Basic Band Structure Concepts



Crystals: periodic boundary conditions, Bravais lattices, Reciprocal Lattice, Brillouin Zone, Bloch Theorem.

Energy in an infinite solid: PlaneWave expansion, Ewald sums, BZ sampling.

Band structure of materials: metal, insulators, partial occupations, (fictitious) temperature

All-electrons vs Pseudopotential methods

Cohen-Bergstressen empirical pseudopotential, Norm-Conserving PP, Ultra-Soft PP, PAW



Infinite Solid with Periodic Boundary Conditions

Real crystals are finite in size and can present many defects (vacancies, impurities, ...). However many properties of a solid, the **bulk properties**, can be studied in the ideal model of an infinite crystal where an elementary unit (one or more atoms) is repeated throughout space.

The resulting periodicity greatly simplifies the problem.



Infinite Solid with Periodic Boundary Conditions

In three dimensions the infinite periodic solid is defined by three fundamental lattice vectors a_1 , a_2 , a_3 , and by the positions of the atoms in the unit cell ($n_{at} = #$ of atoms in the unit cell).

The general atom position R_{ion} is given by



NB: atoms at the same position T_s in different unit cells are of the same atomic kind.



Born-von Kármán Periodic Boundary Conditions

It is convenient to view the infinite solid as a <u>three dimensional</u> <u>thorus</u> containing $N = N_1 \times N_2 \times N_3$ cells with <u>periodic boundary</u> <u>conditions</u>. Crystal sums are finite, wfc are normalized. The limit of large N_i is understood.



Crystal lattice

A regular array of atoms periodically repeated in space



The **crystal structure** is defined by

1) Bravais lattice : regular periodic arrangement of points in space defined by the *primitive* translation vectors (cell shape)

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$



Crystal lattice

A regular array of atoms periodically repeated in space



The vectors $\underline{R}=n_1 \underline{a_1} + n_2 \underline{a_2} + n_3 \underline{a_3}$ are the direct lattice vectors; they define the crystal lattice. Translation by any lattice vector leaves the crystal unchanged. <u>This is by far the most important</u> <u>symmetry of the crystal</u> => Bloch Theorem. Notice that this symmetry only applies to infinite crystals (or crystals with BvK periodic boundary conditions) which is why they have been introduced !



Primitive unit cell



- can be defined by three fundamentale lattice vectors **a**₁, **a**₂, **a**₃ three lenghts (a,b,c) and three angles (α, β, γ) contains exactly one lattice point
- !! the choice of primitive vectors is not unique !!
- volume of the primitive cell is independent on that choice $\Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$

The Wigner-Seitz cell (the region closer to the origin than to any other lattice point) is the most symmetric choice

Wigner-Seitz cell

Figure 4.15

The Wigner-Seitz cell for the body-centered cubic Bravais lattice (a "truncated octahedron"). The surrounding cube is a conventional body-centered cubic cell with a lattice point at its center and on each vertex. The hexagonal faces bisect the lines joining the central point to the points on the vertices (drawn as solid lines). The square faces bisect the lines joining the central point to the central points in each of the six neighboring cubic cells (not drawn). The hexagons are regular (see Problem 4d).



FCC



Figure 4.16

Wigner-Seitz cell for the face-centered cubic Bravais lattice (a "rhombic dodecahedron"). The surrounding cube is *not* the conventional cubic cell of Figure 4.12, but one in which lattice points are at the center of the cube and at the center of the 12 edges. Each of the 12 (congruent) faces is perpendicular to a line joining the central point to a point on the center of an edge.



Crystal lattice

A regular array of atoms periodically repeated in space

The **crystal structure** is defined by

1) Bravais lattice : regular periodic arrangement of points in space defined by the *primitive* translation vectors (cell shape)

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

2) Basis : position of the atoms in the *primitive* cell

• $\mathbf{R}_{n}^{(1)} = \overline{\tau_{1}} + n_{1}\mathbf{a}_{1} + n_{2}\mathbf{a}_{2} + n_{3}\mathbf{a}_{3}$ • $\mathbf{R}_{n}^{(2)} = \overline{\tau_{2}} + n_{1}\mathbf{a}_{1} + n_{2}\mathbf{a}_{2} + n_{3}\mathbf{a}_{3}$ • $\mathbf{R}_{n}^{(3)} = \overline{\tau_{3}} + n_{1}\mathbf{a}_{1} + n_{2}\mathbf{a}_{2} + n_{3}\mathbf{a}_{3}$





Graphene

hexagonal + basis





Crystal Symmetry

!! symmetry of the crystal goes beyond translational invariance => point group operations !!



Crystal Symmetry

!! symmetry of the crystal goes beyond translational invariance => point group operations !!

The complete group of coordinate transformation of a crystal (its **space group**) is smaller than the space group of its lattice The presence of more than one atom in the unit cell can only reduce the number of symmetry operations of the lattice.

32 point groups

230 space groups: 73 symmorphic, 157 non-symmorphic

14 Bravais lattices: 7 crystal systems



14 Bravais Lattices grouped in 7 crystal systems





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Primitive vs conventional cell

Conventional cells are often used instead of the primitive cell



1 atom/cell

$$\mathbf{a}_{1} = \frac{a}{2}(0, 1, 1)$$
$$\mathbf{a}_{2} = \frac{a}{2}(1, 0, 1)$$
$$\mathbf{a}_{3} = \frac{a}{2}(1, 1, 0)$$

$$\mathbf{a}_1 = a(1, 0, 0)$$

 $\mathbf{a}_2 = a(0, 1, 0)$
 $\mathbf{a}_3 = a(0, 0, 1)$



Reciprocal Lattice

Besides the Bravais lattice it is useful to introduce its dual the *reciprocal lattice*

Defined by $RL = \{\mathbf{G} | \exp(+i \mathbf{G} \cdot \mathbf{R}) = 1 \forall \mathbf{R} \in BL \}$ if $\mathbf{R}_{n} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$

then $G_m = m_1 b_1 + m_2 b_2 + m_3 b_3$





- points defined as $\mathbf{G}_m = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3$
- spacing in the RL is inversely proportional to the spacing in the BL
- the primitive cell contains exacly one ${\bf G}$ point
- the choice of primitive cell is not unique but defined by the choice made for the direct lattice
- the volume of the primitive cell is $\ \ \Omega$

$$\Omega_{BZ} = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{\Omega}$$



Brillouin Zone

*BZ is the Wigner-Seitz cell of the reciprocal lattice
 *Obtained by bisecting with perpendicular planes the vectors connecting nearest neighbor lattice points
 * Shape of BZ reflects symmetry of the direct lattice

"Best" primitive cell

*Any point of the first BZ is closer to a given lattice point than to any other *Bragg scattering







External potential

Electrons in a crystal are not free but subject to the strong potential from the periodically arranged nuclei



The electronic band structure arises in response to the periodic potential



Kohn-Sham equations in a periodic solid

Periodic solid: atoms in periodically repeated positions

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

$$V_{ext}(\mathbf{r}) = \sum_{R,s} V_s(|\mathbf{r} - (\mathbf{R} + \tau_s)|) \qquad V_s(r) = -\frac{Z_s e^2}{r}$$

is periodic, hence so is $ho(\mathbf{r}) \Longrightarrow V_H(\mathbf{r}), V_{xc}(\mathbf{r})$



Periodic effective potential

The effective potential represents the effect of the ions on the electrons and has the same periodicity of the crystal

