Density Functional Theory: from theory to Applications

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Solving the electronic problem in practice

All electrons vs pseudopotentials

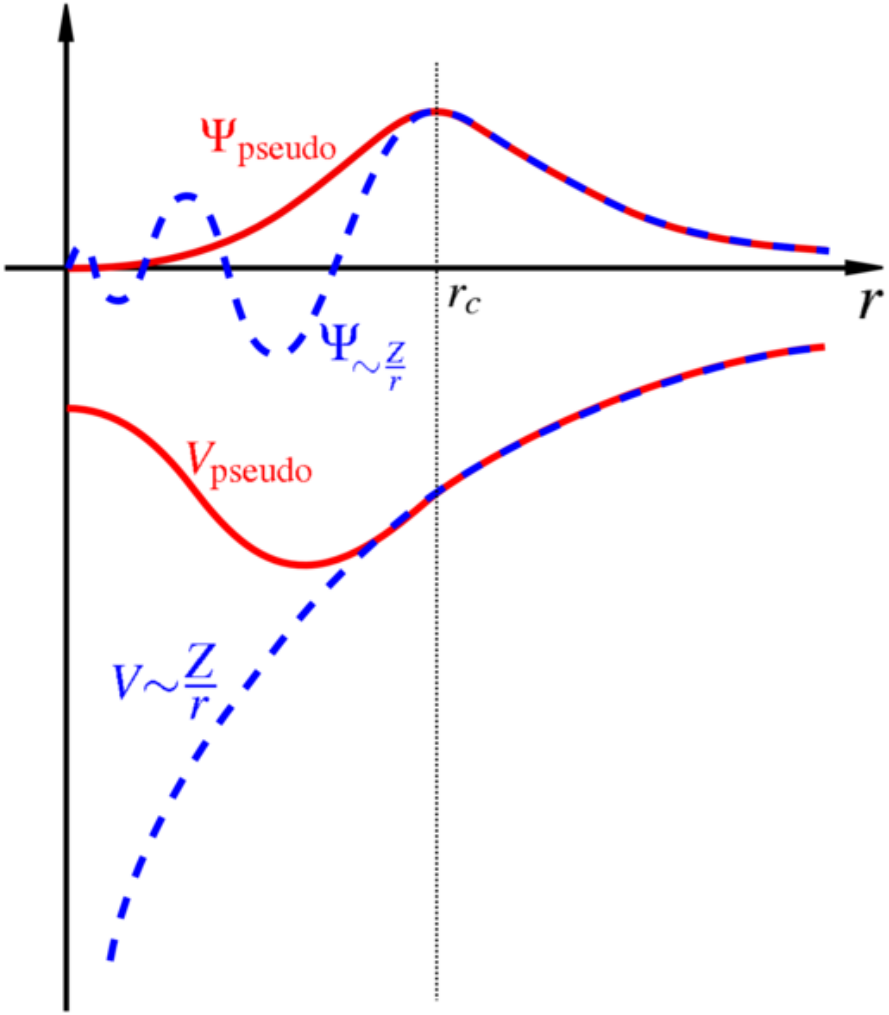
There are two classes of electrons: *valence electrons* (participate to chemical bonds) and *core electrons* (tightly bound to the nuclei). Eventually *semi-core electrons* (close in energy to valence states to feel the presence of the environment)

All-electron methods

- fixed orbital basis set: core electron minimal number of basis function to reproduce atomic features, valence and semi-core more complete basis set to describe the chemical bond.
- augmented basis set. Divide the space into spherical regions around the atoms and interstitial regions and requesting that the basis functions are continuous and differentiable across the boundaries.

Pseudopotential methods

- Core electrons are eliminated. Nuclei effective charge $Z_V = Z - Z_{core}$.
- Number of electron treated explicitly is reduced
- The bare Coulomb potential is replaced by a screened Coulomb potential
- Inner solution, inside the core radius, is replaced with a smooth, node-less pseudo-wave function
- Pseudopotentials are usually chosen to be dependent on the angular momentum.
  E.g. for Pt 6p orbitals are quite external and peaked at around 3.9Å, the 6s peak at around 2.4 Åand the main peak of 5d is located ate 1.3 Å.


Ψ_{pseudo}
r_c
r
$\Psi_{\sim\frac{Z}{r}}$
V_{pseudo}
$V\sim\frac{Z}{r}$

Classes of Basis-set

- *Extended basis set*: delocalized, such as plane waves, useful for condensed phase systems. Tends to be inefficient for molecular systems.
- *Localized basis set*: mainly centered at the atomic positions (but also at position of "ghost" atoms). Mainly used for molecular systems
- *Mixed basis set*: designed to take best of the two worlds (delocalized + localized). There can be some technical issues (over-completeness).
- *Augmented basis set*: where an extended or atom centered basis set is augmented with atomic like wf in spherical regions around the nuclei.

Condensed phase: Bloch's th and PBC

Condensed phase: problem of choosing the size of the simulation cell. For periodic system: unit of Wigner-Seitz cell, the minimal choice that contains the whole symmetry of the system. Sometimes it is convenient to choose a larger cell to simplify description of symmetry properties. In an external periodic potential $v(\mathbf{r}) = v(\mathbf{r} + \mathbf{a}_i)$ the wf can be written as:

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r}) \tag{1}$$

with $u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{a}_i)$.

$$\psi_k(\mathbf{r} + \mathbf{a}_i) = e^{i\mathbf{k}\cdot\mathbf{a}_i} \psi_k(\mathbf{r}) \tag{2}$$

So that the probability density is $|\psi_k(\mathbf{r})|^2$ is exactly the same.

Looking at

$$\psi_k(\mathbf{r}+\mathbf{a}_i) = e^{i\mathbf{k}\cdot\mathbf{a}_i}\psi_k(\mathbf{r})$$

we notice that there is a a class of vectors $\mathbf{k}$ such that

$$e^{i\mathbf{k}\cdot\mathbf{a}_i} = 1 \tag{3}$$

The reciprocal lattice vectors are defined by

$$\mathbf{a_i}\cdot\mathbf{b_j} = 2\pi\delta_{ij} \tag{4}$$

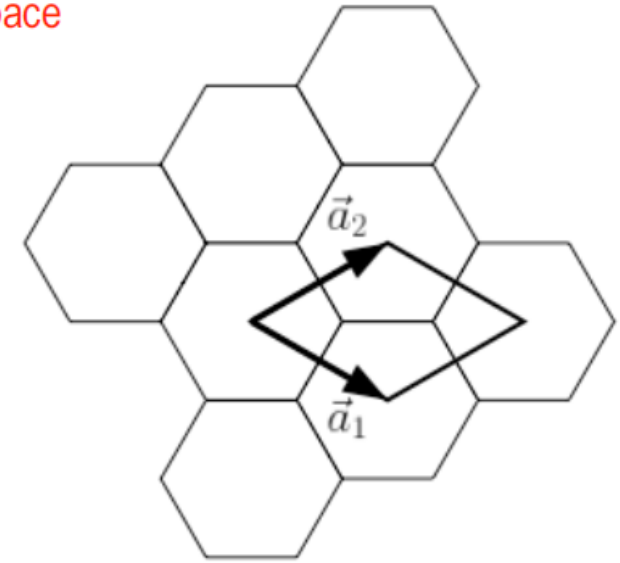
and

$$\mathbf{b_1} = 2\pi\frac{\mathbf{a_2}\times\mathbf{a_3}}{\Omega};\ \mathbf{b_2} = 2\pi\frac{\mathbf{a_3}\times\mathbf{a_1}}{\Omega};\ \mathbf{b_3} = 2\pi\frac{\mathbf{a_1}\times\mathbf{a_2}}{\Omega} \tag{5}$$

The reciprocal lattice vectors define the first Brillouin Zone (BZ).

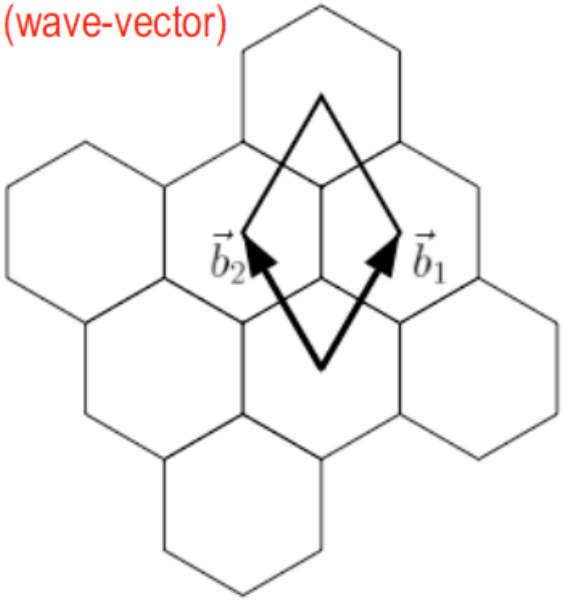
- Example: honeycomb lattice

real space



Lattice vectors a_1, a_2, a_3
Unit cell volume Ω
Crystallographic basis consisting of two atoms

Reciprocal (wave-vector) space



Reciprocal-lattice vectors b_1, b_2, b_3, each perpendicular to a pair of lattice vectors

$$\vec{b}_i = \frac{2\pi}{\Omega}(\vec{a}_j \times \vec{a}_k)$$

Bloch's theorem indicates that it is not necessary to determine the electronic wavefunction everywhere in space. It is sufficient to know the solution in the unit cell.
Using the fact that a periodic function can be represented by a Fourier series:

