

# de la recherche à l'INDUSTRIE Numerical solid-state physics within Plane-Wave basis

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## **KS HAMILTONIAN**

Energies are in Hartree = 27.211 eV Lengths are in Bohr = 0.5219 Angstrom

Hydrogen atom ground state energy = -0.5 Ha = -13.6 eV etc...

The KS Hamiltonian reads

$$H_{\rm KS} = -\frac{\nabla_r^2}{2} + v_{n-e}(\mathbf{r}) + v_H[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r})$$



Main stream

Numerous codes available for free or for \$\$\$





#### Main stream

### Numerous codes available for free or for \$\$\$



G. Kresse Institut für Theoretische Physik, Technische Universität Wien, Wiedner Hauptstraße 8-10/136, A-1040 Wien, Austria

> J. Furthmüller Institut für Festkörpertheorie und Theoretische Optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, D-07743 Jena, Germany (Received 13 December 1995; revised manuscript received 30 May 1996)

We present an efficient scheme for calculating the Kohn-Sham ground state of metallic systems using pseudopotentials and a plane-wave basis set. In the first part the application of Pulay's DHS method (direct ~71 000 citations

# The most cited paper in science

# cea

# **FIRST DFTK TUTORIAL**



Tutorial

```
Problems and plane-wave discretisations
```

```
Introductory resources
```

#### Basic DFT calculations

Temperature and metallic systems

Collinear spin and magnetic systems

Creating and modelling metallic supercells

Modelling a gallium arsenide surface

Graphene band structure

Geometry optimization

Response and properties

Polarizability by linear response

Polarizability using automatic differentiation

Eigenvalues of the dielectric matrix

For our discussion we will use the classic example of computing the LDA ground state of the silicon crystal. Performing such a calculation roughly proceeds in three steps.

using DFTK using Plots using Unitful using UnitfulAtomic

By default, all numbers passed as arguments are assumed to be in atomic units. Quantities such as temperature, energy cutoffs, lattice vectors, and the k-point grid spacing can optionally be annotated with Unitful units, which are automatically converted to the atomic units used internally. For more details, see the Unitful package documentation and the UnitfulAtomic.jl package.

```
(ili)
# Load HGH pseudopotential for Silicon
Si = ElementPsp(:Si, psp=load_psp("hgh/lda/Si-q4"))
# Specify type and positions of atoms
atoms
         = [Si, Si]
positions = [ones(3)/8, -ones(3)/8]
# 2. Select model and basis
model = model_LDA(lattice, atoms, positions)
kgrid = [4, 4, 4]  # k-point grid (Regular Monkhorst-Pack grid)
Ecut = 7
                   # kinetic energy cutoff
# Ecut = 190.5u"eV" # Could also use eV or other energy-compatible units
basis = PlaneWaveBasis(model; Ecut, kgrid)
# Note the implicit passing of keyword arguments here:
# this is equivalent to PlaneWaveBasis(model; Ecut=Ecut, kgrid=kgrid)
# 3. Run the SCF procedure to obtain the ground state
scfres = self_consistent_field(basis, tol=1e-8);
```

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# **1. Plane-wave basis in 1D**

- 2. Plane-wave basis in 3D
- 3. Pseudopotentials
- 4. Kohn-Sham hamiltonian and self-consistency

5. Further reading tips



. . .

# 1-D "CRYSTAL"

An atomic chain:





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. . .

The Hamiltonian is periodic:

H(x+a)=H(x)

What is the form of the wavefunction?

$$\psi(x+a) = \psi(x)$$
 ?



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. . .

The wavefunction is not an observable in quantum-mechanics, however its square-module is

$$|\psi(x+a)|^2 = |\psi(x)|^2 \qquad \Longrightarrow \qquad \psi(x+a) = e^{i\theta} \psi(x)$$



### **Bloch theorem:**

The eigenfunctions of a periodic hamiltonian H(x+a)=H(x)are of the form  $\psi_k(x)=\frac{1}{\sqrt{N}}e^{ikx}u_k(x)$ where  $u_k(x+a)=u_k(x)$ 





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$$\psi_k(x+a) = \frac{1}{\sqrt{N}} e^{ik(x+a)} u_k(x+a)$$





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$$= \frac{1}{\sqrt{N}} e^{ika} e^{ikx} u_{k}(x)$$

$$= e^{ika} \psi_{k}(x)$$
The phase factor is



e<sup>ika</sup>



 $\psi(x + \mathbf{N} a) = \psi(x)$ 



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But from Bloch theorem,

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$$\psi(x+Na)=\psi(x)$$

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$$\psi_k(x+a) = e^{ika} \psi_k(x) \qquad \longrightarrow \qquad \psi_k(x+Na) = e^{ikNa} \psi_k(x)$$