 $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$

can be expanded in plane waves COMPATIBLE with the periodicity of the crystal

$$V(\mathbf{r}) = \sum_{\mathbf{G}_m} V(\mathbf{G}_m) \exp(i\mathbf{G}_m \cdot \mathbf{r})$$



Bloch Theorem

 $\mathbf{k} \in BZ \quad \text{is a good quantum number to label the} \\ \text{eigenfunctions of a periodic crystal}$

$$\mathcal{T}_{\mathbf{R}}: \qquad \mathcal{T}_{\mathbf{R}}\phi(\mathbf{r}) = \phi(\mathbf{r} + \mathbf{R}) \qquad ext{is a symmetry op.}$$

$$\forall \mathbf{R} \quad [H_{KS}, \mathcal{T}_{\mathbf{R}}] = 0 \quad \Longrightarrow \quad \phi(\mathbf{r} + \mathbf{R}) = \alpha(\mathbf{R}) \ \phi(\mathbf{r})$$

$$\mathcal{T}_{\mathbf{R}}\mathcal{T}_{\mathbf{R}'} = \mathcal{T}_{\mathbf{R}+\mathbf{R}'} \implies \alpha(\mathbf{R})\alpha(\mathbf{R}') = \alpha(\mathbf{R}+\mathbf{R}')$$

$$\alpha(\mathbf{R}) = e^{i\mathbf{k}\mathbf{R}} \quad \text{with} \quad \mathbf{k} \in BZ$$
$$\phi_{\mathbf{k},i}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\mathbf{R}}\phi_{\mathbf{k},i}(\mathbf{r})$$

BvK boundary conds:

$$\mathbf{k} = \frac{m_1}{N_1} \mathbf{b}_1 + \frac{m_2}{N_2} \mathbf{b}_2 + \frac{m_3}{N_3} \mathbf{b}_3, \quad m_i = 0, 1, \dots, N_i - 1$$

There are as many ${\bf k}$ points in the BZ as cells in the BL

Bloch Theorem

 $\mathbf{k} \in BZ$ is a good quantum number to label the eigenfunctions of a periodic crystal $\phi_{\mathbf{k},i}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\mathbf{R}}\phi_{\mathbf{k},i}(\mathbf{r})$

Crystal periodicity imposes that the crystal wavefunctions are linear combinations of PWs with wave-vector ${\bf k} + {\bf G}$

$$\phi_{\mathbf{k},i}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},i}(\mathbf{G}) \frac{e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}}{\sqrt{\mathcal{V}}} = \sum_{\mathbf{G}} c_{\mathbf{k},i}(\mathbf{G}) \langle \mathbf{r} | \mathbf{k} + \mathbf{G} \rangle$$

Wavefunctions are PWs modulated by a periodic function

$$\phi_{\mathbf{k},i}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k},i(\mathbf{r})}$$

with

 $u_{\mathbf{k},i}(\mathbf{r}) = \sum_{\mathbf{c}} c_{\mathbf{k},i}(\mathbf{G}) \; \frac{e^{i\mathbf{Gr}}}{\sqrt{\mathcal{V}}} \quad \text{manifestly periodic}$



To solve the problem a basis set is introduced in order to expand the wavefunctions (in Bloch form) Q(r) = Z civ br(r) kv == 1 brow basis function La expansion coefficient This brings the eigenvalues problem to matrix form [H(F,P)-EKN] Q(F) =0 NG $\sum \left[H_{ij}^{(k)} - \varepsilon_{kv} S_{ij}^{(k)} \right] C_{kv}^{j} = 0$ $H_{ci}^{(k)} = \langle 5_{.}^{(k)} | H | 5_{.}^{(k)} \rangle$ $S_{ij}^{(k)} = \langle 5_{i}^{(k)} | 5_{ij}^{(k)} \rangle$

A natural chance for a periodic system is given by the Plane Wave basis set $b_i^{(u)}(\vec{r}) = \langle r | \kappa + G_i \rangle = \frac{1}{\sqrt{u}} e^{+i(\kappa + G)r}$ D... 2. = 20 J. with $G_i = m_2 b_1 + m_2 b_2 + m_2 b_2$ reciprocal lattice vectors Pu's form on infinite (and complete) orthogonal basis set. A finite basis set is selected requiring K (x+G:) < Ecutoff It has several advantages - It is unbiased : has the same spatial resolution. in every point and for every configuration + an be improved easily and systematically by in crossing Ecutoff Matrix dements are very simple to akulate

Matrix dements are very simple to alculate $\langle \kappa + G | - \frac{\hbar^2}{2m} \sqrt{12} | \kappa + G' \rangle = \frac{\hbar^2}{2m} (\kappa + G)^2 \int_{GG'}$ $\langle k+G | v(r) | k+G' \rangle = \frac{1}{V} (VF) e^{-i(G-G')r_{a}^{2}} = V(G-G')$ Allows the use of FFT to go back and forth between direct and reciprocal space $\nabla V_{\mu}(r) = -4\pi e^2 n(r)$ $h(r) \xrightarrow{FFT} h(G) \longrightarrow V_{H}(G) = \frac{4\pi e^{2}}{G^{2}}h(G) \xrightarrow{FFT} V_{H}(r)$ NEyN $(H \varphi)(\kappa+G): T \varphi = \frac{k^2}{2m}(\kappa+G)^2 \varphi(\kappa+G) N \varphi$ $\varphi(w+G) \xrightarrow{\text{PFT}} (\varphi(r) \xrightarrow{i} V(r) \varphi(r) \xrightarrow{\text{FFT}} [V\varphi](w+G)$ NBmN N NPONN Dual Space Formalism

Bloch Theorem

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\mathbf{r})\right]\phi_{\mathbf{k}v}(\mathbf{r}) = \varepsilon_{\mathbf{k}v} \ \phi_{\mathbf{k}v}(\mathbf{r})$$

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

$$\begin{aligned} \langle \mathbf{k} + \mathbf{G} | V_{eff} | \mathbf{k} + \mathbf{G'} \rangle &= \frac{1}{\mathcal{V}} \int_{\mathcal{V}}^{V_{eff}} (\mathbf{r}) e^{-i(\mathbf{G} - \mathbf{G'})\mathbf{r}} d\mathbf{r} \\ &= \frac{1}{\Omega} \int_{\Omega}^{V_{eff}} (\mathbf{r}) e^{-i(\mathbf{G} - \mathbf{G'})\mathbf{r}} d\mathbf{r} = V_{eff} (\mathbf{G} - \mathbf{G'}) \end{aligned}$$

$$\sum_{\mathbf{G}'} \left[\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} + V_{eff}(\mathbf{G} - \mathbf{G}') \right] c_{\mathbf{k}v}(\mathbf{G}') = \varepsilon_{\mathbf{k}v} \ c_{\mathbf{k}v}(\mathbf{G})$$



Band Structure

Energy states available to the electrons: $\epsilon_{i,k}$



- each completely filled band contains 2 electrons/cell -

Band Structure

Energy states available to the electrons: $\epsilon_{i,\mathbf{k}}$





Charge Density of infinite periodic solid

$$\rho(\mathbf{r}) = 2 \sum_{\mathbf{k}v} |\phi_{\mathbf{k}v}(\mathbf{r})|^2$$

where
$$\phi_{\mathbf{k}v}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}v}(\mathbf{G}) \frac{e^{+i(\mathbf{k}+\mathbf{G})\mathbf{r}}}{\sqrt{\mathcal{V}}}$$

is normalized in the whole crystal volume

$$\rho(\mathbf{r}) = \frac{2}{N} \sum_{\mathbf{k}v} |\tilde{\phi}_{\mathbf{k}v}(\mathbf{r})|^2$$

where $\tilde{\phi}_{\mathbf{k}v}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}v}(\mathbf{G}) \frac{e^{+i(\mathbf{k}+\mathbf{G})\mathbf{r}}}{\sqrt{\Omega}}$

is normalized in the unit cell volume



BZ integrals

$$\frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} f(\mathbf{k}) = \langle f \rangle_{BZ}$$

$$f(\mathbf{k}) = \sum_{\mathbf{R}} f_{\mathbf{R}} e^{+i\mathbf{k}\mathbf{R}} \quad \Rightarrow \quad \langle f \rangle_{BZ} = f_{\mathbf{0}}$$

Assuming $f(\mathbf{k})$ has the full symmetry of the crystal if we can find a point where $f(\mathbf{k}) = \langle f \rangle$ we only need to compute the function f in that single point !