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} C_{\mathbf{k}+\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \tag{6}$$

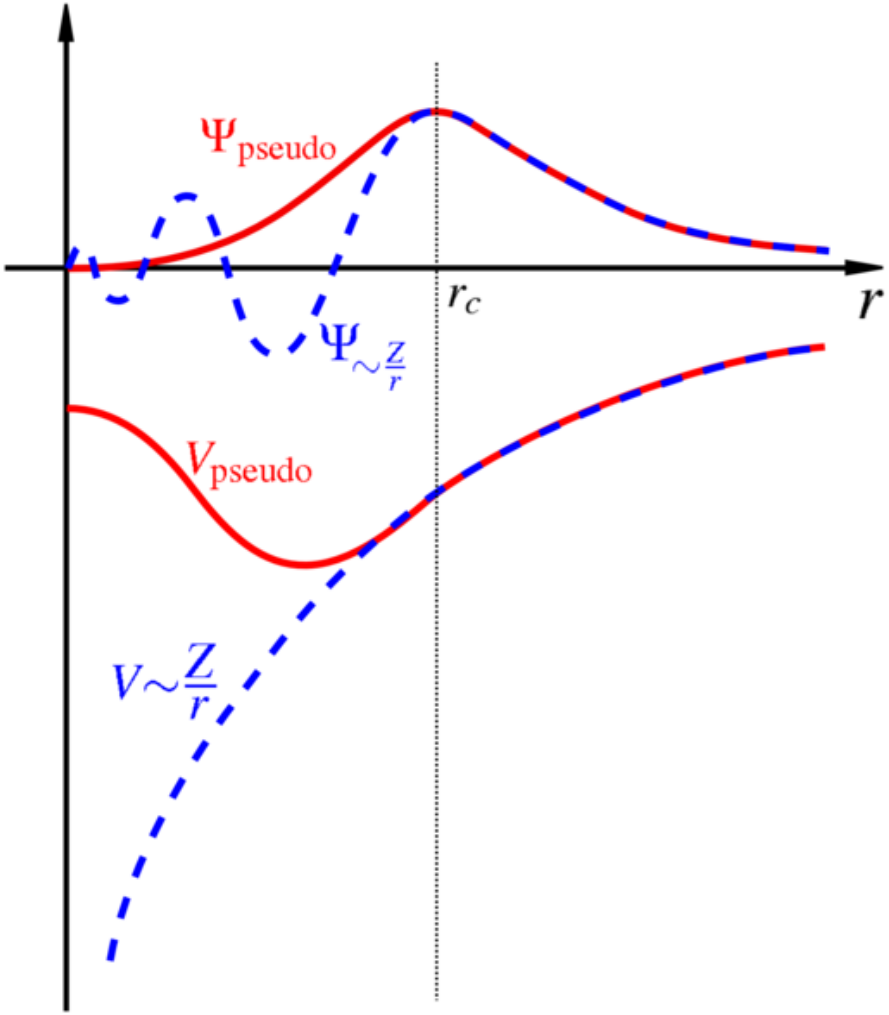
where the sum is over $G = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$, the reciprocal lattice vectors.
$\mathbf{k}$ is restricted to all the vectors in the first Brillouin zone. In practice calculations are done only for a finite number of $\mathbf{k}$.
The number of $\mathbf{k}$ points depends on the systems we want to study.

Aperiodic systems: molecules, surfaces and defects

- supercell approach with PBC, making sure that required physical and chemical properties are converged with respect to the size of the supercell.
- For surfaces and molecules, e.g., introduce a a vacuum region large enough that there so interaction between images.
- For charged systems difficulties due to the electrostatic interactions (long range). A uniform neutralizing background is introduced.

- Only the chemically active electrons are considered explicitly.
- The core electrons are eliminated within the frozen-core approximation and are considered together with the nuclei as rigid non-polarizable ion cores.
- The Pauli repulsion largely cancels the attractive parts of the true potential in the core region, and is built into the therefore rather weak pseudopotentials.

Hamann-Schlüter-Chiang pseudopotentials
Bachelet, Kerker, Martin-Troulliers

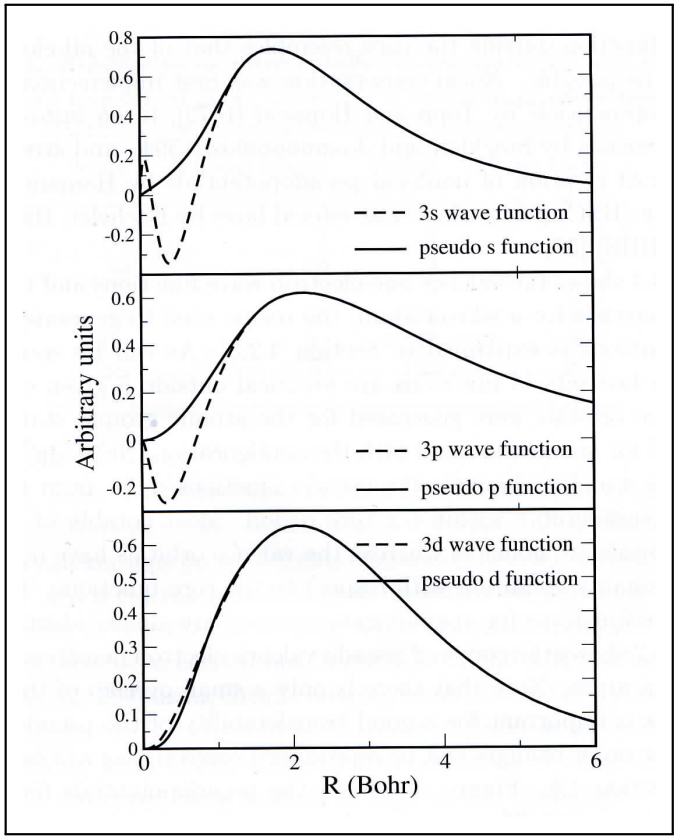


Why Pseudopotentials?

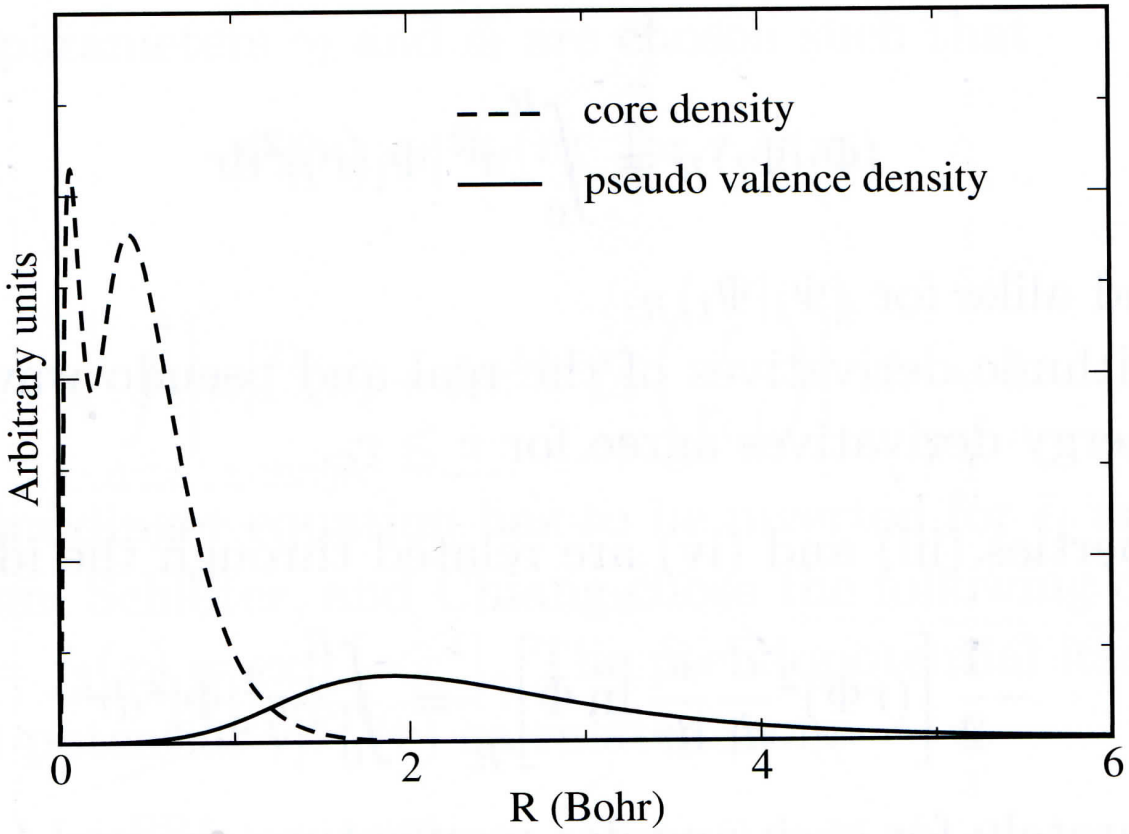
- Reduction of the number of electron in the systems, faster calculation for large systems
- Relativistic effects depending on the core electrons treated incorporated indirectly in the pseudopotentials
- In the frame of plane wave basis set: reduction of the basis set size introducing smoother functions which requires a lower cutoff
- The number of plane waves needed for a certain accuracy increases with the square of the nuclear charge.

