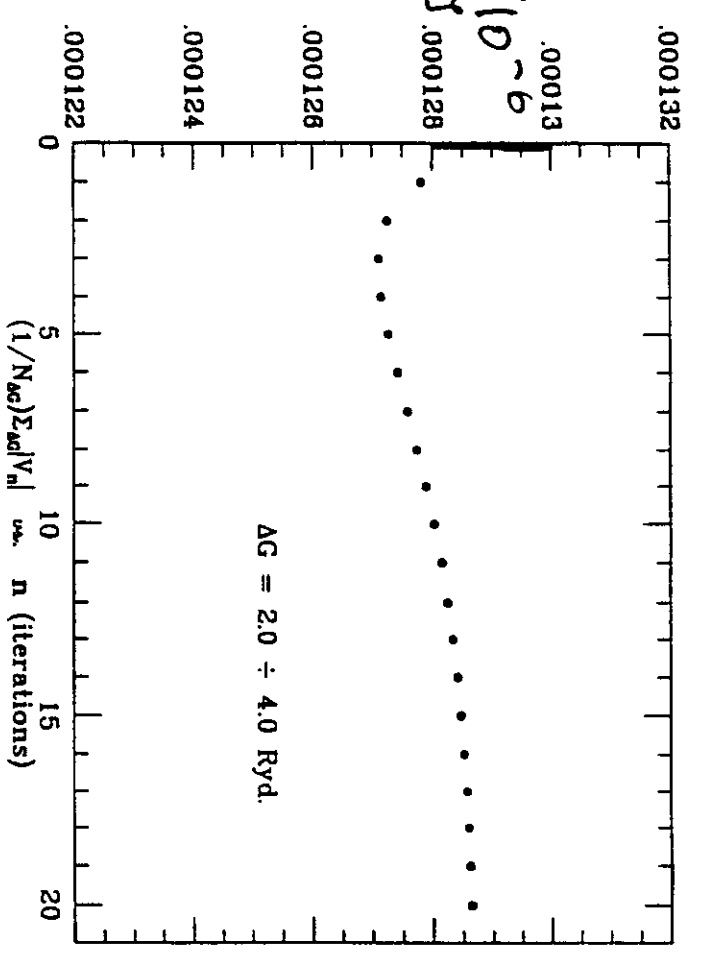
- Operation count: \$\$\$ $\propto \alpha N_G^3 + \beta N_{el} N_G^2$
 - $N_{el} \propto N_{at}$
 - $N_G \propto \text{Volume} \propto N_{at}$
 - \$\$\$ $\propto N_{at}^3$

Iterative Methods



- Operation Count:
\$\$\$ $\approx N_{it} (\alpha N_{el} N_G (\log N_G) + \beta N_{el}^2 N_G) \propto N_{at}^3$





ACCELERATING THE CONVERGENCE - II

$$V_e^h = C^h (V_e^h + V_{ext}^h)$$

$$\bar{V}_e^h = C^h (\bar{V}_e^h + V_{ext}^h) + R^h$$

$$V_e^h = C^h (V_e^h + V_{ext}^h) + \bar{V}_e^h - C^h (\bar{V}_e^h + V_{ext}^h) - R^h$$