• A. Baldereschi Phys. Rev. B7, 5212 (1973) "Hean-Value Point in the Brilloum Zone"



how one can i	Z int	egrals	t. mea	n-value p	6. 2'
(fco)	G(k)	G (k) Z,	G (4) Zz	G(4) Z3	
K= (0.6223, 0.2953, 0)	1	-0	0	¥0	
$K_{1}^{=}(\frac{1}{4},\frac{1}{4},\frac{1}{4})$	1	6	0	0	
$K_{2}^{=}(\frac{1}{4},\frac{1}{4},\frac{3}{4})$	1	-2	0	0	
4(K1) + 3 f(k2)	1	0	ð	0	141
Actually it is zer	ro up to	Σ_7 !			
· D.J. Chadi "Special	and 1 Points	M. Cohen Phys. Rev in the	Brilloviu	5747 (19 , Zone"	73)

• A. Baldereschi Phys. Rev. B7, 5212 (1973) "Hean-Value Point in the Brilloum Zone"

• D.J. Chadi and H. Cohen Phys. Rev. B<u>8</u>,5747 (1973) "Special Points in the Brillouin Zone"

• H.J. Monkhorst and J.D. Pack Phys. Rev. B 13, 5188 (1976) "Special Points for Brillovin-zone integrations"

• D.J. Chadi and M. Cohen Flys. Rev. B 16, 1746 (1977) "Special Points for Brillowin zone integrations "

· J. J. Pack and H.J. Monkhorst Phys. Rev. B 16, 1748 (1977) "Special Points for BZ integrations" - a reply

S.L. Cumingham, Phys. Rev B 10, 4988 (1974) for special points in the hexagonal lattice.


BZ integrals

$$\frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} f(\mathbf{k}) = \langle f \rangle_{BZ}$$

$$f(\mathbf{k}) = \sum_{\mathbf{R}} f_{\mathbf{R}} e^{+i\mathbf{k}\mathbf{R}} \quad \Rightarrow \quad \langle f \rangle_{BZ} = f_{\mathbf{0}}$$

A regular grid of k-points with $\Delta \mathbf{k} = \frac{2\pi}{a} \frac{1}{N}$ integrates exactly up to $R_{max} = \frac{Na}{2}$ (in a cubic system)



Monkorst-Pack meshes

•Regular equispaced meshes in the Brillouin Zone





Monkorst-Pack meshes

•Symmetry is exploited in order to reduce the number of inequivalent points to be considered

$$\begin{split} \rho(\vec{r}) &= \sum_{n,\vec{k}} \left\| \Psi_{n,\vec{k}}\left(\vec{r}\right) \right\|^2 \\ \Psi_{n,\vec{k}}\left(S^{-1}\vec{r}\right) &= \Psi_{n,S\vec{k}}\left(\vec{r}\right) \\ \rho(\vec{r}) &= \sum_{n,\vec{k}} \left\| \Psi_{n,\vec{k}}\left(\vec{r}\right) \right\|^2 &= \sum_{n,S,\vec{k}_{inr}} \left\| \Psi_{n,S\vec{k}_{inr}}\left(\vec{r}\right) \right\|^2 \\ &= \sum_{n,S,\vec{k}_{inr}} \left\| \Psi_{n,\vec{k}_{inr}}\left(S^{-1}\vec{r}\right) \right\|^2 \end{split}$$



Brillouin Zone integration

•In insulators the quantity to be integrated is smooth across the BZ (exponentially localized Wannier functions)

$$\rho(\mathbf{r}) = \frac{2}{N} \sum_{\mathbf{k},v} |\tilde{\phi}_{\mathbf{k},v}(\mathbf{r})|^2$$
$$\rho(\mathbf{r}) = 2 \sum_{\mathbf{R},m} |W_m(\mathbf{r} - \mathbf{R})|^2$$



•The integral is computed exactly if the WF are localized inside the SuperCell corresponding to the k-point grid



Brillouin Zone integration

 Sampling at the Gamma point (isolated molecules, clusters)
 Sampling on a regular grid (Baldereschi, Chadi-Cohen, Monkhorst-Pack)

•In metallic systems, the function to be intergrated is sharply varying across the Fermi surface. Integration can be improved by introducing a finite (ficticious) temperature.







Brillouin Zone sampling

•In metals the quantity to be integrated is discontinuous due to the presence of the Fermi surface



Brillouin Zone sampling

•Integration is improved by introducing a finite (ficticious) temperature. [Fermi-Dirac, Gaussian, Methfessel-Paxton, Marzari-Vanderbilt]



$$\mathcal{I}_{n,\mathbf{k}=\frac{1}{1+\exp[\beta(\varepsilon_{n,\mathbf{k}}-\varepsilon_{F})]}}$$



$$\rho(\mathbf{r}) = \frac{2}{N_k} \sum_{\mathbf{k}v} \vartheta(\varepsilon_F - \varepsilon_{\mathbf{k}v}) |\phi_{\mathbf{k}v}(\mathbf{r})|^2$$

The step function makes the integral badly convergent



The larger is σ the smoother is the function and therefore smaller is the number of k-points in the grid needed to integrate accurately



$$\rho(\mathbf{r}) = \frac{2}{N_k} \sum_{\mathbf{k}v} \vartheta(\varepsilon_F - \varepsilon_{\mathbf{k}v}) |\phi_{\mathbf{k}v}(\mathbf{r})|^2$$

The step function makes the integral badly convergent



Unfortunately, the larger is σ the more the function differs from the original one and the integral deviates from the $\sigma \to 0$ limit that corresponds to the physical situation.



