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Computational methods for electronic structure

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COMPUTATIONAL METHODS

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LECTURE 3

KOHN-SHAM EQUATIONS

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(r,R) + \int \frac{\rho(r')}{|r-r'|}dr' + \mu_{xc}[\rho]\right\}\varphi_i(r) = \varepsilon_i \varphi_i(r)$$

WITH:

$$\rho(r) = \sum_{i=1}^{N_{occ}} \underbrace{f_i}_{\text{occupation numbers}} |\varphi_i(r)|^2 \qquad \text{DENSITY}$$

AND:

$$\int \varphi_i^*(r)\varphi_j(r)\,dr = \delta_{ij} \qquad \text{ORTHOGON.}$$

SOLVE EIGENVALUE EQUATION SELF-CONSISTENTLY.

TWO CHOICES

① NUCLEAR-ELECTRON INTERACTIONS

ALL-ELECTRON VS. PSEUDOPOT.

② BASIS SET

$$\varphi_j(r) = \sum_{i=1}^{M \to \text{SIZE}} C_{jm}\,\phi_m(r) \qquad \text{BASIS FCT.}$$

COEFF.

ALL-ELECTRON METHODS: Core, semicore, and valence electrons treated on the same footing. Bare Coulomb interaction used.

- Localized basis sets (Quantum chemistry)

  GTO - STO - LCAO (explicit)

- Muffin Tin orbitals (secular equation)

  KKR - LMTO (Haukels)

  APW - LAPW (Plane waves)

CORE ELECTRONS DO NOT PARTICIPATE IN CHEMICAL BONDING.

⇓

PSEUDOPOTENTIALS

Only valence electrons are explicitly considered. The nucleus is replaced by (nucleus + core electrons) ⇒ ⇒ ionic cores. Screened Coulomb interactions used.

Valence wfn are "hard" close to the nucleus (orthogonalization ⇒ nodes)

↳ Forget about what happens inside r_c, and replace the true potential with a pseudopotential, so that the pseudo wfn is nodeless and smooth.

Constructing pseudopotential theories

1. Remove core electrons from the calculation
2. Replace the bare nucleus-electron potential with a screened ion-electron potential (V_{sc})

   Electrons of $\neq$ angular momentum feel $\neq$ potentials

   $\Rightarrow V_{sc}(r) \rightarrow V_{sc}^{l}(r)$

   For each l: the valence wave function should be the Ground state of $V_{sc}^{l}(r)$ (core states don't appear any longer)

Si(Be)	Si(P)
$1s^2 2s^2 2p^6$	–
$3s^2 3p^2$	$1s^2 2p^2$

3. Replace the screened (true) potential with a weaker pseudopotential whose GS is a pseudo wfn. (nodeless)

   Be careful that the scattering properties (phase shifts) are not modified by pseudization.

Phillips-Kleinman (1959)

ψ_v with ψ_c.

(ψ_v = true wfn.; ϕ_v = pseudo wfn.)

$$\underbrace{\psi_v}_{\text{orthogonal with } \psi_c} = \underbrace{\phi_v}_{\text{smooth, non-orthogonal to core states. (nodeless)}} - \sum_c \alpha_{cv} \psi_c \quad \text{to orthog.}$$

Enormous freedom!!

$$\left\{ \hat{H} + \sum_c (\varepsilon_v - \varepsilon_c) |\psi_c\rangle\langle\psi_c| \right\} \phi_v = \varepsilon_v \phi_v$$

Pseudo wfn.

Pseudo hamiltonian

↳ Acts $\neq$ on different l-states.

same eigenvalue as the true ψ_v

Non-local pseudopotentials

$$V_{PS}(\bar{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} |lm\rangle V_{PS}^{l}(r) \langle lm| =$$

($V_{PS}^{l}(r)$: semilocal)

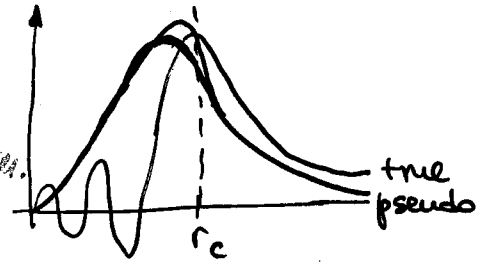
$$= V_{loc}(r) + \sum_{l=0}^{l_{max}} \Delta V_{PS}^{l}(r)\, \hat{P}_l$$

$$= V_{PS}^{l}(r) - V_{loc}(r)$$

(Empirical)

Phillips-Kleinman: the pseudo wfn. has ≠ amplitude than the true wfn.

wrong valence charge distribution.



Hamann, Schlüter and Chiang (1979): NORM-CONSERVING PSEUDOPOTENTIALS

True and pseudo wfn. are equal for $r > r_c$

⇒ scattering properties are the same.

How to do that?

1. $\phi_{PS} = \begin{cases} \tilde{\phi}_{PS}(r) & r < r_c \\ \phi_{ae}(r) & r \geq r_c \end{cases}$
2. $\phi_{PS}(r)$ and $\phi'_{PS}(r)$ cont. at r_c
3. $\varepsilon_{PS} = \varepsilon_{ae}$
4. $\int_0^{r_c} |r\phi_{PS}(r)|^2 dr = \int_0^{r_c} |r\phi_{ae}(r)|^2 dr$ NORM CONSERV.