Norm-conserving pseudopotentials

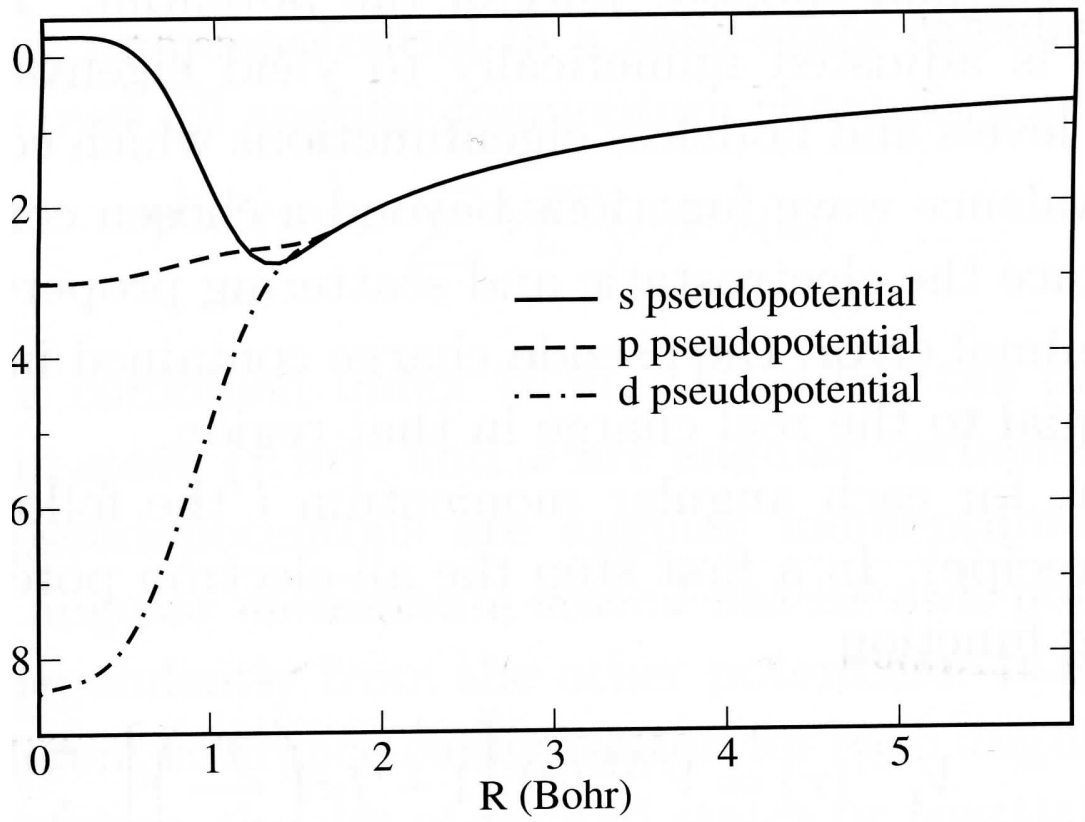
Norm-conserving pseudopotentials conserves the normalization of the pseudo wf in the core region so that the wf outside resembles that of the all-electrons as closely as possible.



Valence and pseudo wf of a Si atom, generated according to Martin-Troullier scheme.



Ground state core density (dashed line) and pseudo valence density (solid line) for a Si atom.



Note: The pseudopotentials converge to the limit $-Z/r$ outside the core radius.

Hamann-Schlüter-Chiang conditions[1]

Norm-conserving pseudos are derived from atomic reference state:

$$(T + V^{AE})|\Psi_l >= \epsilon_l|\Psi_l > . \tag{7}$$

This is replaced by the "valence electrons only"

$$(T + V^{val})|\Phi_l >= \tilde{\epsilon}_l|\Phi_l > . \tag{8}$$

Imposing the following:

- $\epsilon_l = \tilde{\epsilon}_l$ for a chosen prototype atomic configuration.
- $\Psi_l(r) = \Phi_l(r)$ for $r \geq r_c$.
- Norm conservation, $< \Phi_l|\Phi_l >_R =< \Psi_l|\Psi_l >_R$ for $R \geq r_c$.
- Log derivative of Φ_l equal to that of Ψ_l.

[1] Hamann-Schlüter-Chiang, *Phys. Rev. Lett.*, 43, 1494 (1979)

Hamann-Schlüter-Chiang recipe

- First step: the all-electron wf is multiplied by a smoothing function f_1 to remove strongly attractive and singular part of the potential:

$$V_l^{(1)}(r) = V^{AE}(r)\left[1 - f_1\left(\frac{r}{r_{c,l}}\right)\right] \tag{9}$$

- Then a function f_2 is added in order to obtain $\epsilon_l = \tilde{\epsilon}_l$

$$V_l^{(2)}(r) = V_l^{(1)}(r) + c_l f_2\left(\frac{r}{r_{c,l}}\right) \tag{10}$$

$$\left(T + V_l^{(2)}(r)\right) w_l^{(2)}(r) = \tilde{\epsilon}_l w_l^{(2)}(r) \tag{11}$$

This determines the value of c_l.

Hamann-Schlüter-Chiang recipe

- The valence wf is defined as

$$\Phi_l(r) = -\gamma_l \left[w_l^{(2)}(r) + \delta_l r^{l+1} f_3 \left(\frac{r}{r_{c,l}} \right) \right] \tag{12}$$

where γ_l and δ_l are chosen such that
$\Phi_l(r) \to \Psi_l(r)$ for $R \geq r_c$.
And

$$\gamma_l^2 \int |w_l^{(2)}(r) + \delta_l r^{l+1} f_3 \left(\frac{r}{r_{c,l}} \right) |^2 i dr = 1 \tag{13}$$

Hamann-Schlüter-Chiang recipe

- Given Φ_l and $\tilde{\epsilon}_l$ the equation:

$$(T + V^{val})|\Phi_l >= \tilde{\epsilon}_l|\Phi_l > .$$

  is inverted to get $V^{val}(r)$.

Hamann-Schlüter-Chiang chose $f_1(x) = f_2(x) = f_3(x) = exp[-x^4]$.

$$V_l^{PP}(r) = V_l^{val}(r) - V_H(n_V) - V_{xc}(n_V) \tag{14}$$

The total atomic pseudopotential then takes the form of a sum over all angular momentum channels:

$$V^{PP}(\mathbf{r}) = \sum_L V_L^{PP}(r)\mathbf{P}_L(\omega) \tag{15}$$

where $\mathbf{P}_L(\omega)$ is the projector on the angular momentum state L, defined by $\{l, m\}$ and ω are angular variables.

Bachelet-Hamann-Schlüter pseudopotentials

Bachelet et proposed an analytic form to fit the pseudos generated by Hamann-Schlüter-Chiang of the form:

$$V^{PP}(r) = V^{core}(r) + \sum_L \Delta V_L^{ion}(r) \tag{16}$$

$$V^{core}(r) = -\frac{Z_V}{r}\left[\sum_{i=1}^{2} c_i^{core} erf(\sqrt{\alpha_i^{core}}r)\right] \tag{17}$$

$$V_L^{ion}(r) = \sum_{i=1}^{3}(A_i + r^2 A_{i+3})exp[-\alpha_i r^2] \tag{18}$$

the advantage here is that this form allow an easy implementation in plane-wave code, since the Fourier transform can be also written analytically.

Kerker pseudopotentials

In the Kerker approach[2] psedupotentials are constructed to satisfy HSC conditions, but replacing the AE wf inside r_c with a smooth analytic function that matches the AE wf at r_c.

- r_c is generally larger than that used in HSC

The analytic form proposed by Kerker is

$$\Phi_l(r) = r^{l+1} exp[p(r)] \text{ for } r < r_{c,l} \tag{19}$$

with l-dependent cut-off radii $r_{c,l}$ and

$$p(r) = \alpha r^4 + \beta r^3 + \gamma r^2 + \delta \tag{20}$$

The method of Kerker was generalized by Troullier and Martins to polynomials of higher order[3]

[2] Kerker, *J. of Phys. C* 13; L189 (1980)
[3] *Phys. rev. B*, 43: 1993. (1991).

An Example: pseudos for carbon

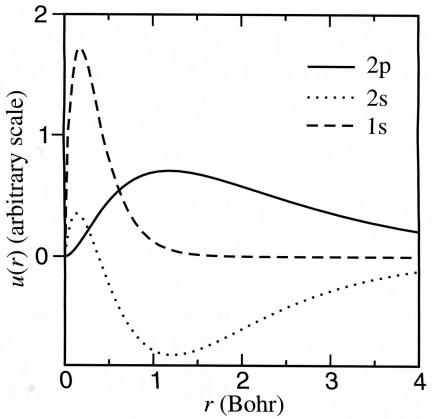


Fig. 4.6. All-electron wave functions $u(r) = r\Psi(r)$ for the carbon atom in the ground state.