$$h \rightarrow H$$

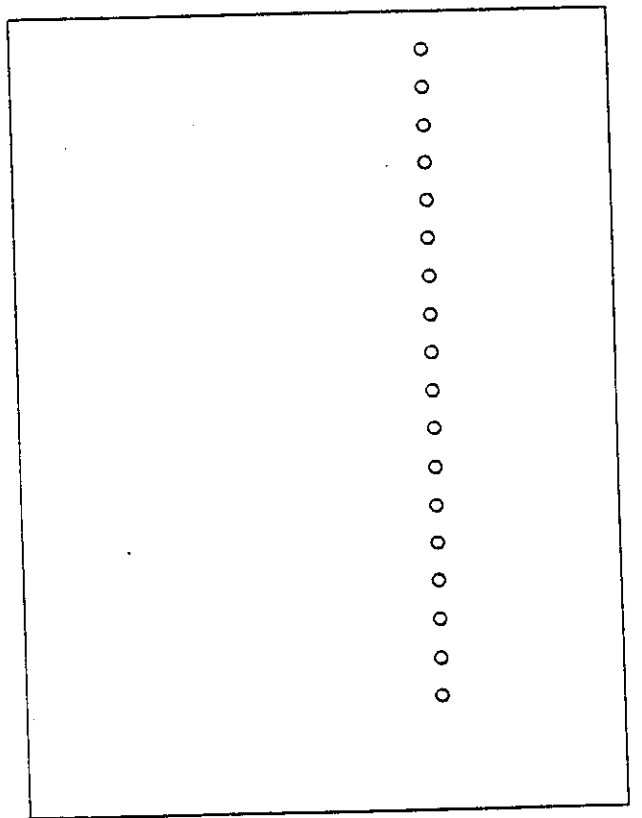
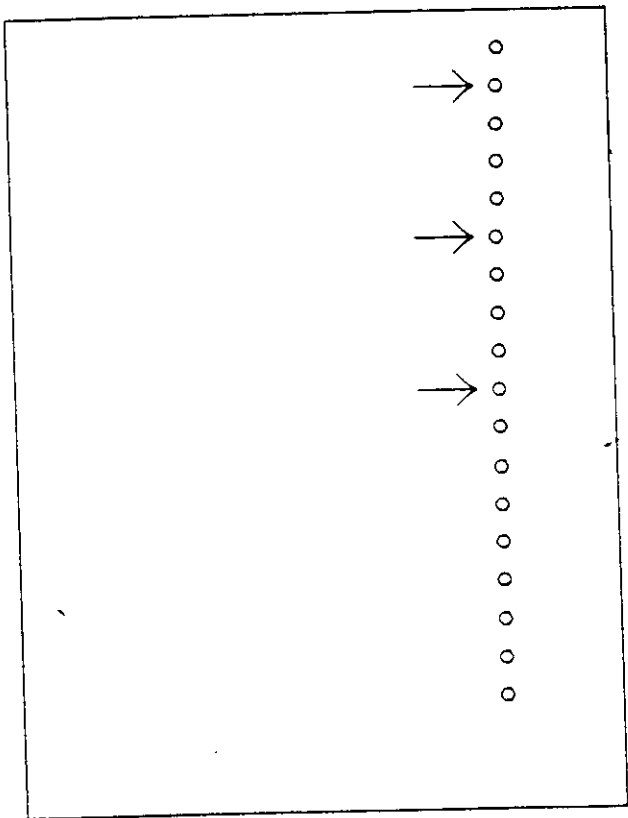
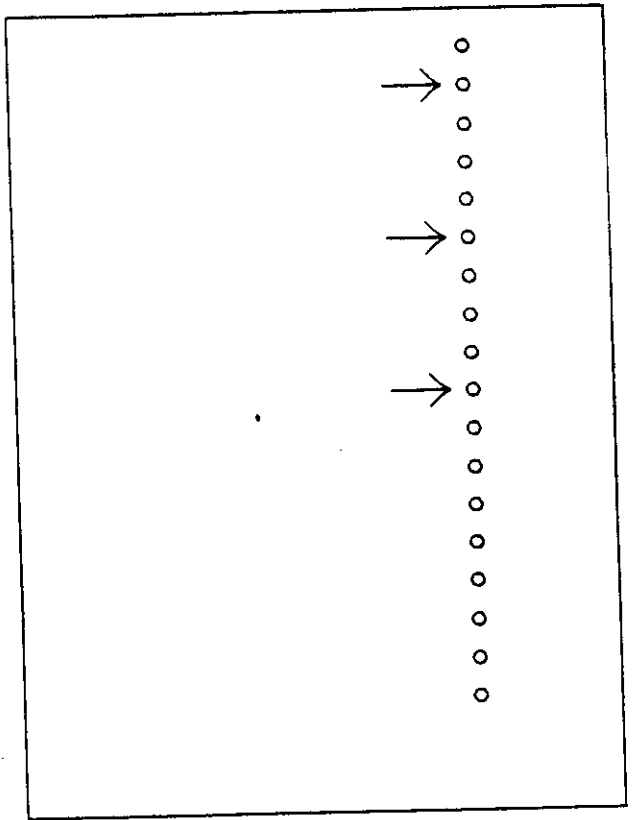