TRANSF.

V_{PS} and V_{ae} have the same 1st order variation in energy (Eig.)

General procedure

1. Solve all-electron radial Schrödinger eq. for the atom in some electronic configuration:

$$\left\{-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V[\rho,r]\right\} r R^{AE}_{nl}(r)=\varepsilon_{nl}\, r R^{AE}_{nl}(r)$$

$$V[\rho,r]=-\frac{Z}{r}+\int\frac{\rho(r')}{|\vec{r}-\vec{r}'|}dr'+\mu_{xc}[\rho]$$

2. Construct the pseudo wave function according to some prescription (BHS - Troullier-Martins - Kerker - ...)

3. Invert the radial Schrödinger eq. for the screened pseudopotential:

$$V^{PP}_{sc\,nl}(r)=\varepsilon_{nl}-\frac{l(l+1)}{2r^2}+\frac{1}{2rR^{PP}_{nl}(r)}\frac{d^2}{dr^2}\left[rR^{PP}_{nl}(r)\right]$$

4. Unscreen the pseudopotential:

$$V^{PP}_{nl}(r)=V^{PP}_{sc\,nl}(r)-\int\frac{\rho_v(r')dr'}{|\vec{r}-\vec{r}'|}-\mu_{xc}[\underbrace{\rho_v}_{\text{valence charge dens.}}]$$

BACHELET - HAMANN - SCHLÜTER (1982)

$$V^l_{ps}(r)=-\frac{Z_v}{r}\left[C\,\mathrm{erf}\left(\sqrt{\alpha_1^{loc}}\,r\right)+(1-C)\,\mathrm{erf}\left(\sqrt{\alpha_2^{loc}}\,r\right)\right]+$$

$$+\sum_{i=1}^{3}\left(A_{l,i}+r^2A_{l,i+3}\right)e^{-\alpha_{l,i}r^2}$$

Troullier-Martins (PRB 43, 1993 ('91)).

$R_l^{PS}(r) = r^l e^{p(r)}$ → No singularity at $r=0$.

$p(r) = c_0 + \sum_{i=2}^{n} c_i r^i$

odd coeff $(c_{i+1}) = 0 \Rightarrow$ SMOOTH.

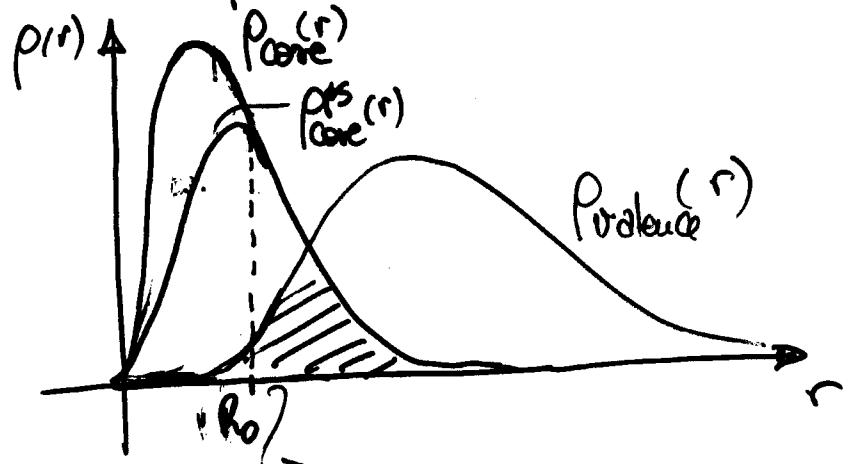
TM: $n = 12$.

1) Norm conservation within r_c
2) Continuity of R and its first 4 derivatives at r_c
3) Zero curvature at the origin ($V''_{sc,l}(0) = 0$)
   $\Rightarrow c_2^2 + c_4(2l+5) = 0$. (SMOOTHNESS).

ULTRASOFT (VANDERBILT / RKKJ) PSEUDOS.

NON-LINEAR CORE CORRECTIONS.

Louie, Froyen & Cohen, PRB 26, 1738 (82)



overlap of core and valence charge densities.

V_H, V_{ext} are linear in ρ, but not V_{xc}

1) $V_\ell^{ps}(r) = V_{sc,\ell}^{ps} - \int \frac{\rho_{ir}(r')\,dr'}{|r-r'|} - \mu_{xc}[\rho_v + \rho_c]$

2) Compute μ_{xc} for $\rho_v + \rho_c$, ρ_c = frozen core charge density.