Several smearing functions have been proposed Fermi - Dirac $\delta(x) = \frac{1}{2 + e^{RP(x)} + e^{RP(x)}}$ Gaussian: Fu and Ho, PRB 28, 5480 (1983) $S(x) = \frac{1}{12x} e^{-\frac{x}{2}}$ 9(x)=A.erf(*) Gaussian times polynomials Methfessel and Paxton PRB 40 3616(1989) Marzari and Vanderbilt PRL 82 3296(1999) $S(x) = \frac{1}{12\pi} e^{-\frac{x}{2}} P(x)$ J(x)= (S(Y)dy





SMEARING FUNCTIONS

• Fermi-Dirac

$$\tilde{\delta}(x) = \frac{1}{e^x + e^{-x} + 2}; \qquad \tilde{\theta}(x) = \frac{1}{e^x + 1}$$
$$\sigma = K_B T; \quad T = 300K \Longrightarrow \sigma = 0.026 \text{eV}$$

• Gaussian

$$\tilde{\delta}(x) = \frac{1}{\sqrt{2\pi}} e^{-x^2/2}, \qquad \tilde{\theta}(x) = \frac{1}{2}(1 + \exp(x/\sqrt{2}))$$

• Hermite Polynomial \times Gaussian (HG_N) : M.Methfessel and A.Paxton, **PRB 40**, 3616 (1989).

$$\tilde{\delta}(x) = \sum_{n=0}^{N} A_n H_{2n}(x) e^{-x^2}, \quad A_n = \frac{(-1)^n}{n! 4^n \sqrt{\pi}}$$

$$\tilde{\theta}(x) = \tilde{\theta}_0(x) - \sum_{n=1}^N A_n H_{2n-1}(x) e^{-x^2}$$

with $\tilde{\theta}_0(x) = \frac{1}{2}(1 + \operatorname{erf}(x))$

THE ENERGY

Kohn-Sham (KS) kinetic energy functional

$$T_{s}[n] = \int_{-\infty}^{\varepsilon_{F}} \varepsilon n(\varepsilon) d\varepsilon - \int V^{KS}(\mathbf{r}) \ n(\mathbf{r}) d\mathbf{r}$$
$$= \sum_{i} \left[-\frac{\hbar^{2}}{2m} \tilde{\theta}(\frac{\varepsilon_{F} - \varepsilon_{i}}{\sigma}) \langle \phi_{i} | \nabla^{2} | \phi_{i} \rangle + \sigma \tilde{\theta}_{1}(\frac{\varepsilon_{F} - \varepsilon_{i}}{\sigma}) \right]$$
$$\tilde{\sigma}(\varepsilon) = \int_{-\infty}^{\infty} \tilde{\sigma}(\varepsilon) d\varepsilon$$

$$\tilde{\theta}_1(x) = \int_{-\infty}^x y \tilde{\delta}(y) dy$$

Total Energy

$$E_{tot} = T_s[n] + E_{Hxc} + \int V^0(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{ion}$$

KS equations

 $\left[-\frac{\hbar^2}{2m}\nabla^2 + V^0(\mathbf{r}) + V_{Hxc}(\mathbf{r}) - \varepsilon_i\right]\phi_i(\mathbf{r}) = 0$



It can be shown that the "correct" energy is

$$E = 2\sum_{k,r} \mathcal{D}\left(\frac{E_{k}-E_{k,r}}{\sigma}\right) < 4_{k,r} \left|\frac{h^{2}}{2kr}\right|^{2} |4_{k,r}\rangle + \int V_{0}(r) n(r) d^{2}r + \frac{e^{2}}{2} \int \frac{n(r)}{|r-r'|} d^{2}d^{2}r' + E_{k}(n) + 5\sum_{k,r} \mathcal{D}_{1}\left(\frac{E_{r}-E_{k,r}}{\sigma}\right)$$
for Fermi-Dirde smearing

$$\mathcal{D}_{1}(k) = \int \mathcal{Y}_{0}^{d} \left(\frac{1}{1+e^{2}r}\right) d\mathcal{Y} = \frac{x}{1+erq(-x)} - \ln\left(1+exp(x)\right)$$

$$= \mathcal{D}(n\mathcal{F} + (1-\mathcal{F})) \ln(1-\mathcal{F})$$
that is the expression for the entropy for non-inherboring all chroms.
In fact in this case E is scheelly the Free Energy



since dF =- S we have (also for general smearing) $\frac{dE}{d\sigma} = \sum_{kv} \mathcal{D}_{\pm} \left(\frac{\varepsilon_{F} - \varepsilon_{kv}}{\varepsilon} \right) \cong \int d\varepsilon \ h(\varepsilon) \int \frac{(\varepsilon_{F} - \varepsilon)/\sigma}{\frac{1}{2} \sqrt{\frac{1}{2} \sqrt{\frac{1}{2$ $= -\sum_{k=0}^{\infty} \frac{2^{k+1}}{(2^{k+1})!} \frac{C_{k+1}}{d\epsilon^{2^{k}}} \frac{d^{k}}{d\epsilon^{2^{k}}} = \frac{1}{2^{k+1}} \frac{d^{k}}{d\epsilon^{2^{k}}} =$ $G_{k} = \int_{x}^{2k} S(x) dx$



$$\begin{split} \frac{dE_{tot}}{d\sigma} &= \frac{\partial E_{tot}}{\partial\sigma} \\ &= \sum_{i} \tilde{\theta}_{1} (\frac{\varepsilon_{F} - \varepsilon_{i}}{\sigma}) = \int_{-\infty}^{\infty} d\varepsilon \, \hat{n}_{\sigma}(\varepsilon) \int_{-\infty}^{\frac{\varepsilon_{F} - \varepsilon}{\sigma}} y \tilde{\delta}(y) dy \\ &= -\sum_{k=0}^{\infty} \sigma^{2k+1} \frac{c_{k+1}}{(2k+1)!} \left. \frac{d^{2k} \hat{n}_{\sigma}}{d\varepsilon^{2k}} \right|_{\varepsilon_{F}} = -c_{1} n \langle \varepsilon_{F} \rangle^{\sigma} - \frac{c_{2} n \langle \varepsilon_{F} \rangle^{\sigma}}{3!} + \cdots \end{split}$$

where
$$c_k = \int x^{2k} \tilde{\delta}(x) dx$$

positive definite smearing functions (Fermi-Dirac, Gaussian): $c_1 \neq 0$ $E_{tot} \approx E_{tot}^{\sigma=0} - \frac{c_1}{2}n(\varepsilon_F)\sigma^2$

non positive definite smearing functions, (HG1): $c_1 = 0$ $E_{tot} \approx E_{tot}^{\sigma=0} - \frac{c_2}{4!} n''(\varepsilon_F) \sigma^4$



Brillouin Zone sampling

•Integration is improved by introducing a finite (ficticious) temperature. [Fermi-Dirac, Gaussian, Methfessel-Paxton, Marzari-Vanderbilt]



FIG. 1. Total energy per atom of fcc-Pb crystal as a function of the smearing linewidth and for two different smearing functions: the Hermite-Gaussian function of order 1 (solid line) and the simple Gaussian function (dashed line).



Brillouin Zone sampling





Step 1 : defining V ext construct V_ext guess rho_in compute V_KS diagonalize H_KS compute rho_out mix to get no <u>rho_in = rho_out ?</u> new rho_in yes compute forces, stress, and other properties



The external potential

Electrons experience a Coulomb potential due to the nuclei.

This has a known simple form.

For a single atom it is

$$V_{nuc}(r) = -\frac{Ze^2}{|r|}$$



$$\begin{aligned} & \text{Periodic potential} \\ V(r) &= \sum_{s} \sum_{R} V_{s}(|r - R - \tau_{s}|) \\ & V(G) &= \frac{1}{\mathcal{V}} \int_{\mathcal{V}} \sum_{s} \sum_{R} V_{s}(|r - R - \tau_{s}|) \exp(-iGr) dr \\ & V(G) &= \sum_{s} \int_{\mathcal{V}} V_{s}(|r|) \exp(-iGr) dr \quad \sum_{R} \frac{\exp(-iG(R + \tau_{s}))}{N\Omega} \\ & \mathcal{V} &= N\Omega \end{aligned}$$



nuclear potential

The Coulomb potential due to any single atom is

$$V_{nuc}(|r|) = -\frac{Ze^2}{|r|} \longrightarrow V_{nuc}(|G|) = -Z\frac{4\pi e^2}{|G|^2}$$

The direct use of this potential in a Plane Wave code leads to computational difficulties!