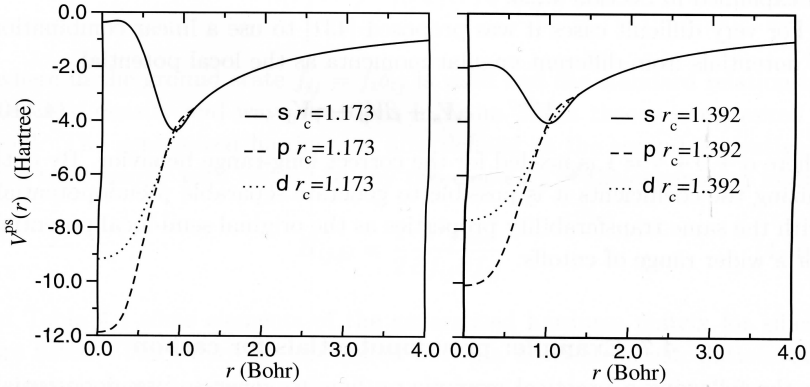
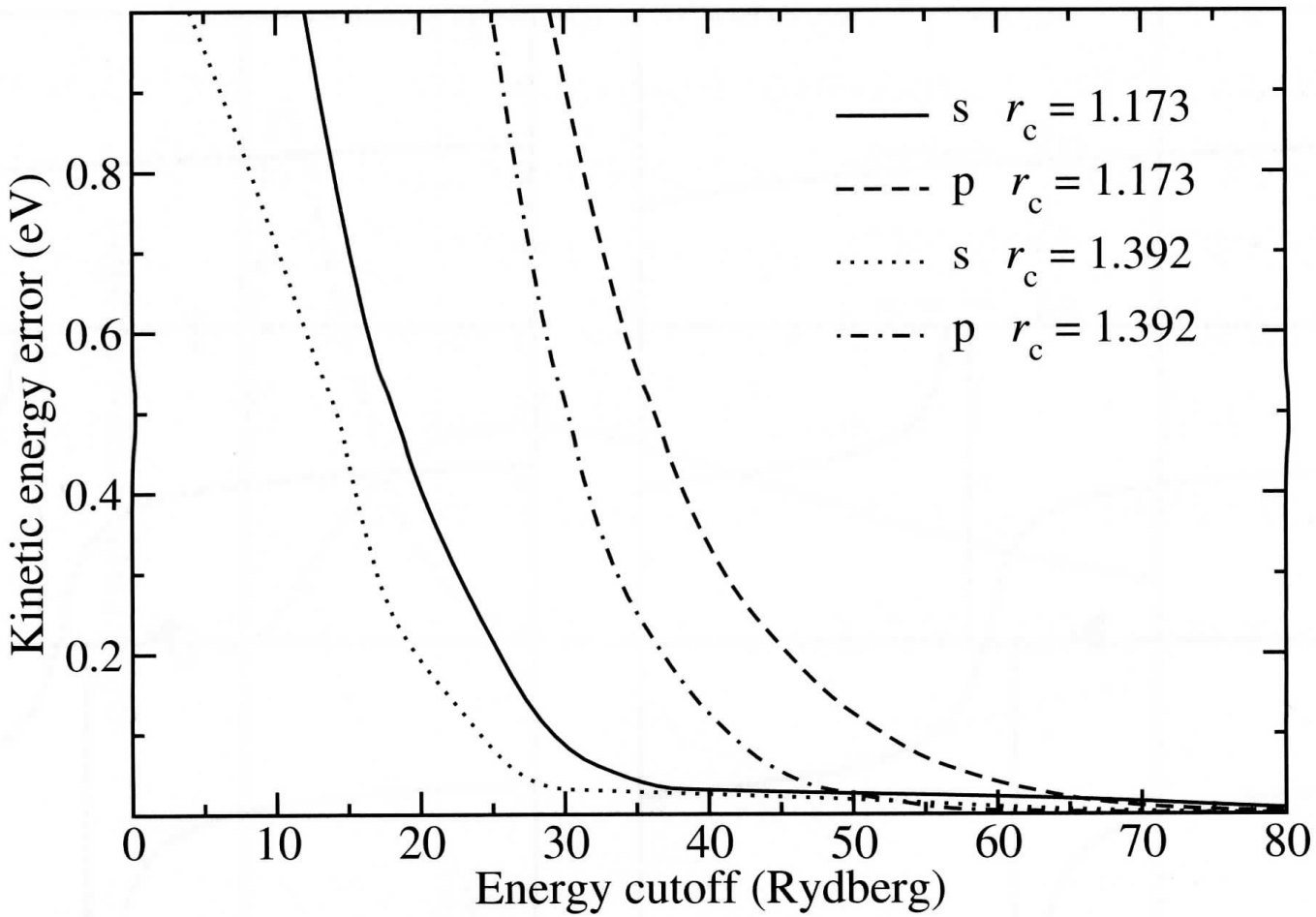


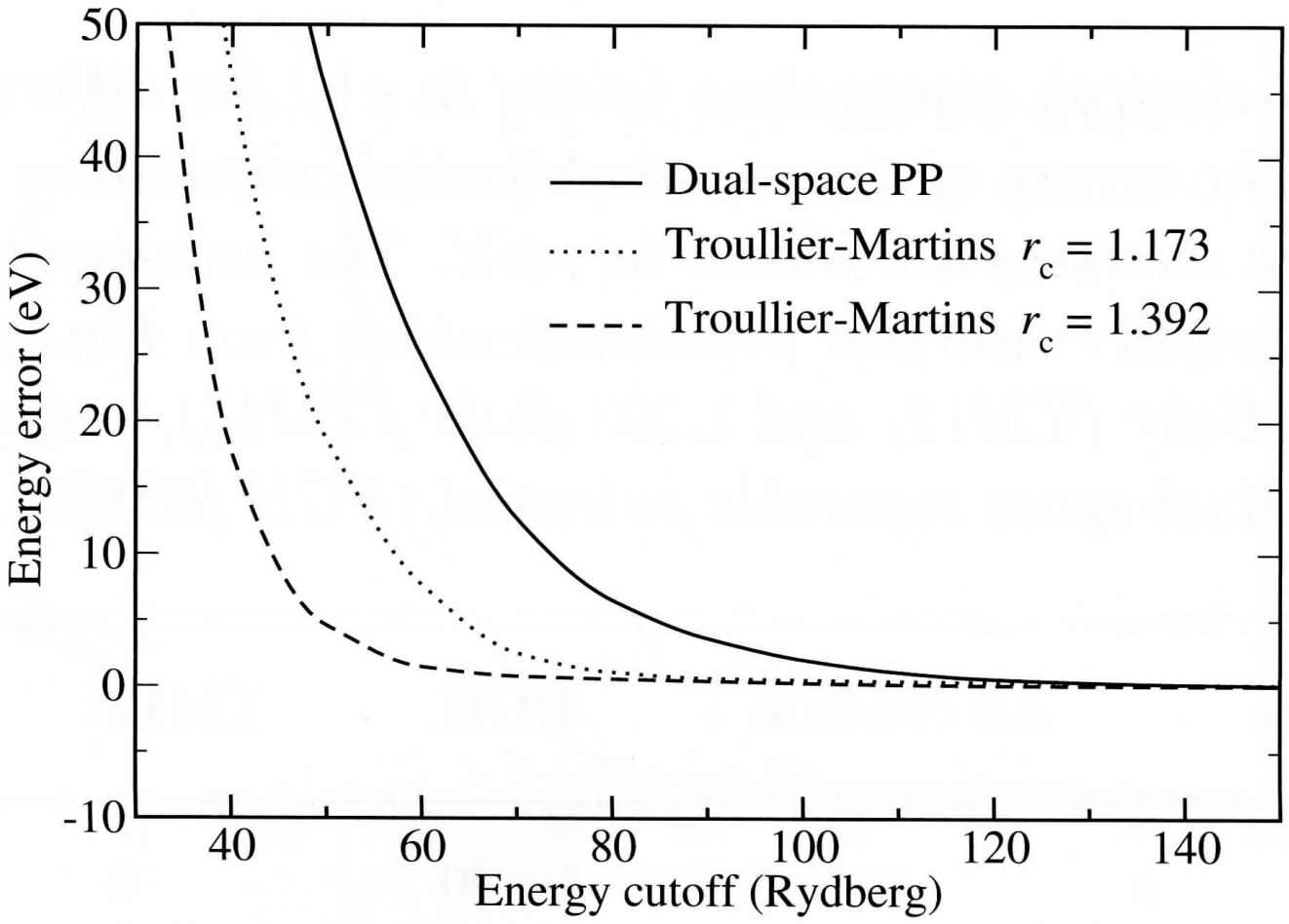
Fig. 4.7. Two sets of Troullier–Martins pseudopotentials for carbon generated by using two different cutoff radii r_c as indicated in the panels.

Martin-Troulliers pseudopotential for carbon in the LDA.

reference configuration: $1s^2 2s^2 2p^2$



Convergence of the kinetic energy for carbon atom as function of the cutoff.



Convergence of the total energy of diamond as function of the cutoff.