3) $\rho_c(r)$ is "hard" $\Rightarrow$

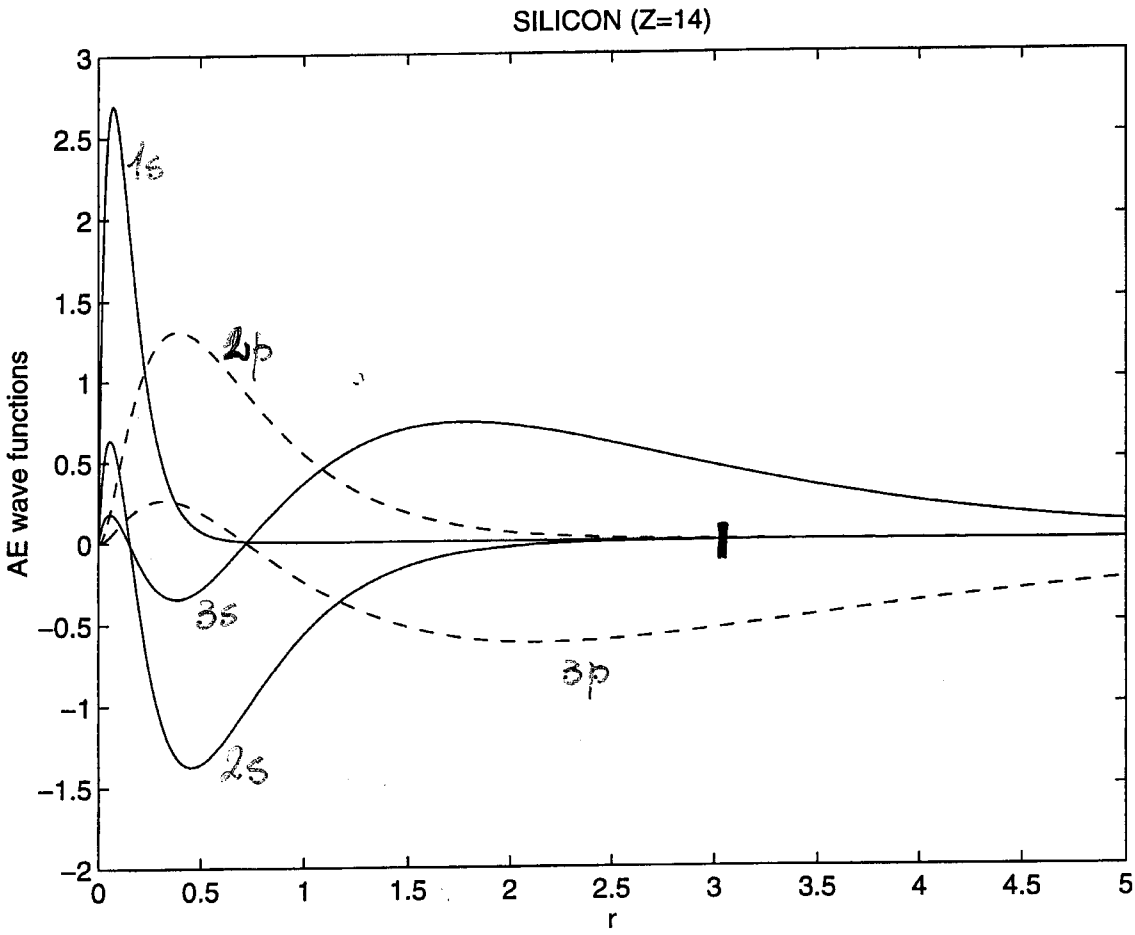
$\Rightarrow$ pseudize it for $r < R_o$.

$$\tilde{\rho}_c(r) = \begin{cases} \rho_c(r) & r > R_o \\ A\,\dfrac{\sin(Br)}{r} & r \le R_o \end{cases}$$