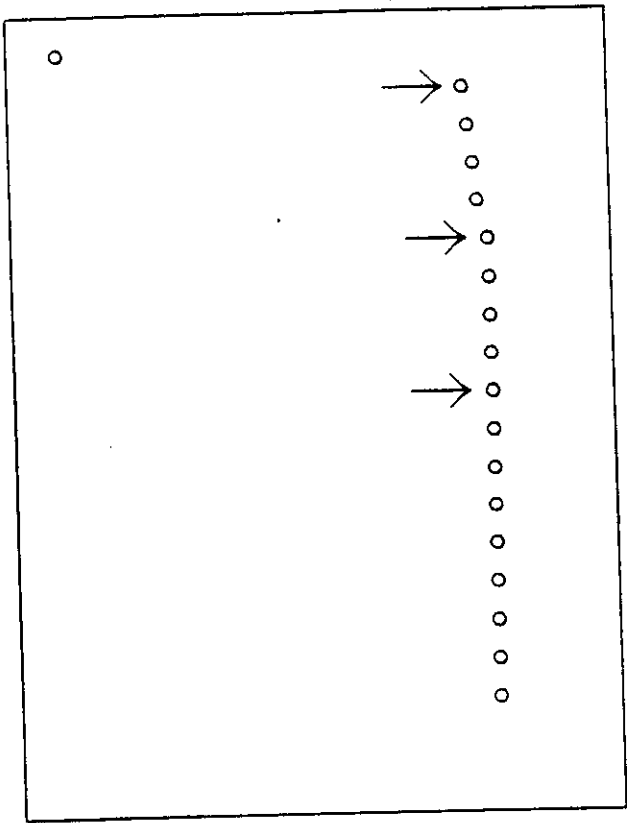
$$V_e^H = C^H (V_e^H + V_{ext}^H) + I_h^H \bar{V}_e^h - C^H (I_h^H \bar{V}_e^h + V_{ext}^H) - I_h^H R^h$$