Controlling temperature: thermostats
Controlling pressure: barostats

Zero or small electronic gaps: thermostatted electrons

- One way to (try to) overcome the problem in coupling of electronic and ionic dynamics is to thermostat also the electrons (Blöchl & Parrinello, PRB 1992)
- Thus electrons cannot heat up; if they try to, thermostat will adsorb the excess heat
- Target fictitious kinetic energy $E_{kin,0}$ instead of temperature
- Mass of thermostat to be selected appropriately:
  Too light: Adiabacity violated (electrons may heat up)
  Too heavy: Ions dragged excessively
- Note: Introducing the thermostat the conserved quantity changes

$$M_I \ddot{\mathbf{R}}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I} < \Psi_0 | H_e^{KS} | \Psi_0 > -M_I \dot{R}_I \dot{x}_R \quad (21)$$

$$\mu \ddot{\phi}_i(t) = -H_e^{KS} \phi_i + \sum_j \Lambda_{ij} \phi_j - \mu \dot{\phi}_i \dot{x}_e \quad (22)$$

in blue are the frictious terms governed by the following equations:

$$Q_e \ddot{x}_e = 2 \left[\sum_i \mu \dot{\phi}^2 - E_{kin,0} \right] \quad (23)$$

$$Q_R \ddot{x}_R = 2 \left[\sum_I \frac{1}{2} M_I \dot{R}^2 - \frac{1}{2} g K_B T \right] \quad (24)$$

The masses Q_e and Q_R determines the time scale for the thermal fluctuations. The conserved quantity is now:

$$E_{tot} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu < \dot{\phi}_i | \dot{\phi}_i > + < \Psi_0 | H_e^{KS} | \Psi_0 >$$
$$+ \frac{1}{2} Q_e \dot{x}_e^2 + 2 E_{kin,0} x_e + \frac{1}{2} Q_R \dot{x}_R^2 + g K_B T x_R \quad (25)$$

Standard Nose'-Hoover thermostat suffers from non-ergodicity problems for certain classes of Hamiltonian, so a closely related technique has been proposed, the Nose'-Hoover chain thermostat. For the nuclear part:

$$M_I \ddot{\mathbf{R}}_I = -\nabla E^{KS} - M_I \dot{\xi}_1 \dot{\mathbf{R}}_I \tag{26}$$

$$Q_1^n \ddot{\xi}_1 = \left[\sum_I M_I \dot{R}_I^2 - g K_B T \right] - Q_1^n \dot{\xi}_1 \dot{\xi}_2 \tag{27}$$

$$Q_k^n \ddot{\xi}_k = 2 \left[Q_{k-1}^n \dot{\xi}_{k-1}^2 - K_B T \right] - Q_k^n \dot{\xi}_k \dot{\xi}_{k+1} (1 - \delta_{kK}) \tag{28}$$

For the electronic part:

$$\mu \ddot{\phi}_i = -H_e^{KS} \phi_i + \sum_{ij} \Lambda_{ij} \phi_j - \mu \dot{\eta}_1 \dot{\phi}_i \tag{29}$$

$$Q_1^e \ddot{\eta}_1 = \left[\sum_i^{occ} \mu < \phi_i | \phi_i > - T_1^0 \right] - Q_1^e \dot{\eta}_1 \dot{\eta}_2 \tag{30}$$

$$Q_l^n \ddot{\eta}_l = 2 \left[Q_{l-1}^n \dot{\eta}_{l-1}^2 - \frac{1}{\beta_e} \right] - Q_l^e \dot{\eta}_l \dot{\eta}_{l+1} (1 - \delta_{lL}) \tag{31}$$

- Separate chains composed of K and L coupled thermostats are attached to the nuclear and electronic equations of motion, respectively
- Masses for the thermostats are chosen so that there overlap of the thermostat and system power spectra.

$$Q_1^n = \frac{gK_B T}{\omega_n^2}, \ \dots \ Q_k^n = \frac{gK_B T}{\omega_n^2}, \tag{32}$$

$$Q_1^e = \frac{2T_e^0}{\omega_e^2}, \ \dots \ Q_l^e = \frac{2T_e^0}{\omega_e^2} \tag{33}$$

- massive thermostatting method: NH chains for individual nuclear degree of freedom. Accelerate expensive equilibration periods

Energy and Momentum conservation

In micro-canonical classical molecular simulations the total energy and the total momentum are conserved.
In the case of thermostatted NVT simulations the constant of motion is:

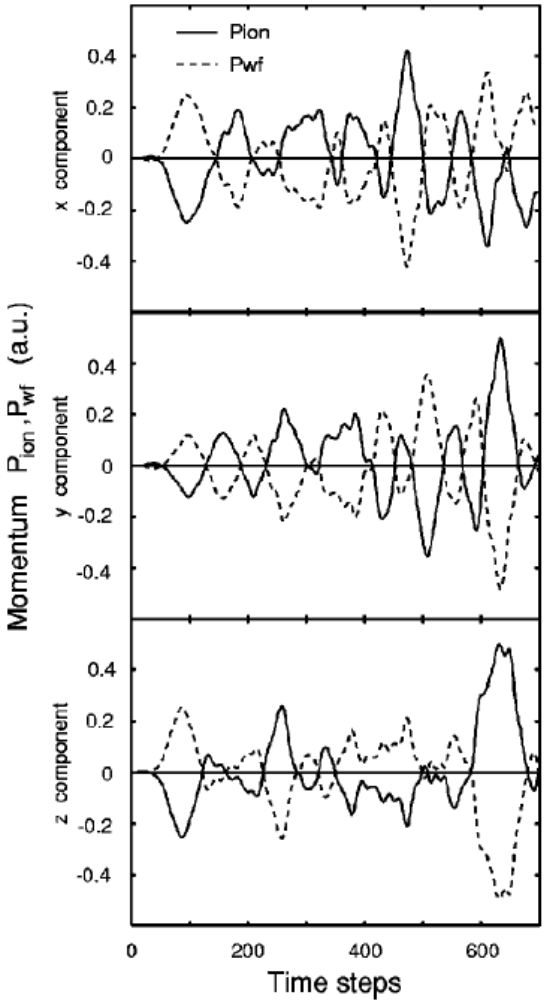
$$E_{cons}^{NVT} = \sum_{i}^{occ} \mu < \dot{\phi}_i | \dot{\phi}_i > + \sum_{I} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + E^{KS}\left[\{\phi_i\}, \{\mathbf{R}_I\}\right] \quad (34)$$

$$+ \sum_{l=1}^{L} \frac{1}{2} Q_l^e \dot{\eta}_l^2 + \sum_{l=2}^{L} \frac{\eta_l}{\beta_e} + 2 T_e^0 \eta_1 + \sum_{k=1}^{K} \frac{1}{2} Q_k^n \dot{\xi}_k^2 + \sum_{k=2}^{K} K_b T \xi_k + g K_b T \xi_1 \quad (35)$$

In micro-canonical CPMD a generalized linear momentum is conserved:

$$\mathbf{P}_{CP} = \mathbf{P}_n + \mathbf{P}_e = \sum_{I} \mathbf{P}_I + \sum_{i}^{occ} \mu < \dot{\phi}_i | -\frac{1}{2} \nabla_r | \phi_i > + c.c. \quad (36)$$

where $\mathbf{P}_I = M_I \dot{\mathbf{R}}_I$.



Time evolution of P_{ion} (solid line) and P_{wf} (dashed line) in the diamond structure of Si. From the upper panel, three components, x, y, z, are shown, respectively. (*Morishita and Nose'Phys Rev B , 59, 15126 (1999)*)

Imposing pressure: barostats

Original version from Andersen[4] devised to allow isotropic fluctuations in the volume of the supercell. Variable cell approach: allows structural phase transition in solids at finite temperature. Parrinello-Rahman[5]
Built an extended Lagrangian with additional dynamical variables $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, the primitive Bravais lattice vectors.
Using the $3X3$ matrix $\mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$ which define the volume Ω, the scaled coordinates $\mathbf{S}$ are defined by $\mathbf{R}_I = \mathbf{h}\mathbf{S}_I$.
the normalized original orbitals are transformed according to:

$$\phi_i(\mathbf{r}) = \frac{1}{\Omega}\phi_i(\mathbf{s}) \tag{37}$$

The cell-variable extended Lagrangian is:

$$\begin{aligned} \mathcal{L} &= \sum_i \mu < \dot{\phi}(\mathbf{s})_i | \dot{\phi}_i(\mathbf{s}) > - E^{KS}[\{\phi_i\}, \{\mathbf{h}\mathbf{S}_I\}] \\ &+ \sum_{ij} \Lambda_{ij}(< \phi_i(\mathbf{s}) | \phi_j(\mathbf{s}) > - \delta_{ij}) + \sum_I \frac{1}{2} M_I (\dot{\mathbf{S}}_I^T \mathbf{h}^T \mathbf{h} \dot{\mathbf{S}}_I) + \frac{1}{2} W Tr \dot{\mathbf{h}}^T \dot{\mathbf{h}} - p\Omega \end{aligned} \tag{38}$$

$$\mathcal{L} = \sum_i \mu < \dot{\phi}(\mathbf{s})_i | \dot{\phi}_i(\mathbf{s}) > - E^{KS}[\{\phi_i\}, \{\mathbf{h}\mathbf{S}_I\}] \tag{39}$$
$$+ \sum_{ij} \Lambda_{ij}(< \phi_i(\mathbf{s}) | \phi_j(\mathbf{s}) > - \delta_{ij}) + \sum_I \frac{1}{2} M_I (\dot{\mathbf{S}}_I^T \mathbf{h}^T \mathbf{h} \dot{\mathbf{S}}_I) + \frac{1}{2} W Tr \dot{\mathbf{h}}^T \dot{\mathbf{h}} - p\Omega$$

- nine additional degrees of freedom associated with lattice vectors of supercell **h**.
- This constant-pressure CPMD reduce to constant-volume CPMD in the limit $\dot{\mathbf{h}} \to 0$ (apart from a constant term $p\Omega$
- W is the fictious mass that controls the timescale of the cell dynamics