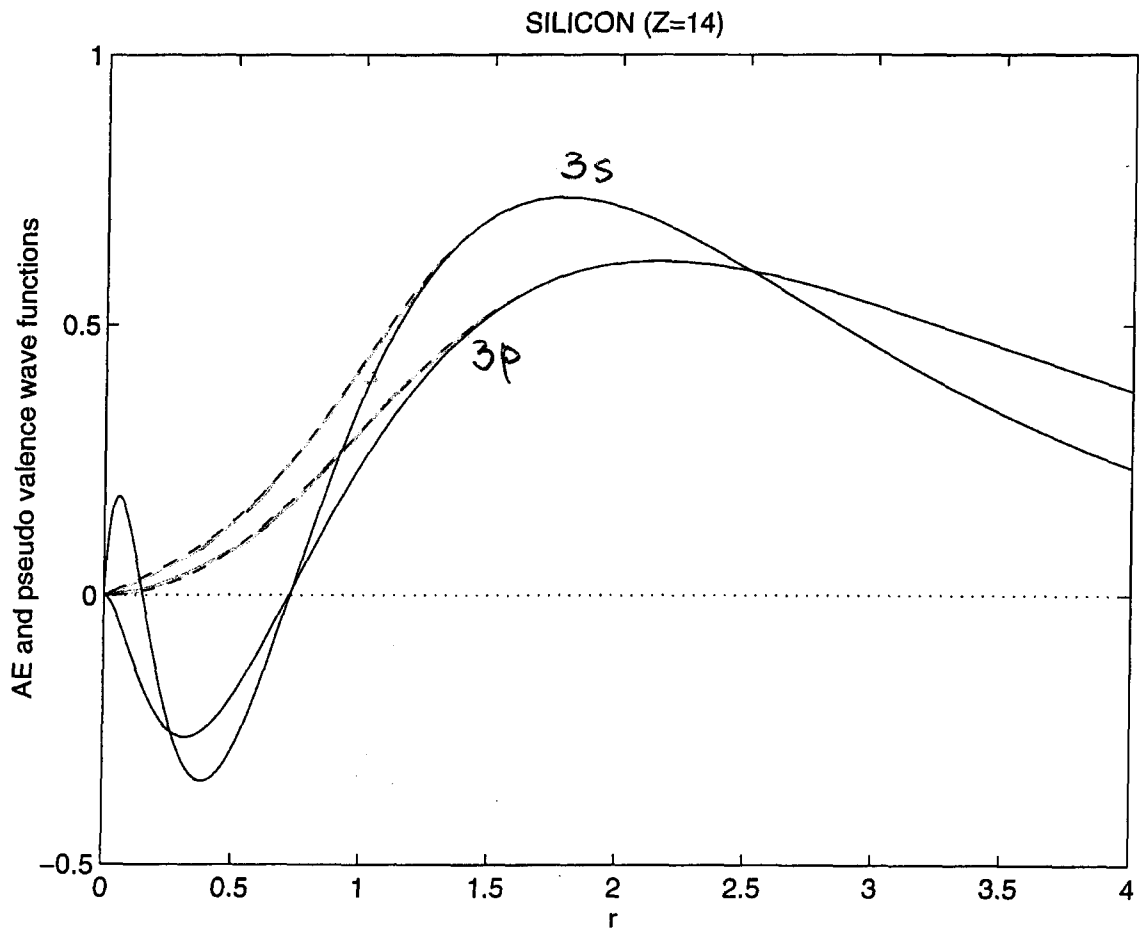
Silicon : Atomic Wave functions

$\varepsilon(1s) = -65.184$
$\varepsilon(2s) = -5.074$
$\varepsilon(2p) = -3.514$
} core

$\varepsilon(3s) = -0.398$
$\varepsilon(3p) = -0.154$
} valence



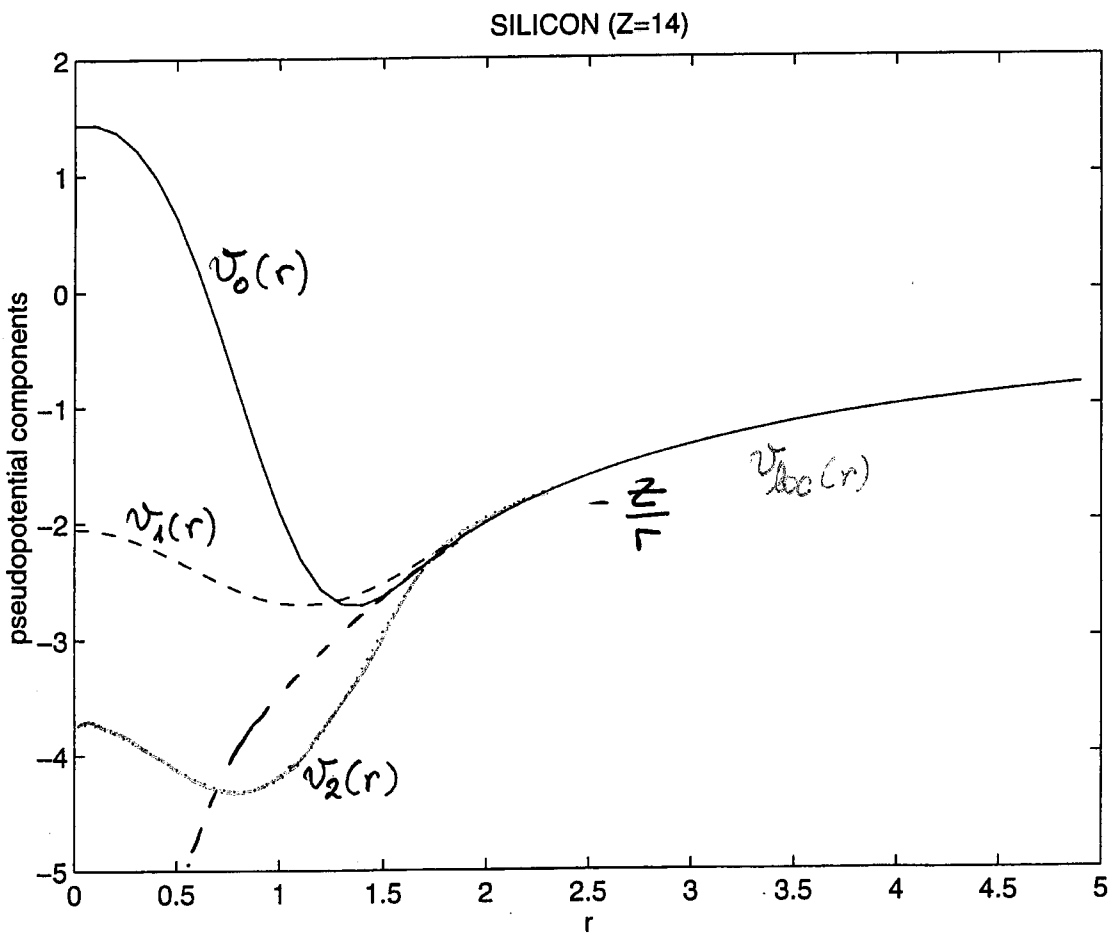
Silicon: Atomic and Pseudoatomic wave functions (valence)