Problems for a Plane-Wave based code

Core wavefunctions: Sharply peaked close to nuclei due to deep Coulomb potential. Valence wavefunctions: Lots of wiggles near nuclei due to orthogonality to core wavefunctions



<u>High Fourier components are present</u> <u>i.e. large kinetic energy cutoff needed</u>

$$r_{1s} \approx 1/Z$$
 $Ecut \approx \left(\frac{2\pi}{r_{1s}}\right)^2 \approx 40Z^2$



strategies here been followed 1000 (1) Abandon puis picture near nuclei pw GE APW: Augmented Plane Weres $\psi(r) = \sum_{i} c_i(k) A(k+G_i,r)$ atomic line ups LAPW: Lineanized APW $R_e(\varepsilon,r) \cong R_e(\varepsilon_o,r) + (\varepsilon-\varepsilon_o) R_e(\varepsilon_o,r)$ $R' = \frac{dR}{de}$ FLAPW full potential LAPW (No atomic sphere approx) Similarly MTO -> LMTO -> FLMTO KKR All-electron methods these 2 P

2 Inhoduce Pseudo Potentials core dectrons do not participate to thending - " frozen core" zaproxination eliminate the core states and modify the potential in such a way that the valence who are smooth in the core region and coincide with the true valence wfe autside the core regron. ex! Berillium [1s2]2s2 25 25 Ground Skite for the pseudoaton 15

An analogy!

- "Dummy cops" used by many law-enforcement agencies!
- Don't care about internal structure as long as it works right!
- But cheaper!!
- Obviously it can't reproduce all the functions of a real cop, but should be convincing enough to produce desired results....





Solutions for a Plane-Wave based code

Core wavefunctions: Sharply peaked close to nuclei due to deep Coulomb potential. Valence wavefunctions: Lots of wiggles near nuclei due to orthogonality to core wavefunctions

Don't solve for core wavefunction



Remove wiggles from valence wavefunctions

<u>Replace hard Coulomb potential</u> <u>by smooth PseudoPotentials</u>

This can be done on an empirical basis by fitting experimental band structure data ..



Empirical PseudoPotentials

$$V(G) = \sum_{s} V_s(|G|) \ S_s(G)$$

	the second se		
	V_3 ^S	$V_8{}^S$	$V_{11}s$
Si	-0.21	+0.04	+0.08
Ge	-0.23	+0.01	+0.06
Sn	-0.20	0.00	+0.04

Cohen & Bergstresser, PRB 141, 789 (1966)



FIG. 1. Band structure of Si.



transferability to other systems is problematic

Let's consider an atomic problem ...

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{|r|} + e^2 \int \frac{\rho(r')}{|r-r'|} d^3r' + v_{xc}[\rho(r)]\right]\varphi_i(r) = \varepsilon_i \ \varphi_i(r)$$

... in the frozen core approximation: $\rho(r) = \rho_v(r) + \rho_c(r)$

$$\begin{bmatrix} -\frac{\hbar^2}{2m}\nabla^2 + e^2\left(-\frac{Z}{|r|} + \int \frac{\rho_c(r')}{|r-r'|} d^3r'\right) + e^2\int \frac{\rho_v(r')}{|r-r'|} d^3r' \\ + v_{xc}[\rho_v(r) + \rho_c(r)] \end{bmatrix} \varphi_i(r) = \varepsilon_i \ \varphi_i(r)$$

if $\rho_v(r)$ and $\rho_c(r)$ do not overlap significantly:

 $v_{xc}[\rho_v(r) + \rho_c(r)] \approx v_{xc}[\rho_v(r)] + v_{xc}[\rho_c(r)]$



ab initio Norm Conserving PseudoPotentials ... hence $\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{Z_v}^{PS}(|r|) + e^2 \int \frac{\rho(r')}{|r-r'|} d^3r' + v_{xc}[\rho_v(r)] \right] \varphi_i(r) = \dots$ $V_{Z_v}^{PS}(|r|) = e^2 \left(-\frac{Z}{|r|} + \int \frac{\rho_c(r')}{|r-r'|} d^3r' \right) + v_{xc}[\rho_c(r)]$ with with a Coulomb tail corresponding to $Z_v = Z - N_{core}^{el}$ or in case of overlap we have (*non-linear core correction*) $\left[\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{Z_v}^{PS}(|r|) + e^2 \int \frac{\rho(r')}{|r-r'|} d^3r' + v_{xc} [\rho_v(r) + \rho_c(r)] \right] \varphi_i(r) = \frac{1}{2m} \nabla^2 + V_{Z_v}^{PS}(|r|) + e^2 \int \frac{\rho(r')}{|r-r'|} d^3r' + v_{xc} [\rho_v(r) + \rho_c(r)] \right] \varphi_i(r) = \frac{1}{2m} \nabla^2 + V_{Z_v}^{PS}(|r|) + e^2 \int \frac{\rho(r')}{|r-r'|} d^3r' + v_{xc} [\rho_v(r) + \rho_c(r)] \left[\frac{\rho(r')}{|r-r'|} + \frac{\rho(r'$ $V_{Z_v}^{PS}(|r|) = e^2 \left(-\frac{Z}{|r|} + \int \frac{\rho_c(r')}{|r-r'|} d^3 r' \right)$ with

 $V_{Z_v}^{PS}(|r|)$ is further modified in the core region so that the reference valence wavefunctions are nodeless and smooth and properly normalized (norm conservation) so that the valence charge density (outside the core) is simply:

$$\rho_v(r) = \sum_v |\varphi_v(r)|^2$$

The norm-conservation condition ensures correct electrostatics outside the core region and that atomic scattering properties are reproduced correctly

$$4\pi \int_0^R |\varphi(r)|^2 r^2 dr = 2\pi \left[r^2 |\varphi(r)|^2 \frac{d}{d\varepsilon} \frac{d}{dr} \ln \varphi(r) \right]_{r=R}$$

this determines *transferability*



An example: Mo





Hamann, schlueter & Chiang, *PRL* **43**, 1494 (1979) FIG. 2. Energy dependence of logarithmic derivatives at r = 3.0 a.u. for Mo *ab initio* full-core atomic wave functions (broken lines) and pseudo wave functions (solid lines) as shown in Fig. 1.

semilocal form

$$V_{Z_v}^{PS}(r,r') = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \Delta V_l(|r|)\delta(|r|-|r'|)P_l(r,r')$$

7

where
$$P_l(r, r') = \sum_m Y_{lm}(r) Y_{lm}^*(r')$$
 projects over $L^2 = l(l+1)$
 $V^{loc}(|r|)$ is local with a Coulomb tail $Z_v = Z - N_{core}^{el}$

 $\Delta V_l(|r|)$ is local in the radial coordinate, short ranged and l-dependent

$$\langle q | V_{Z_v}^{PS} | q' \rangle = V^{loc}(q - q') + \sum_{l=0}^{l_{max}} \Delta V_l(|q|, |q'|) P_l(q, q')$$

is a full matrix ! NO use of dual-space approach

from semilocal form ...