The resulting equations of motion are:

$$M_I \ddot{S}_{I,u} = -\sum_{v=1}^{3} \frac{\partial E^{KS}}{\partial R_{I,v}} (\mathbf{h}^T)^{-1}_{v,u} - M_I \sum_{v=1}^{3} \sum_{s=1}^{3} \mathcal{G}^{-1}_{uv} \dot{\mathcal{G}}_{vs} \dot{S}_{I,s} \quad (40)$$

$$\mu \ddot{\phi}_i(\mathbf{s}) = -\frac{\partial E^{KS}}{\partial \phi_i^*(\mathbf{s})} + \sum_j \Lambda_{ij} \phi_j(\mathbf{s}) \quad (41)$$

$$W \ddot{h}_{uv} = \Omega \sum_{s=1}^{3} (\Pi^{tot}_{us} - p\delta_{us})(\mathbf{h}^T)^{-1}_{sv} \quad (42)$$

where the total stress tensor is:

$$\Pi^{tot}_{us} = \frac{1}{\Omega} \sum_I M_I (\dot{\mathbf{S}}_I^T \mathcal{G} \dot{\mathbf{S}}_I)_{us} + \Pi_{us} \quad (43)$$

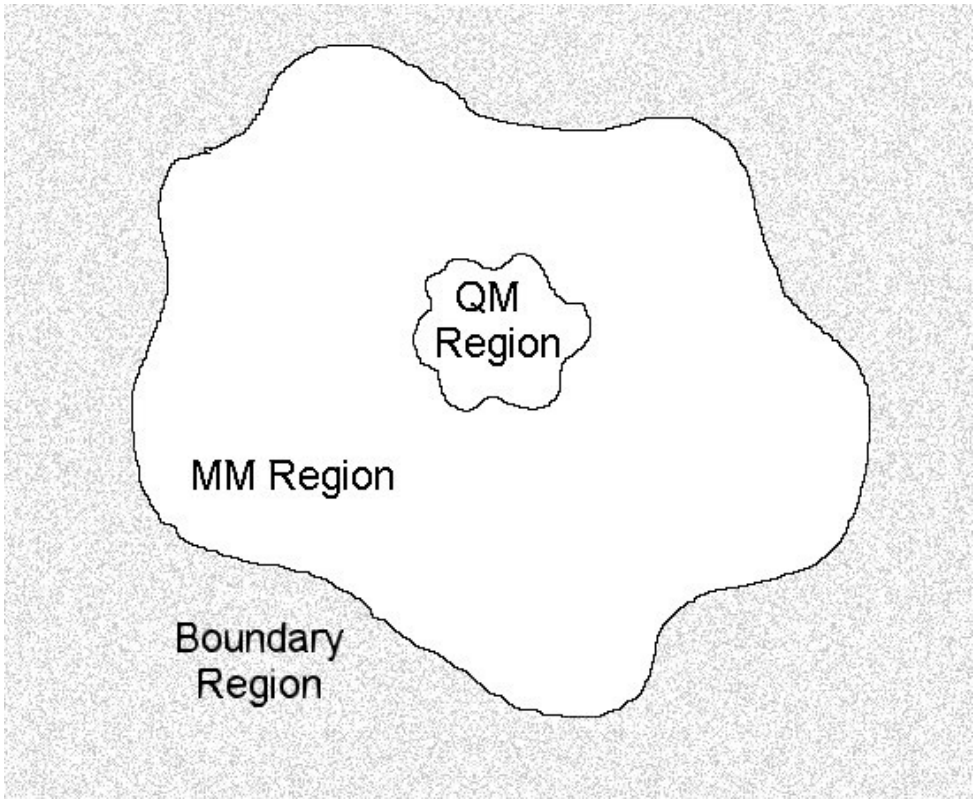
and Π_{us} is electronic stress tensor:

$$\Pi_{us} = -\frac{1}{\Omega} \sum_v \frac{\partial E_{tot}}{\partial h_{uv}} h^T_{vs} \quad (44)$$

- frictional feedback mechanism
- Parrinello-Rahman used in connection with metadynamics
- practical issue: basis set error, when using a fixed cutoff in plane wave with a varying cell

Alternative approach for clusters[6].

Idea: surrounding the finite cluster by a pressurizing medium described by N_L classical point particles.i (e.g. liquid of purely repulsive soft spheres).



[6] R. Martonak, C. Molteni and M. Parrinello, Comp Mat Science 20 (3-4) 2001, 293-299

Alternative approach for clusters[7].

Idea: surrounding the finite cluster by a pressurizing medium described by N_L classical point particles.i (e.g. liquid of purely repulsive soft spheres). The corresponding Lagrangian is:

$$\mathcal{L} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu < \dot{\phi}(\mathbf{r})_i | \dot{\phi}_i(\mathbf{r}) > - E^{KS}[\{\phi_i\}, \{\mathbf{R}_I\}] \quad (45)$$

$$+ \sum_{ij} (< \phi(\mathbf{r})_i | \phi_j(\mathbf{r}) > - \delta_{ij}) + \sum_\alpha \frac{1}{2} M_\alpha \dot{\mathbf{X}}_\alpha^2 \quad (46)$$

$$+ - \sum_{I,\alpha} V_{C-L}(|\mathbf{R}_I - \mathbf{X}_\alpha|) - \sum_{\alpha<\beta} V_{L-L}(|\mathbf{X}_\alpha - \mathbf{X}_\beta|) \quad (47)$$

where M_α is the mass of a liquid particle at position $\mathbf{X}_\alpha$ and V_{C-L} and V_{L-L} are model pair potential to describe the cluster-liquid and the liquid-liquid interactions.

[7] R. Martonak, C. Molteni and M. Parrinello, Comp Mat Science 20 (3-4) 2001, 293-299

How is the pressure controlled?

For purely repulsive soft spheres:

$$V_{L-L}(r) = \epsilon_{L-L} \left(\frac{\sigma_{L-L}}{r} \right)^{12} \tag{48}$$

the equation of state gives:

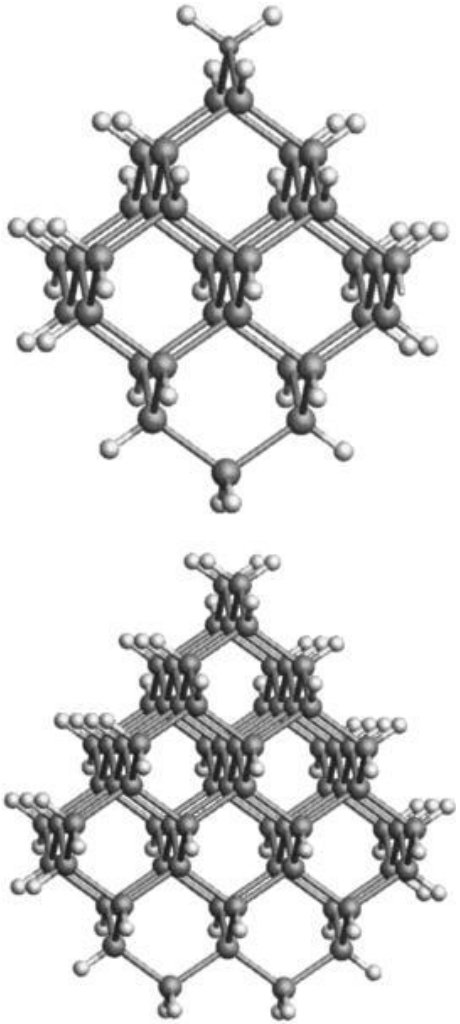
$$p = \frac{N_L K_B T}{\Omega_L} \xi(\tilde{\rho}) \tag{49}$$

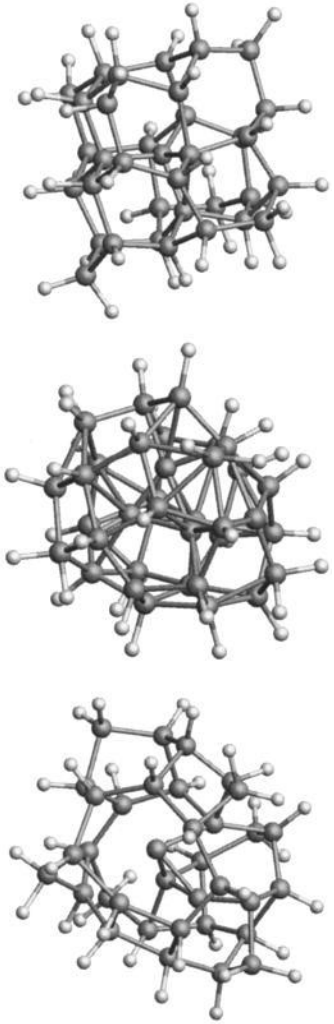
where

$$\xi(\tilde{\rho}) = \frac{N_L}{\Omega_L} \frac{\sigma_{L-L}^3}{\sqrt{2}} \left(\frac{\epsilon_{L-L}}{K_B T} \right)^{1/4} \tag{50}$$

the pressure is adjusted tuning ϵ_{L-L}.