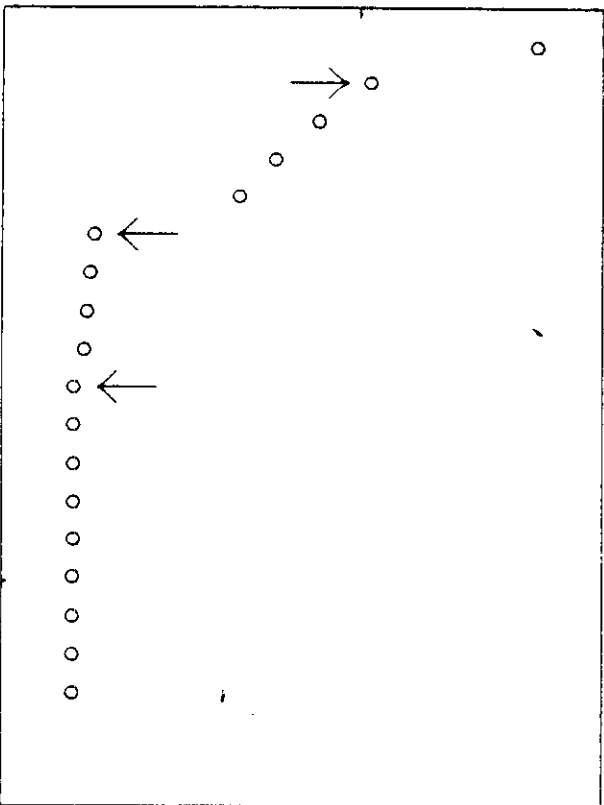
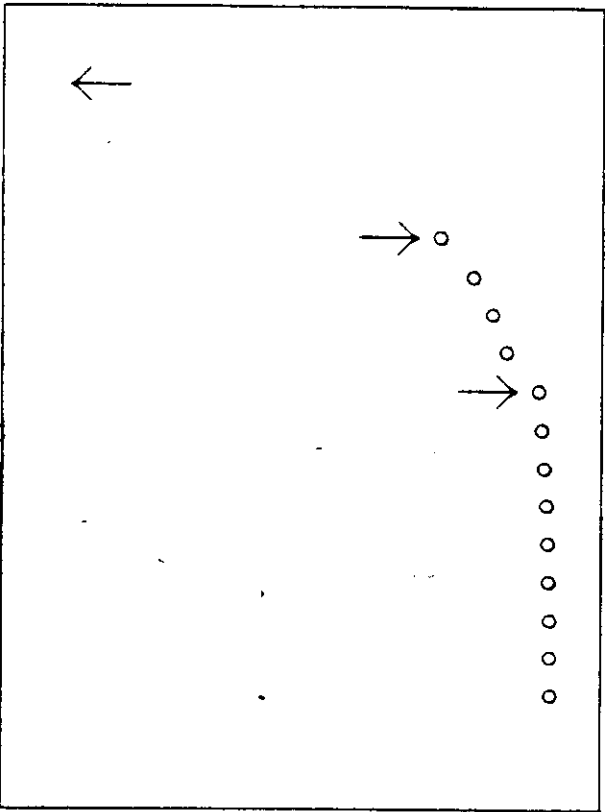
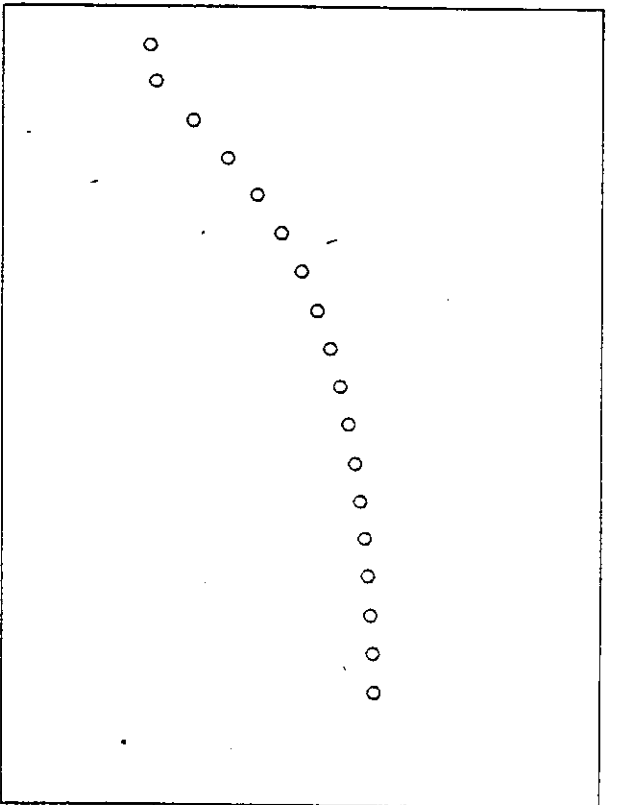
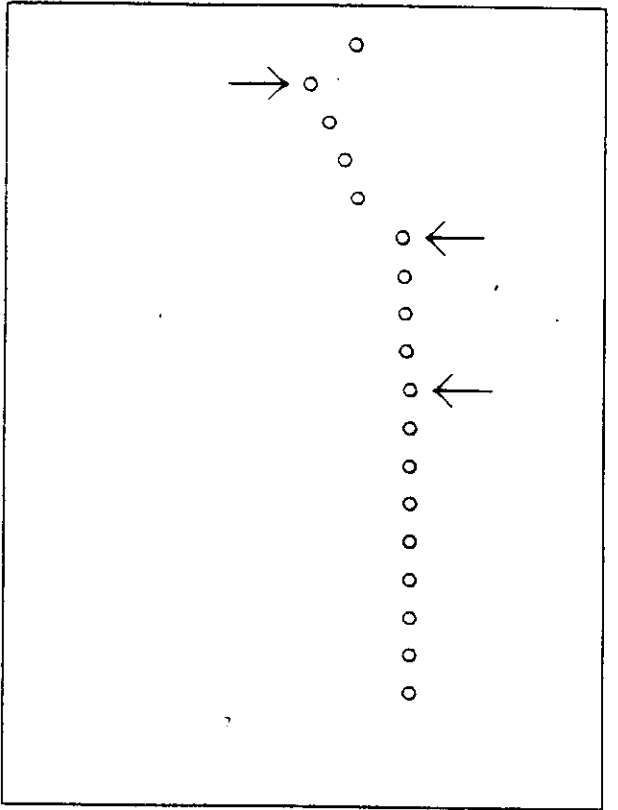
ΔV_{ext}^H