$$V_{Z_v}^{PS}(r,r') = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \Delta V_l(|r|)\delta(|r|-|r'|)P_l(r,r')$$

... to Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS}(r,r') = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm} \rangle D_l \langle \beta_{lm}|r' \rangle$$

 $V^{loc}(|r|)$ is local with a Coulomb tail $Z_v = Z - N^{el}_{core}$

 $\begin{aligned} \langle r|\beta_{lm}\rangle &= \Delta V_l(r)\phi_l(r)Y_{lm}(r) & \text{ are localized radial functions} \\ & \text{ such that the transformed pseudo acts in the same} \\ & \text{ way as the original form on the reference config.} \\ & \text{ One has } D_l = \langle \phi_l | \Delta V_l | \phi_l \rangle^{-1} \end{aligned}$



Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS} = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm} \rangle \ D_l \ \langle \beta_{lm}|r' \rangle$$

 $V^{loc}(|r|)$ is local with a Coulomb tail $Z_v = Z - N^{el}_{core}$

 $\langle r|\beta_{lm}\rangle = \Delta V_l(r)\phi_l(r)Y_{lm}(r)$ are localized radial functions such that the transformed pseudo acts in the same way as the original form on the reference config.

One has $D_l = \langle \phi_l | \Delta V_l | \phi_l \rangle^{-1}$

The pseudopotential reduces to a sum of dot products l_{max}

$$\tilde{V}_{Z_v}^{PS}|\psi\rangle = V^{loc}(|r|)\langle r|\psi\rangle + \sum_{l=0}^{max} \sum_{m=-l}^{max} \langle r|\beta_{lm}\rangle D_l \langle \beta_{lm}|\psi\rangle$$


ab initio Norm Conserving PseudoPotentials

Kleinman-Bylander fully non-local form

$$\tilde{V}_{Z_v}^{PS} = V^{loc}(|r|)\delta(r-r') + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \langle r|\beta_{lm} \rangle D_l \langle \beta_{lm}|r' \rangle$$

The KB form is more efficiently computed than the original semi-local form.

By construction it behaves as the original form on the reference configuration ... but ... there is no guarantee that the reference configuration is the GS of the modified potential.

When this happens the pseudopotential has GHOST states and should not be used.



ab initio Norm Conserving PseudoPotentials

Desired properties of a pseudopotential are

- *Transferability* (norm-conservation, small core radii, non-linear core correction, multi projectors)

- *Softness* (various optimization/smoothing strategies, large core radii)

For some elements it's easy to obtain "soft" Norm-Conserving PseudoPotentials.

For some elements it's instead very difficult!

Expecially for <u>first row elements</u> (very localized 2p orbitals) and <u>1st row transition metals</u> (very localized 3d orbitals)



Norm-Conserving PseudoPotentials basic literature

<1970 empirical PP. es: Cohen & Bergstresser, PRB **141**, 789 (1966)

1979 Hamann, Schlueter & Chang, PRL 43, 1494 (1979), ab initio NCPP
1982 Bachelet, Hamann, Schlueter, PRB 26, 4199 (1982), BHS PP table
1982 Louie, Froyen & Cohen, PRB 26, 1738 (1982), non-linear core corr.
1982 Kleinman & Bylander, PRL 48, 1425 (1982), KB fully non local PP

1985 Vanderbilt, PRB **32**, 8412 (1985), optimally smooth PP 1990 Rappe,Rabe,Kaxiras,Joannopoulos, PRB **41**, 1227 (1990), optm. PP 1990 Bloechl, PRB **41**, 5414 (1990), generalized separable PP 1991 Troullier & Martins, PRB **43**, 1993 (1991), efficient PP

1990 Gonze, Kackell, Scheffler, *PRB* **41**, 12264 (1990), *Ghost states*

1991 King-Smith, Payne, Lin, PRB **44**, 13063 (1991), PP in real space



In spite of the devoted effort NCPP's are still "hard" and require a large plane-wave basis sets (Ecut > 70Ry) for first-row elements (in particular N, O, F) and for transition metals, in particular the 3d row: Cr, Mn, Fe, Co, Ni, ...



Even if just one atom is "hard", a high cutoff is required.

2.0

1.0

a.u.

(r)≯

UltraSoft (Vanderbilt) PseudoPotentials (USPP) are devised to overcome such a problem.

Oxygen 2p orbital <u>nodeless</u>

FIG. 1. Oxygen 2p radial wave function (solid line), and corresponding pseudo-wave-functions generated using HSC (dotted line) and current (dashed line) methods.

Vanderbilt, *PRB* **41**, 7892 (1991)



$$\rho(r) = \sum_{i} |\psi_{i}(r)|^{2} + \sum_{i} \sum_{lm} \langle \psi_{i} | \beta_{l} \rangle Q_{lm}(r) \langle \beta_{m} | \psi_{i} \rangle$$

where the "augmentation charges" are

$$Q_{lm}(r) = \phi_l^*(r)\phi_m(r) - \phi_l^*(r)\phi_m(r)$$

 $|\beta_l\rangle$ are projectors

 $|\phi_l\rangle$ are atomic states (not necessarily bound)

 $|\phi_l\rangle$ are pseudo-waves (coinciding with $|\phi_l\rangle$ beyond some *core radius*)

$$\hat{V}^{USPP} = V_{loc}(r) + \sum_{lm} |\beta_l\rangle D^0_{lm} \langle \beta_m |$$

Orthogonality with USPP:

$$\begin{split} \langle \psi_i | S | \psi_j \rangle &= \langle \psi_i | \psi_j \rangle + \sum_{lm} \langle \psi_i | \beta_l \rangle q_{lm} \langle \beta_m | \psi_j \rangle = \delta_{ij} \\ \end{split}$$
 where $q_{lm} = \int Q_{lm}(r) dr$

leading to a generalized eigenvalue problem

$$[H_{KS} - \varepsilon_i S] |\psi_i\rangle = 0$$



There are additional terms in the density, in the energy, in the hamiltonian in the forces, ...

$$E = \sum_{i} \langle \psi_{i} | \hat{T}_{s} + \hat{V}^{USPP} | \psi_{i} \rangle + E_{Hxc}[\rho] - \sum_{ij} \lambda_{ij} (\langle \psi_{i} | S | \psi_{j} \rangle - \delta_{ij})$$
where
$$\rho(r) = \sum_{i} |\psi_{i}(r)|^{2} + \sum_{i} \sum_{lm} \langle \psi_{i} | \beta_{l} \rangle Q_{lm}(r) \langle \beta_{m} | \psi_{i} \rangle$$

$$\frac{\delta E}{\delta \psi_{i}^{*}} = 0 \qquad [H_{KS} - \varepsilon_{i}S] |\psi_{i} \rangle = 0$$

$$H_{KS} = -\frac{\hbar^{2}}{2m} \nabla^{2} + V_{loc}(r) + V_{Hxc}(r) + \sum_{lm} |\beta_{l} \rangle D_{lm} \langle \beta_{m} |$$

$$D_{lm} = D_{lm}^{0} + \int V_{Hxc}(r) Q_{lm}(r) dr$$

There are additional terms in the density, in the energy, in the hamiltonian in the forces, ...

Electronic states are orthonormal with a (configuration dependent) overlap matrix

The "augmentation charges" typically require a larger cutoff for the charge density:

<u>QE Input parameter:</u> ecutrho (SYSTEM namelist)

Default value is ecutrho = $4 \times \text{ecutwfc}$ (OK for NC PP)

For USPP a larger value ecutrho is often needed.