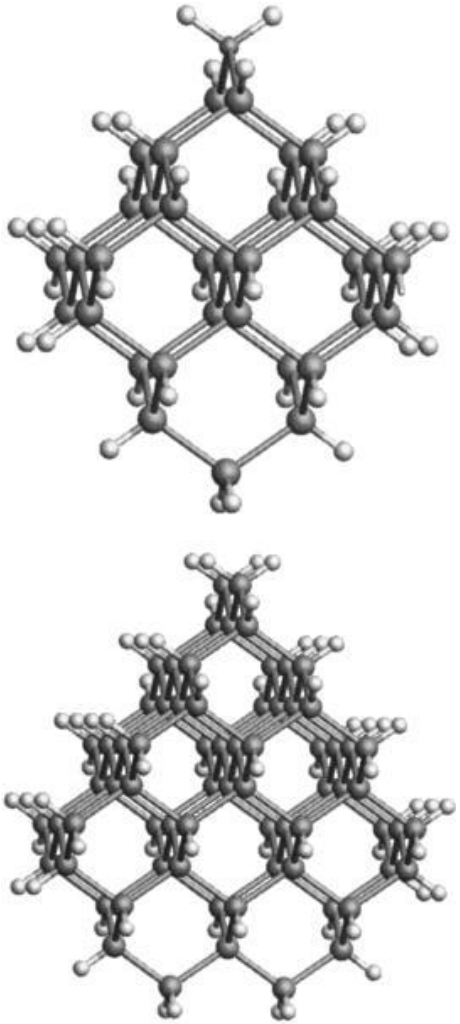
Alternative approach for clusters

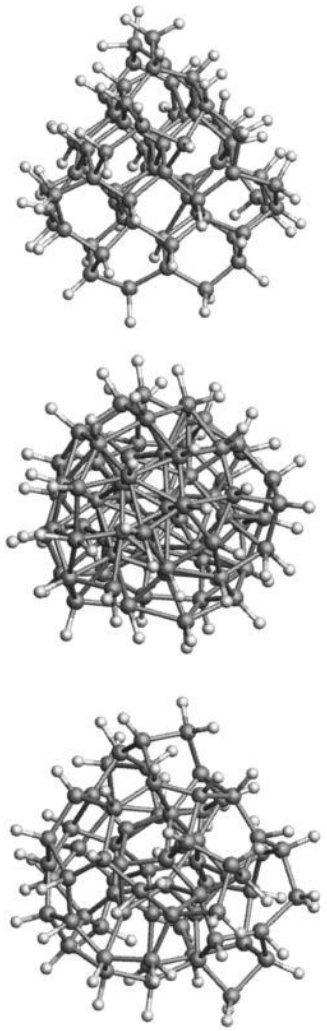




$Si_{35}H_{36}$ at 25 GPa (top), 35 GPa (center), and 5 GPa (after the

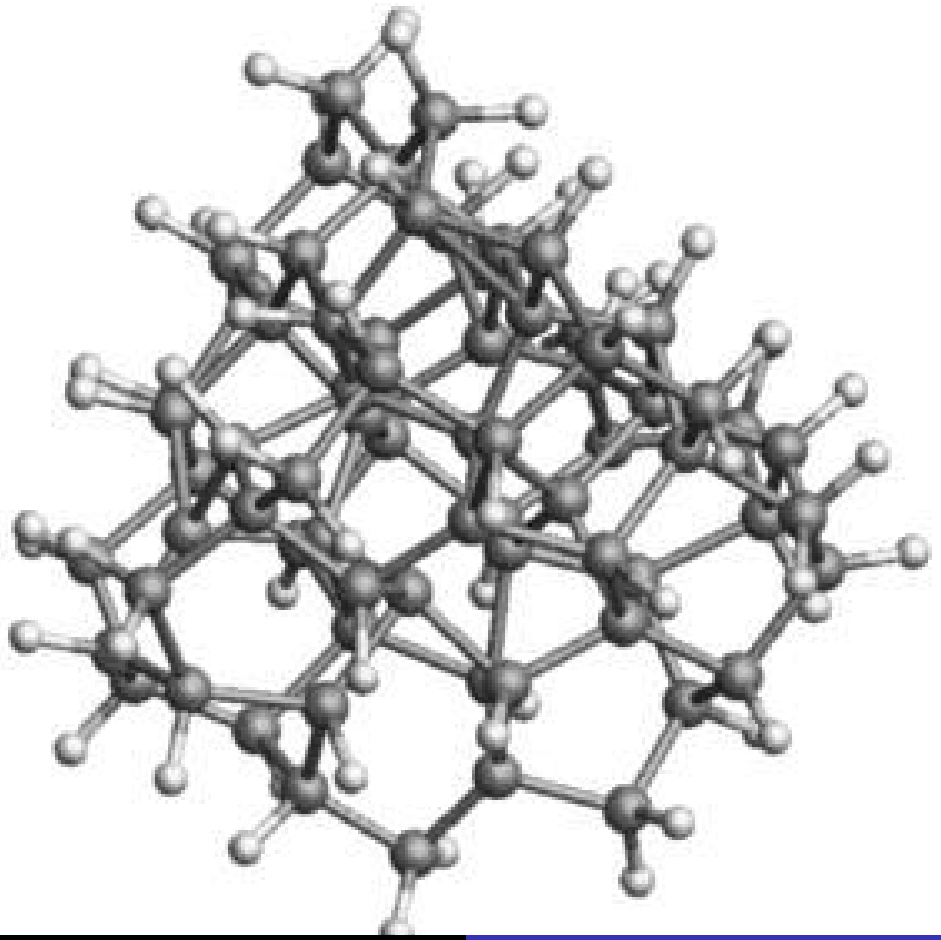
Alternative approach for clusters



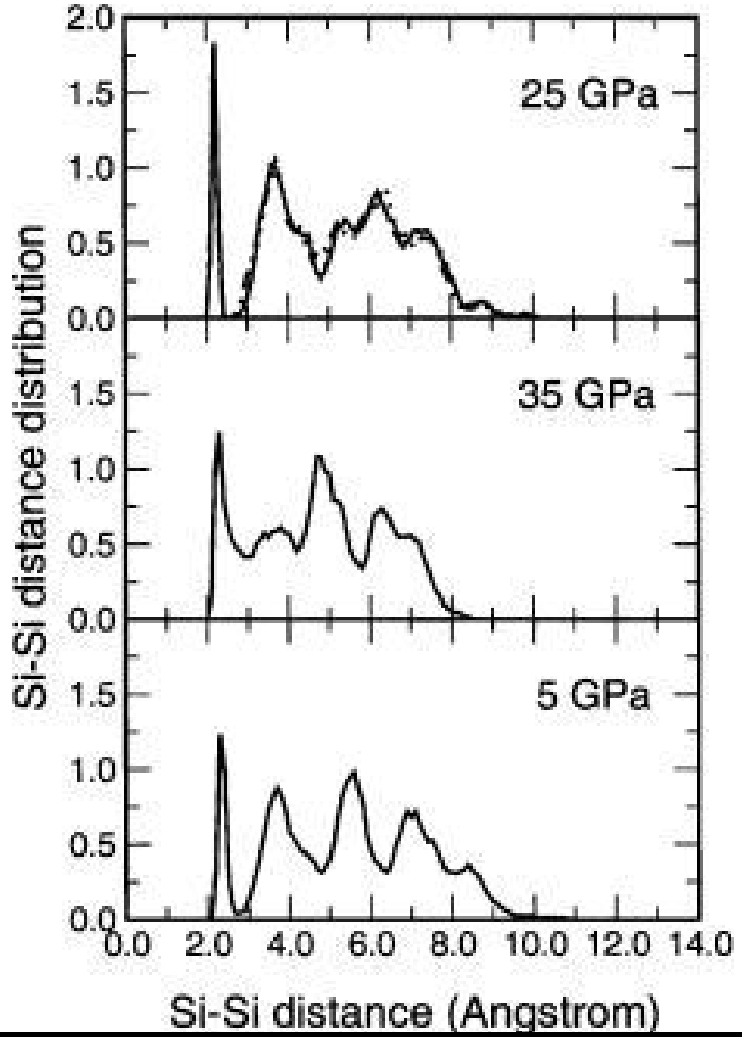


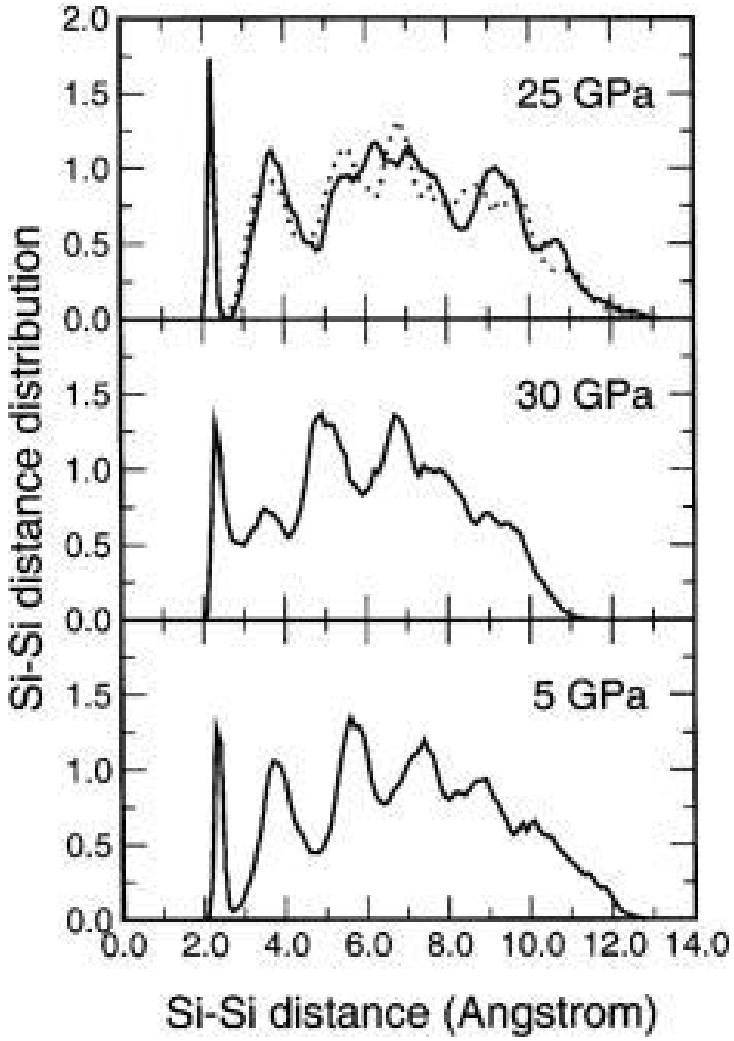
$Si_{71}H_{60}$ at 25 Gpa (top), 30 GPa (center), and 5 GPa (after the

In both clusters, up to 25 GPa, a distorted but predominantly tetrahedral coordination is maintained, with no sign of a transformation to a different structure. This also holds for the case with the vacancy, even if with a higher degree of disorder.