Silicon: Pseudopotentials

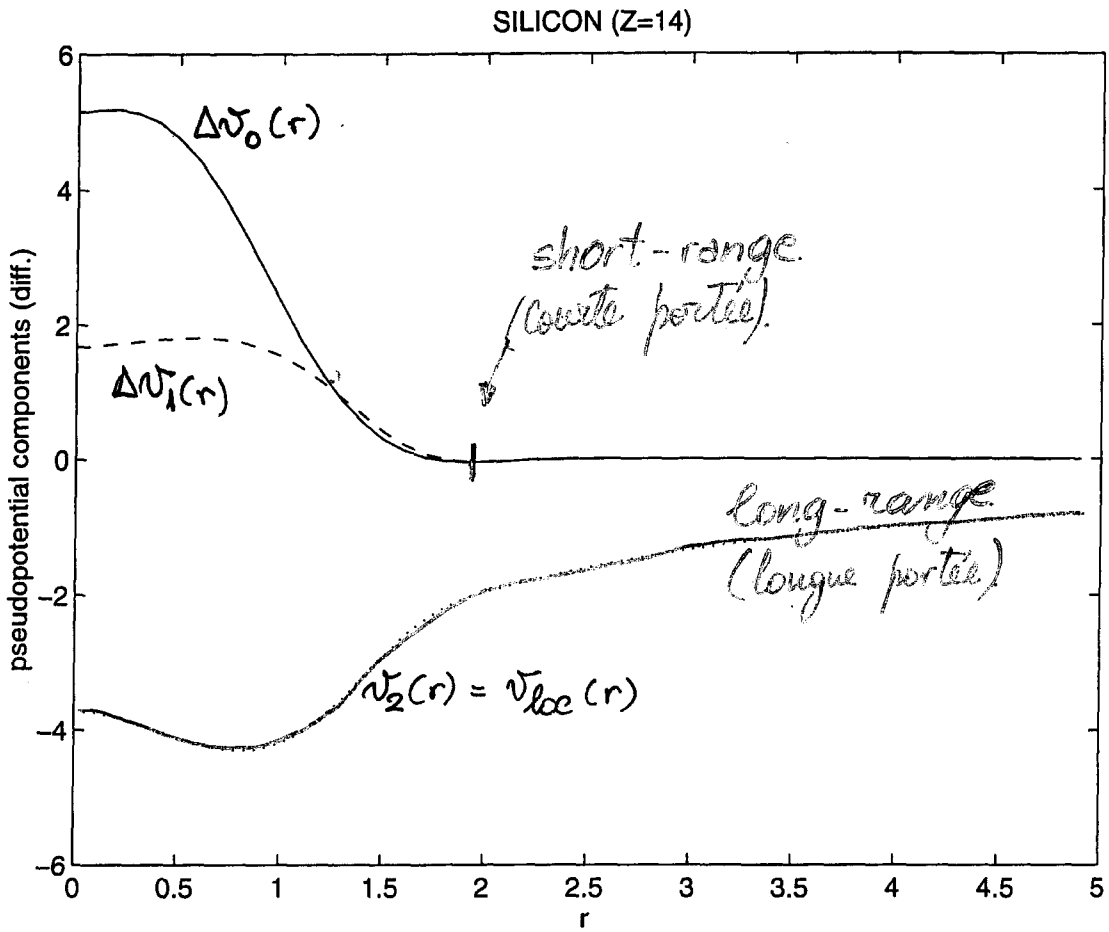
$$\hat{v}_{PS}(\vec{r}) = \sum_{l=0}^{\infty} v_l(|\vec{r}|)\,\hat{P}_l =$$

$$\approx v_{loc}(r) + \sum_{l=0}^{l_{max}} \Delta v_l(r)\,\hat{P}_l$$



Silicon: Local and Non-local pseudos.

$$\hat{v}_{PS}(\vec{r}) = \underline{v_2(r)} + \sum_{\ell=0}^{1} \Delta v_\ell(r) \hat{P}_\ell$$



BASIS SETS

— [redacted] $\varphi_j(\Sigma) = \sum_{\alpha=1}^{M} c_{j\alpha} \underline{\phi_\alpha(\Sigma)}$

BASIS FUNCTIONS

$\phi_\alpha(\Sigma)$ CAN DEPEND ON ENERGY, BUT IT'S MESSY. IF NOT, THEN KS EQUATIONS BECOME A GENERALISED EIGENVALUE PROBLEM:

$$\sum_{\beta=1}^{M} (\underline{\underline{H}}_{\alpha\beta} - \varepsilon_j \underline{\underline{S}}_{\alpha\beta}) c_{j\beta} = 0$$

Hamiltonian, overlap

$$H_{\alpha\beta} = \int \phi_\alpha^*(\Sigma)\, \hat{H}\, \phi_\beta(\Sigma)\, d\Sigma$$

$$S_{\alpha\beta} = \int \phi_\alpha^*(\Sigma)\, \phi_\beta(\Sigma)\, d\Sigma \quad (\neq \delta_{\alpha\beta})$$

SAME CAN BE DONE FOR HARTREE-FOCK → ROOTHAAN-HALL EQUATIONS.