It is always possible to express the AE wfc via augmentation of a smooth (pseudo) wfc using atomic reference states

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_{l} \left(|\phi_l\rangle - |\tilde{\phi}_l\rangle \right) \langle \beta_l |\tilde{\psi}\rangle = (1+T)|\tilde{\psi}\rangle$$

where

 $|\psi
angle$ all-electron wave function

 $|\psi
angle$ pseudo wave function

 $\{ |\phi_l\rangle, l = 1, ..., N_{proj} \}$ all-electron atomic partial waves

 $\{ \ | \tilde{\phi}_l
angle, l = 1, ..., N_{proj} \}$ pseudo atomic partial waves

 $\{ |\beta_l\rangle, l = 1, ..., N_{proj} \} \text{ localized projectors on the atomic} \\ \text{partial waves such that } \langle \beta_l | \tilde{\phi}_m \rangle = \delta_{lm}$



It is always possible to express the AE wfc via augmentation of a smooth (pseudo) wfc using atomic reference states

$$\begin{split} |\psi\rangle &= |\tilde{\psi}\rangle + \sum_{l} \left(|\phi_l\rangle - |\tilde{\phi}_l\rangle \right) \langle \beta_l |\tilde{\psi}\rangle = (1+T) |\tilde{\psi}\rangle \\ \text{pictorially} \end{split}$$



T is a localized operator !

 $|\phi_l\rangle$'s and $|\phi_l\rangle$'s coincide outside the core region and we can truncate them The $|\beta_l\rangle$'s projectors are localized in the core region...

AE matrix elements of any operator can then be computed as

$$\langle \psi | A | \psi \rangle = \langle \tilde{\psi} | (1 + T^{\dagger}) A (1 + T) | \tilde{\psi} \rangle = \langle \tilde{\psi} | \tilde{A} | \tilde{\psi} \rangle$$

if the $|\beta_l\rangle$ expansion is complete

$$\sum_{l} |\tilde{\phi}_{l}\rangle \langle \beta_{l}| \approx I_{\Omega_{core}}$$

for local operators (kinetic energy, potential,...) one can show

$$\tilde{A} = A + \sum_{lm} |\beta_l\rangle \left(\langle \phi_l | A | \phi_m \rangle - \langle \tilde{\phi}_l | A | \tilde{\phi}_m \rangle \right) \langle \beta_m |$$

and normalization of wfc is computed with

$$= 1 + \sum_{lm} |\beta_l\rangle \left(\langle \phi_l | \phi_m \rangle - \langle \tilde{\phi}_l | \tilde{\phi}_m \rangle \right) \langle \beta_m |$$



AE results can be computed from the PS matrix elements augmented by KB-like contributions that can be computed from atomic AE and PS reference calculations.

$$\langle \psi | A | \psi \rangle = \langle \tilde{\psi} | A | \tilde{\psi} \rangle + \sum_{lm} \langle \tilde{\psi} | \beta_l \rangle \left(\langle \phi_l | A | \phi_m \rangle - \langle \tilde{\phi}_l | A | \tilde{\phi}_m \rangle \right) \langle \beta_m | \tilde{\psi} \rangle$$

$$\langle A \rangle = \langle \tilde{A} \rangle + \sum \left(\langle A \rangle^{at} - \langle \tilde{A} \rangle^{at} \right)$$

The charge density is therefore

$$|\psi_i(r)|^2 = |\tilde{\psi}_i(r)|^2 + \sum_{lm} \langle \tilde{\psi}_i | \beta_l \rangle \left(\phi_l(r) \phi_m(r) - \tilde{\phi}_l(r) \tilde{\phi}_m(r) \right) \langle \beta_m | \tilde{\psi}_i \rangle$$

$$\rho(r) = \tilde{\rho}(r) + \sum \left(\rho^{at}(r) - \tilde{\rho}^{at}(r)\right)$$

The charge density is therefore

$$|\psi_i(r)|^2 = |\tilde{\psi}_i(r)|^2 + \sum_{lm} \langle \tilde{\psi}_i | \beta_l \rangle \left(\phi_l(r) \phi_m(r) - \tilde{\phi}_l(r) \tilde{\phi}_m(r) \right) \left\langle \beta_m | \tilde{\psi}_i \right\rangle$$

but it is convenient to add/subtract a compensating charge so that the AE and PS atomic references have the same Multipole expansion

$$\rho(r) = \tilde{\rho}(r) + \sum \left(\rho^{at}(r) - \tilde{\rho}^{at}(r)\right)$$

The charge density is therefore

$$\begin{split} |\psi_{i}(r)|^{2} &= |\tilde{\psi}_{i}(r)|^{2} + \sum_{lm} \langle \tilde{\psi}_{i} | \beta_{l} \rangle Q_{lm}(r) \langle \beta_{m} | \tilde{\psi}_{i} \rangle \\ &+ \sum_{lm} \langle \tilde{\psi}_{i} | \beta_{l} \rangle \phi_{l}(r) \phi_{m}(r) \langle \beta_{m} | \tilde{\psi}_{i} \rangle \\ &- \sum_{lm} \langle \tilde{\psi}_{i} | \beta_{l} \rangle \left(\tilde{\phi}_{l}(r) \tilde{\phi}_{m}(r) + Q_{lm}(r) \right) \langle \beta_{m} | \tilde{\psi}_{i} \rangle \end{split}$$

$$\rho(r) = \tilde{\rho}(r) + \sum \left(\rho^{at}(r) - \tilde{\rho}^{at}(r)\right)$$

The different energy contributions so become

 $E_{H}[\rho] = E_{H}[\tilde{\rho} + \sum (\rho^{at} - \tilde{\rho}^{at})] = E_{H}[\tilde{\rho}] + \sum (E_{H}^{at}[\rho^{at}] - E_{H}^{at}[\tilde{\rho}^{at}])$ $E_{xc}[\rho] = E_{xc}[\tilde{\rho} + \sum (\rho^{at} - \tilde{\rho}^{at})] = E_{xc}[\tilde{\rho}] + \sum (E_{xc}^{at}[\rho^{at}] - E_{xc}^{at}[\tilde{\rho}^{at}])$ $T_{s}[\rho] = T_{s}[\tilde{\rho} + \sum (\rho^{at} - \tilde{\rho}^{at})] = T_{s}[\tilde{\rho}] + \sum (T_{s}^{at}[\rho^{at}] - T_{s}^{at}[\tilde{\rho}^{at}])$ + $E_{tot} = \tilde{E}_{tot} + \sum \left(E_{tot}^{at} - \tilde{E}_{tot}^{at} \right)$

Finally the KS eigenvalue problem is as for USPP

 $[H_{KS} - \varepsilon_i S] |\psi_i\rangle = 0$ with $S = 1 + \sum |\beta_l\rangle q_{lm} \langle \beta_m |$ lm $H_{KS} = -\frac{\hbar^2}{2m} \nabla^2 + \tilde{V}_{eff}(r) + \sum |\beta_l\rangle D_{lm} \langle \beta_m|$ where lm $q_{lm} = \langle \phi_l | \phi_m \rangle - \langle \tilde{\phi}_l | \tilde{\phi}_m \rangle = \int Q_{lm}(r) dr$ $D_{lm} = D_{lm}^{at} - \tilde{D}_{lm}^{at} + \int \tilde{V}_{eff}(r)Q_{lm}(r)dr$ $D_{lm}^{at} = \langle \phi_l | T_s + V_{eff} | \phi_m \rangle$ $\tilde{D}_{lm}^{at} = \langle \tilde{\phi}_l | T_s + \tilde{V}_{eff} | \tilde{\phi}_m \rangle + \int \tilde{V}_{eff}(r) Q_{lm}(r) dr$

Step 2 : initial guess for rho_in





Initial choice of rho_in

Various possible choices, e.g.,:

- Superpositions of atomic densities.
- Converged n(r) from a closely related calculation (e.g., one where ionic positions slightly different).
- Approximate n(r) , e.g., from solving problem in a smaller/different basis.
- Random numbers.