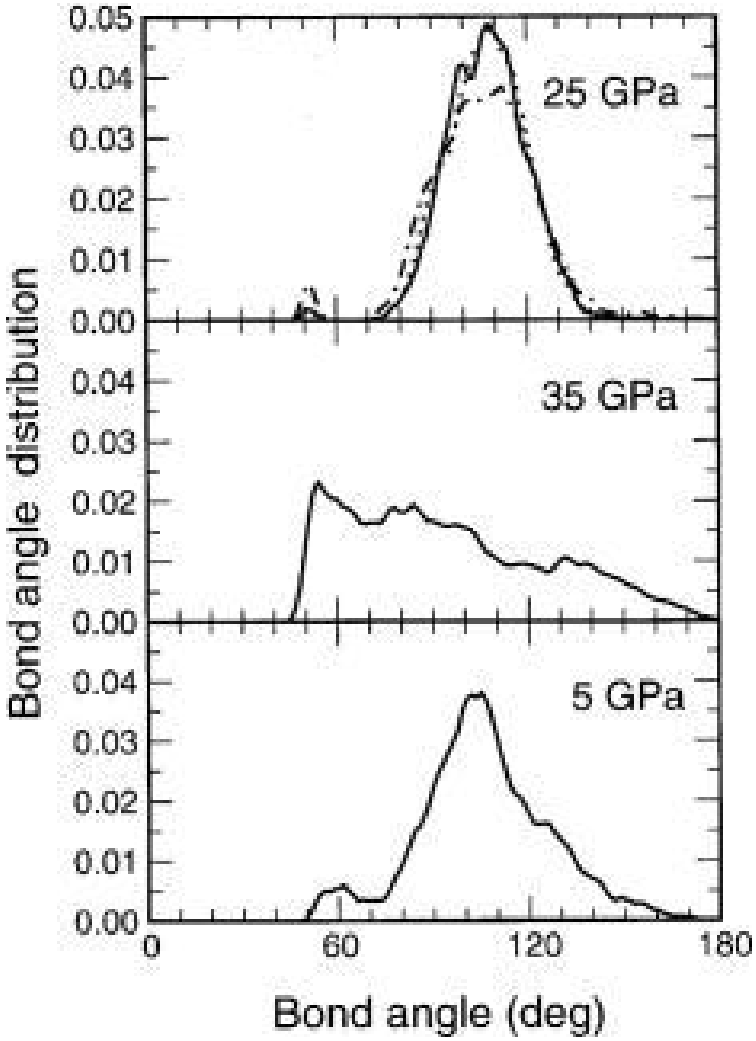


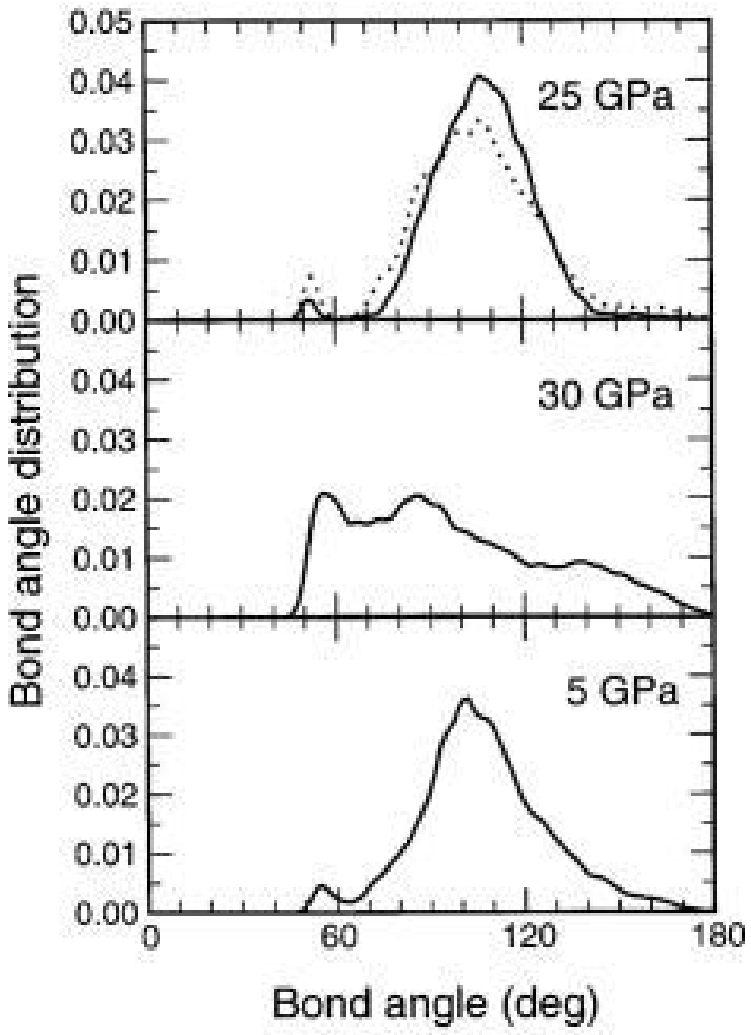
Dramatic structural transformation occurs for Si35H36 at 35 GPa and for Si71H60 at 30 GPa. Shape changes to roughly spherical and the tetrahedral coordination is no longer dominant. (In accord with exps.)



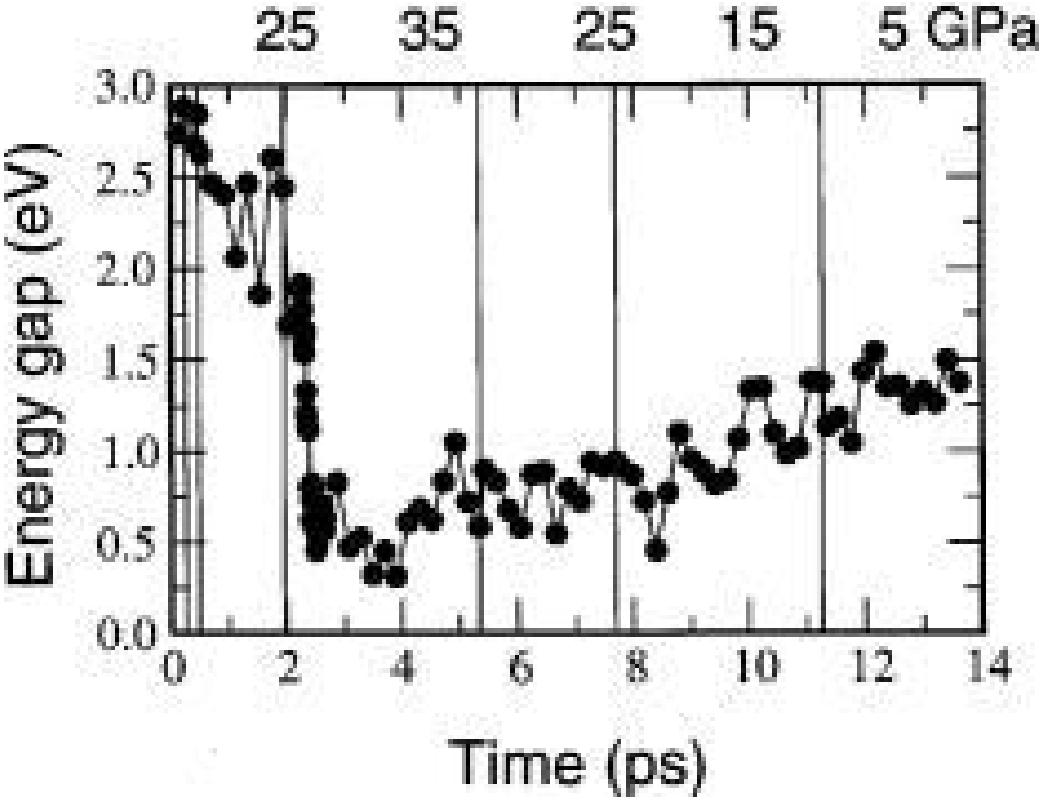


Distributions of the SiSi distances for Si71H60


25 GPa
35 GPa
5 GPa
Bond angle distribution
Bond angle (deg)
0.05
0.04
0.03
0.02
0.01
0.00
0
60
120
180


25 GPa
30 GPa
5 GPa
Bond angle distribution
Bond angle (deg)
0.05
0.04
0.03
0.02
0.01
0.00
0
60
120
180

The change in coordination and shape is accompanied by a change in the electronic properties.
There is a clear qualitative trend toward metallicity at high pressure.



Time evolution of the KohnSham energy gap of Si35H36