PERIODIC SYSTEMS (CRYSTALS)

$$\varphi_j^{(\underline{k})}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}} \sum_{\alpha=1}^{M} C_{j\alpha}^{(\underline{k})} \phi_\alpha(\underline{r})$$

if $\phi_\alpha(r)$ respect PBC

$$\varphi_j^{(\underline{k})}(\underline{r}) = \sum_{\alpha=1}^{M} C_{j\alpha}^{(\underline{k})} \left(\frac{1}{\sqrt{\Omega}} \sum_{\underline{T}} e^{i\underline{k}\cdot\underline{T}} \phi_\alpha(\underline{r}-\underline{T}) \right)$$ BLOCH SUMS

if $\phi_\alpha(r)$ are not periodic (localized)

$\underline{k}$ = VECTORS IN THE BRILLOUIN ZONE

KS EQUATIONS

$$\sum_{\beta=1}^{M} \left(H_{\alpha\beta}^{(\underline{k})} - \varepsilon_j^{(\underline{k})} S_{\alpha\beta}^{(\underline{k})} \right) C_{j\beta}^{(\underline{k})} = 0 .$$

WITH:

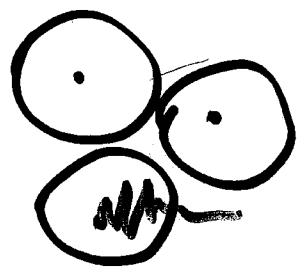
$$\rho(\underline{r}) = \sum_{\underline{k}} w_{\underline{k}} \sum_{i=1}^{N_{\underline{k}}} f_i^{\underline{k}} \left| \varphi_i^{(\underline{k})}(\underline{r}) \right|^2$$

- $w_{\underline{k}}$: weights (symmetry)
- $f_i^{\underline{k}}$: occupation numbers
  - Fermi-Dirac
  - Methfessel-Paxton
  - Marzari-Vanderbilt
  - Tetrahedron
- (choice of k-pts.)
  - Baldereschi
  - Chadi-Cohen
  - Monkhorst-Pack

BASIS FUNCTIONS

1. FLOATING (DON'T MOVE WITH ATOMS)
   - PLANE WAVES
   - ADAPTIVE GRIDS (FINITE DIFFERENCES)
   - FLOATING GAUSSIANS
   - WAVELETS
   - B-SPLINES
   - LAGRANGE POLYNOMIALS
   - SPHERICAL WAVES
2. ATOM-CENTERED (LOCAL ORBITALS)
   - ATOMIC ORBITALS (LCAO)
   - NUMERICAL
   - HYDROGENIC
   - SLATER-TYPE (STO)
   - GAUSSIAN-TYPE (GTO)

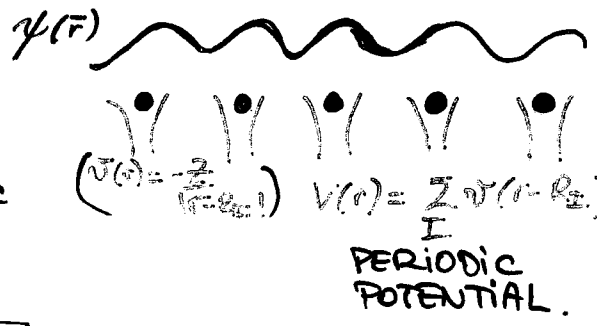
   BSSE
3. MIXED
   - PLANE WAVES + GAUSSIANS



4. AUGMENTED
   - APW - ASW - MTO (Muffin-tin)

PLANE WAVES

Bloch Theorem:



If $V(\vec{r}) = V(\vec{r}+\vec{a})$ is a periodic potential (period $\vec{a}$)

$$\Rightarrow \boxed{\psi_{\underline{k}}(\vec{r}) = e^{i\underline{k}\cdot\underline{r}}\, u_{\underline{k}}(\vec{r})}$$

$u_{\underline{k}}(\vec{r}) = u_{\underline{k}}(\vec{r}+\vec{a})$ is also periodic, with period $\vec{a}$.

$e^{i\underline{k}\cdot\underline{r}}$ comes from the translational symmetry.

$u_{\underline{k}}(\vec{r})$ periodic $\Rightarrow$ Fourier transform:

$$u_{\underline{k}}(\vec{r}) = \int e^{i\vec{g}\cdot\vec{r}}\, \tilde{u}_{\underline{k}}(\vec{g})\, d^3g$$

$$u_{\underline{k}}(\vec{r}+\vec{a}_i) = \int e^{i\vec{g}\cdot\vec{r}}\, \tilde{u}_{\underline{k}}(\vec{g})\, e^{i\vec{g}\cdot\vec{a}_i}\, d\vec{g}$$

$\Rightarrow e^{i\vec{g}\cdot\vec{a}_i} = 1$

$\vec{g}\cdot\vec{a}_i = 2\pi n$

$\Rightarrow$ The FT is, in fact, a Fourier Series:

$$\boxed{u_{\underline{k}}(\vec{r}) = \sum_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}\, u_{\underline{k}}(\vec{G})}$$

expansion in plane waves

with $\vec{G} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3$

$\vec{b}_1, \vec{b}_2, \vec{b}_3$: reciprocal lattice vectors.

$$\vec{b}_i = \frac{\vec{a}_j \times \vec{a}_k}{\Omega}\ (\epsilon_{ijk}) \qquad \Omega = \vec{a}_i\cdot(\vec{a}_j\times\vec{a}_k)$$

volume

Plane wave expansion: $$\psi_{\underline{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}=0}^{\infty} e^{i\vec{G}\cdot\vec{r}} C_{\underline{k}}(\vec{G})$$

Periodic Boundary Conditions (PBC) always satisfied.