$$\underbrace{V_e^H - \Delta V_{ext}^H}_{\tilde{V}_e^H} = C^H \left(\underbrace{V_e^H - \Delta V_{ext}^H}_{\tilde{V}_e^H} + \underbrace{V_{ext}^H + \Delta V_{ext}^H}_{\tilde{V}_{ext}^H} \right)$$

$$\tilde{V}_e^H = C^H (\tilde{V}_e^H + \tilde{V}_{ext}^H)$$

$$V_e^h \approx \bar{V}_e^h + I_h^h \left(\tilde{V}_e^H + \Delta V_{ext}^H - I_h^H \bar{V}_e^h \right)$$





CAR-PARRINELLO-LIKE APPROACHES

- Electronic Structure Calculations as Optimization problems
- Dynamics

$$E[\Psi_n] = -\sum_n \int \Psi_n^*(r) \Delta \Psi_n(r) dr + \\ + E_{xc}[n] + E_H[n] + \\ + \int V_{ext}(r) n(r) dr$$

Minimize $E[\Psi_n]$, subject to
the constraints: $\langle \Psi_n | \Psi_m \rangle = \delta_{nm}$

$$\delta \left(E[\Psi_n] - \sum_{pq} \lambda_{pq} (\langle \Psi_p | \Psi_q \rangle - \delta_{pq}) \right) = 0$$

Simplest approach:

Steepest Descent

SOLVE

$$\dot{\Psi}_n = - \frac{\delta E}{\delta \Psi_n} + \sum_m \Lambda_{nm} \Psi_m$$

- $$\Psi_n(t+\Delta t) \approx \Psi_n(t) + \Delta t \left(-2 H \Psi_n(t) + \sum_m \Lambda_{nm}(t) \Psi_m(t) \right)$$

- Choose $\Lambda_{nm}(t)$ such that

$$\langle \Psi_n(t+\Delta t) | \Psi_m(t+\Delta t) \rangle = \delta_{nm}$$

- Other minimization techniques possible

- Slow for large systems

WHY IS IT SLOW?

Suppose that E is quadratic and there are no constraints

$$E[\psi] = E_0 - \langle \psi | \psi_0 \rangle + \frac{1}{2} \langle \psi | A | \psi \rangle$$

$$\dot{\psi} = - \frac{\delta E}{\delta \psi} = A\psi - \psi_0$$

$$\psi(t) = A^{-1}\psi_0 + e^{-At} \underbrace{(\psi(0) - A^{-1}\psi_0)}_{e(0)}$$

Discretizing:

$$\begin{aligned} \psi(t+\Delta t) &\approx \psi(t) - \Delta t \frac{\delta E}{\delta \psi} \\ &= \psi(t) - \Delta t \underbrace{(A\psi(t) - \psi_0)}_{r(t)} \end{aligned}$$

$$\Delta t < \frac{1}{\rho_{\max}} \ll \frac{1}{\rho_{\min}}$$

MULTI-LEVEL MINIMIZATION

$$\psi = \underbrace{\sum_{|q| \leq \epsilon_1} \psi(q) e^{iqt}}_{\psi^{(1)} \in \mathcal{K}^{(1)}} + \underbrace{\sum_{|q| \leq \epsilon_2} \psi(q) e^{iqt}}_{\psi^{(2)} \in \mathcal{K}^{(2)}}$$

IDEA Evolve in turn, in the whole Hilbert space, $\mathcal{K} = \mathcal{K}^{(1)} + \mathcal{K}^{(2)}$ with time-step $\Delta t_2 < \frac{1}{\epsilon_2}$, and in the reduced one, $\mathcal{K}^{(1)}$, with $\frac{1}{\epsilon_1} > \Delta t_1 > \Delta t_2$

Evolution in $\mathcal{K}^{(1)}$:

$$\frac{\delta E}{\delta \psi^{(1)}} = -2 (H \psi^{(1)} + H \psi^{(2)})$$

$$\dot{\psi}_n^{(1)} = -2 H^{(1)} \psi_n^{(1)} + \sum_m \Lambda_{nm} \psi_m^{(1)} + H^{(2)} \psi_n^{(2)}$$

with constraints:

$$\langle \psi_n^{(1)} | \psi_m^{(1)} \rangle = \delta_{nm} - \underbrace{\langle \psi_n^{(2)} | \psi_m^{(2)} \rangle}_{\text{fixed}}$$