Initial choice of rho_in

Various possible choices, e.g.,:

- Superpositions of atomic densities.
- Converged n(r) from a closely related calculation (e.g., one where ionic positions slightly different).
- Approximate n(r) , e.g., from solving problem in a smaller/different basis.
- Random numbers.

Initial guess of wfc

QE input parameter startingwfc

'atomic' | 'atomic+random' | 'random' | 'file'



Pseudopotentials in Quantum ESPRESSO Go to http://www.quantum-espresso.org/



1 U A N T U M <mark>e s p r e s s o</mark>

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25 May 2011 Version 4.3.1 of Quantum ESPRESSO is available for download.

05 May 2011

The first GPU-enabled beta release of Quantum ESPRESSO is available for download.

01 April 2011

The new release, v.4.3, of the Quantum ESPRESSO distribution is available for download.

13 July 2010

Bugfix release v.4.2.1 of the Quantum ESPRESSO distribution is available for download.

> 10 May 2010 A new version, v.4.2, of the

Quantum ESPRESSO is an integrated suite of computer codes for electronicstructure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials (both norm-conserving and ultrasoft).



Pseudopotentials for Quantum ESPRESSO Click on the element for which the PP is desired

Pa

Th

Ac

U

Np

Pu

Am

URNTUM ESPRESSO

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PSEUDOPOTENTIALS

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Cf

Es

Md

No

Fm

Bk

Cm

Pseudopotentials for Quantum ESPRESSO

Name: Oxygen Symbol: O Atomic number: 8 Atomic configuration: [He] 2s2 2p4 Atomic mass: 15.9994 (3)

Available pseudopotentials:

O.pbe-van_ak.UPF (details)

Perdew-Burke-Ernzerhof (PBE) exch-corr Vanderbilt ultrasoft author: ak

O.pbe-rrkjus.UPF (details)

Perdew-Burke-Ernzerhof (PBE) exch-corr Rabe Rappe Kaxiras Joannopoulos (ultrasoft)

O.pbe-kjpaw.UPF (details)

Perdew-Burke-Ernzerhof (PBE) e Projector Augmented Waves (Kre

O.rel-pz-rrkjus.UPF (details)

rel => full-relativistic Perdew-Zunger (LDA) exch-corr Rabe Rappe Kaxiras Joannopoulos (ultrasoft)

O.pz-rrkjus.UPF (details)

Perdew-Zunger (LDA) exch-corr Rabe Rappe Kaxiras Joannopoulos (ultrasoft) Pseudopotential's name gives Information about

-exchange correlation functional

-type of pseudopotential

Perdew-Burke-Ernzerhof (PBE) exch-corr Rabe Rappe Kaxiras Joannopoulos (ultrasoft)

details

Atomic and V_ion info for QE

QE input card ATOMIC_SPECIES example:

ATOMIC_SPECIES Ba 137.327 Ba.pbe-nsp-van.UPF Ti 47.867 Ti.pbe-sp-van_ak.UPF O 15.999 O.pbe-van_ak.UPF

NOTE

should use the same XC functional for all pseudopentials. ecutwfc, ecutrho depend on type of pseudopotentials used (should test for system & property of interest).



DFT Total Energy in an infinite periodic solid

$$E(R) = \min_{\rho} \left[T_s[\rho] + \frac{1}{2} \int_{\mathcal{V}} V_H(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E_{xc}(\rho) + \int_{\mathcal{V}} V_0(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right]$$
$$+ E_{ion}(R)$$
$$\rho(\mathbf{r}) = 2 \sum_{\mathbf{k}v} |\phi_{\mathbf{k}v}(\mathbf{r})|^2 \implies T_s[\rho] = 2 \sum_{\mathbf{k}v} \sum_{\mathbf{G}} \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 |c_{\mathbf{k}v}(\mathbf{G})|^2$$

$$E_{xc}^{LDA} = \int_{\mathcal{V}} \rho(\mathbf{r}) \ \varepsilon_{xc}^{hom}(\rho(\mathbf{r})) \ d\mathbf{r}$$



DFT Total Energy in an infinite periodic solid

$$\begin{split} \frac{E(R)}{N} &= \min_{\rho} \left[\frac{T_s[\rho]}{N} + \frac{1}{2} \int_{\Omega} V_H(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \frac{E_{xc}(\rho)}{N} + \int_{\Omega} V_0(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right] \\ &\int_{\mathcal{V}} |\phi(\mathbf{r})|^2 d\mathbf{r} = 1 \to \int_{\Omega} |\phi(\mathbf{r})|^2 d\mathbf{r} = 1 \qquad \qquad + \frac{E_{ion}(R)}{N} \\ &\phi(\mathbf{r}) \to \tilde{\phi}(\mathbf{r}) / \sqrt{N} \end{split}$$
$$\rho(\mathbf{r}) &= 2 \sum_{\mathbf{k}v} |\phi_{\mathbf{k}v}(\mathbf{r})|^2 \Longrightarrow \frac{T_s[\rho]}{N} = \frac{2}{N} \sum_{\mathbf{k}v} \sum_{\mathbf{G}} \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 |c_{\mathbf{k}v}(\mathbf{G})|^2 \end{split}$$

$$\frac{E_{xc}^{LDA}}{N} = \int_{\Omega} \rho(\mathbf{r}) \ \varepsilon_{xc}^{hom}(\rho(\mathbf{r})) \ d\mathbf{r}$$



 $\mathbf{k}v$

DFT Total Energy in an infinite periodic solid

$$\frac{E(R)}{N} = \min_{\rho} \left[\frac{T_s[\rho]}{N} + \frac{1}{2} \int_{\Omega} V_H(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \frac{E_{xc}(\rho)}{N} + \int_{\Omega} V_0(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right]$$
$$\int_{\mathcal{V}} |\phi(\mathbf{r})|^2 d\mathbf{r} = 1 \rightarrow \int_{\Omega} |\phi(\mathbf{r})|^2 d\mathbf{r} = 1 \qquad \qquad + \frac{E_{ion}(R)}{N}$$
$$\phi(\mathbf{r}) \rightarrow \tilde{\phi}(\mathbf{r}) / \sqrt{N}$$

$$\rho(\mathbf{r}) = \frac{2}{N} \sum_{\mathbf{k}v} |\tilde{\phi}_{\mathbf{k}v}(\mathbf{r})|^2 \Longrightarrow \frac{T_s[\rho]}{N} = \frac{2}{N} \sum_{\mathbf{k}v} \sum_{\mathbf{G}} \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 |c_{\mathbf{k}v}(\mathbf{G})|^2$$

$$\frac{E_{xc}^{LDA}}{N} = \int_{\Omega} \rho(\mathbf{r}) \ \varepsilon_{xc}^{hom}(\rho(\mathbf{r})) \ d\mathbf{r}$$



THE END