Basis set: $$\phi_{\underline{k}}^{\vec{G}}(\vec{r}) = \frac{e^{i(\vec{k}+\vec{G})\cdot\vec{r}}}{\sqrt{\Omega}}$$

Kinetic operator:

$$T_{\vec{G},\vec{G}'}^{\underline{k}} = \langle k+\vec{G} | -\frac{\hbar^2}{2m}\nabla^2 | \vec{k}+\vec{G}' \rangle = \frac{\hbar^2}{2m} |\vec{k}+\vec{G}|^2 \delta_{\vec{G},\vec{G}'}$$

Potential operator:

$$V_{\vec{G},\vec{G}'}^{\underline{k}} = V_{\vec{G},\vec{G}'} = \langle k+\vec{G} | V | k+\vec{G}' \rangle = \frac{1}{\Omega}\int V(\vec{r}) e^{i(\vec{G}-\vec{G}')\cdot\vec{r}}\, d\vec{r} = \tilde{V}(\vec{G}-\vec{G}')$$

Overlap:

$$S_{\vec{G},\vec{G}'}^{\underline{k}} = \langle k+\vec{G} | k+\vec{G}' \rangle = \delta_{\vec{G},\vec{G}'}$$ orthogonal basis.

Secular equation:

$$\sum_{\vec{G}'} \left[\frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2 \delta_{\vec{G},\vec{G}'} + \tilde{V}_{KS}(\vec{G}-\vec{G}') \right] C_{\underline{k}}(\vec{G}') = \varepsilon_{\underline{k}} C_{\underline{k}}(\vec{G}).$$

ENERGY CUTOFF: Cut the PW expansion at G_{CUT}.

variational. $E(G_{CUT}) < E(G'_{CUT})$ if $G_{CUT} > G'_{CUT}$

Plane Waves

⊕ $\hat{T}$ is diagonal in reciprocal space
$\hat{V}_{loc}$ is diagonal in real space (V_{nl}) $\Big\} \Rightarrow$

$\Rightarrow$ Matrix elements can be calculated where they are diagonal, and the wfn. transformed from real to reciprocal space (and back) using FFT.

⊕ Calculation of energy, matrix elements, forces and stresses is VERY SIMPLE.

⊕ PW basis is "floating" $\Rightarrow$ All regions of space are equally represented (UNBIASED). No "Pulay" forces.

⊕ E_{TOT} is variational in E_{CUT}.

⊖ Waste of effort for isolated systems.

⊖ Large number of PW needed for strong potentials.
(H, first row, TM)

Solving Kohn-Sham equations

$$\sum_{G'} H^{KS}_{K+G,\,K+G'}(\{c\})\, c^{(j)}_{K+G'} = \varepsilon^{(j)} c^{(j)}_{K+G}$$

1. Computation of Matrix elements
2. Solution of eigenvalue equation
3. Self-consistency. (H^{KS} depends on $\{c\}$).

DIAGONALIZATION

DIRECT: Diagonalize full Hamiltonian matrix using Linear Algebra packages

LAPACK - SCALAPACK (parallel)

- Small matrices (small no. basis functions)
- Can be used restricting requested no. eigenstates if too large.

ITERATIVE: Filter out lowest-lying eigenstates

Simple example:

$$\psi^{(n+1)} = e^{-\beta \hat{H}} \psi^{(n)}$$

if $\psi^{(n)} = \sum_{i=1}^{M} c_i^{(n)} \varphi_i \Rightarrow$

$$\Rightarrow \psi^{(n+1)} = \sum_{i=1}^{M} e^{-\beta \varepsilon_i} c_i^{(n)} \varphi_i$$

After m steps: $\psi^{(m)} = \sum_{i=1}^{M} \underbrace{e^{-m\beta\varepsilon_i} c_i^{(0)}}_{c_i^{(m)}} \varphi_i$

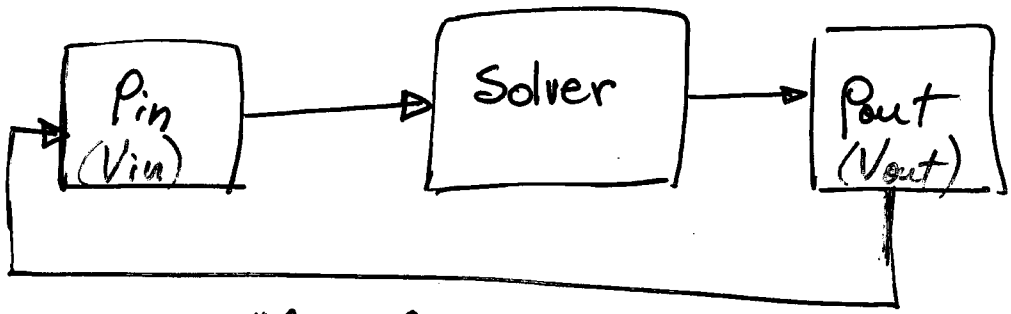
$$\frac{c_i^{(m)}}{c_1^{(m)}} = e^{-m\beta(\varepsilon_i - \varepsilon_1)} \longrightarrow 0 \text{ for large } m. \Rightarrow \psi^{(m)} \to c_1^{(0)} e^{-m\beta\varepsilon_1} \varphi_1$$

Only GS!

MANY STATES, MORE EFFICIENT { LANCZOS, DAVIDSON

SELF-CONSISTENCY

- MIXING SCHEMES
- DIRECT MINIMIZATION OF THE ENERGY FUNCTIONAL.



$$\|\rho_{out} - \rho_{in}\| < \varepsilon$$

$$\Downarrow$$

Self-consistency.

The solver:

$$f(\underline{r},\underline{r}') = \frac{\delta V_{KS}^{out}(\underline{r})}{\delta V_{KS}^{in}(\underline{r}')} = \int \frac{1}{|r-r''|}\left[\frac{\delta \rho_{out}(r'')}{\delta V_{KS}^{in}(\underline{r}')}\right] dr'' +$$

$$+ \frac{d\mu_{KC}[\rho_{out}]}{d\rho_{out}(\underline{r})} \cdot \left[\frac{\delta \rho_{out}(r)}{\delta V_{KS}^{in}(r')}\right] \longrightarrow \chi(\underline{r},\underline{r}')$$

Response function...

$\chi(\underline{r},\underline{r}') < 0$ for the electron gas.

(Increasing $V \Rightarrow$ electrons flow away!)

Finding the fixed point: $V_{KS}^{out} = V_{KS}^{in} \Rightarrow$

$\Rightarrow$ solving $f(x) = x$

In our case: $V_{KS}^{out}(\underline{r}) = \int \underbrace{f(\underline{r},\underline{r}')}_{\text{Kernel.}} V_{KS}^{in}(\underline{r}')\, d\underline{r}'$

If the slope is too large and negative $\Rightarrow$
$\Rightarrow$ it oversluts and diverges.

$f(\underline{r},\underline{r}')$ is negative (χ is negative)
and very large at some points $\left(\frac{1}{|r-r'|}\right)$

$\Rightarrow$ Use mixing of input & output.

SIMPLE MIXING

$$\rho_{in}^{(n+1)}(\underline{r}) = \alpha\, \rho_{out}^{(n)}(\underline{r}) + (1-\alpha)\, \rho_{in}^{(n)}(\underline{r})$$

ANDERSON MIXING

$$\bar{\rho}_{in}(n) = \beta\, \rho_{in}(n) + (1-\beta)\, \rho_{in}(n-1)$$
$$\bar{\rho}_{out}(n) = \beta\, \rho_{out}(n) + (1-\beta)\, \rho_{out}(n-1)$$

Minimize $\| \bar{\rho}_{out} - \bar{\rho}_{in} \| \Rightarrow \beta$ - Then use simple mixing.

PULAY : Generalization of Anderson to mixing of several preceding steps.

BROYDEN. (along the same line).

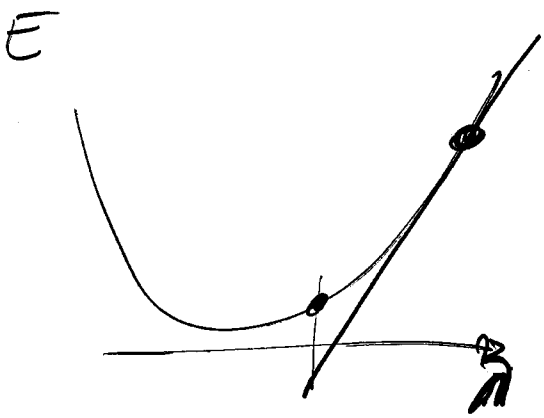
FEMD : - Solve $H\psi = \varepsilon\psi$ using Lanczos (fixed ρ).
- Mix ρ_{in} and ρ_{out} with Anderson or Broyden.

DIRECT MINIMIZATION

$$\varphi_i^{(n+1)} = \varphi_i^{(n)} - \Delta \frac{\delta E[\{\varphi_i^{(n)}\}, R]}{\delta \varphi_i^{*(n)}}$$

Force

steepest Descent.



$$H_{KS}\varphi_i^{(n)} - \sum_j \lambda_{ij}\varphi_j^{(n)}$$

Conjugated Gradients

CODES

- **ALL-ELECTRON**
  - LAPW : WIEN2k (Vienna)
  - LMTO : Stuttgart (O.K. Andersen), M. van Schilfgaarde, S. Savrasov
  - GAUSSIANS : Crystal (Torino), D-mol (Delley), Gaussian, Gamess, NWChem, ~~R~~Gauss, ... (Quantum Chemistry)
- **PSEUDOPOTENTIALS**
  - PLANE WAVES (PAW) : VASP (Vienna), Q-Espresso (Trieste), CPMD (Zürich/Stuttgart), CASTEP (UK), ABINIT (Belgium), FHI
  - LOCAL ORBITALS : SIESTA (Spain) (LCAO), QUICKSTEP (Zurich Stuttgart) (Gauss.), ONETEP (UK) (psinc), CONQUEST (UK) (Splines)