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But from Bloch theorem,

$$\psi_k(x+a) = e^{ika} \psi_k(x) \qquad \longrightarrow \qquad \psi_k(x+Na) = e^{ikNa} \psi_k(x)$$
$$\qquad \longrightarrow \qquad e^{ikNa} = 1$$



$$\psi(x + \mathbf{N} a) = \psi(x)$$

But from Bloch theorem,

$$\psi_{k}(x+a) = e^{ika} \psi_{k}(x) \qquad \longrightarrow \qquad \psi_{k}(x+Na) = e^{ikNa} \psi_{k}(x)$$
$$\implies \qquad e^{ikNa} = 1$$
$$\implies \qquad k = \frac{2\pi}{Na}n \qquad \text{where} \quad n \in Z$$



 $\psi(x + \mathbf{N} a) = \psi(x)$ 

$$\int_{0}^{Na} dx |\psi_k(x)|^2 = 1$$



 $\psi(x + \mathbf{N} a) = \psi(x)$ 



# FOURIER SERIES

Let us gather the results:

$$\psi_k(x) = \frac{1}{\sqrt{Na}} e^{ikx} u_k(x)$$

where

$$k = \frac{2\pi}{Na}n$$

$$u_k(x+a)=u_k(x)$$

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### We can use a Fourier series for



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 $\times b$ 

### We can use a Fourier series for





# **1<sup>ST</sup> BRILLOUIN ZONE**



## 1<sup>ST</sup> BRILLOUIN ZONE



## 1<sup>ST</sup> BRILLOUIN ZONE





## **POWER OF BLOCH THEOREM**

H is block-diagonal:



Diagonalization for each k-point can be conducted independently

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# LINK WITH DFT CODES



# 2. Select model and basis
<pre>model = model_LDA(lattice, atoms, positions)</pre>
<pre>kgrid = [4, 4, 4]  # k-point grid (Regular Monkhorst-Pack grid)</pre>
Ecut = 7 # kinetic energy cutoff
<pre># Ecut = 190.5u"eV" # Could also use eV or other energy-compatible units</pre>
<pre>basis = PlaneWaveBasis(model; Ecut, kgrid)</pre>

$$\psi_k(x) = \frac{1}{\sqrt{Na}} e^{i\frac{n}{N}bx} \sum_{|m| \le m_{\text{max}}} C_n(m) e^{ibmx} \text{ where }$$

$$n \in \left[-\frac{N}{2}+1, \frac{N}{2}\right]$$





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# **REAL LIFE IS 3-D**



# **CRYSTAL LATTICES**

Crystal axis:  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$ 

Direct lattice vector:  $\mathbf{R} = n_1$ 

$$\{n_1 + n_2 a_2 + n_3 a_3 \\ \{n_1, n_2, n_3\} \in \mathbb{Z}^3$$

Periodic hamiltonian:

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

 $\boldsymbol{b}_2 = \frac{2\pi}{V} \boldsymbol{a}_3 \times \boldsymbol{a}_1$ 

 $b_3 = \frac{2\pi}{V} a_1 \times a_2$ 

 $\boldsymbol{b}_1 = \frac{2\pi}{V} \boldsymbol{a}_2 \times \boldsymbol{a}_3$ 

 $\boldsymbol{a}_i \cdot \boldsymbol{b}_i = 2\pi \delta_{ii}$ 

Reciprocal lattice axis:

$$\boldsymbol{G} = h \boldsymbol{b}_1 + k \boldsymbol{b}_2 + l \boldsymbol{b}_3 \qquad \qquad \boldsymbol{e}^{i \boldsymbol{G} \cdot \boldsymbol{R}} = 1$$
$$\{h, k, l\} \in Z^3$$

# FROM 1-D TO 3-D

1-D

 $\psi_k(x) = \frac{1}{\sqrt{Na}} e^{ikx} u_k(x)$  wh

here 
$$u_k(x+a) = u_k(x)$$

Fourier series in 1-D:

$$u_k(x) = \sum_{|\mathbf{m}| < m_{\max}} C_k(\mathbf{m}) e^{i \mathbf{m} b x}$$

3-D 
$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{NV}} e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r})$$

where 
$$u_k(\mathbf{r} + \mathbf{R}) = u_k(\mathbf{r})$$

Fourier series in 3-D:

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{G}| < G_{\text{max}}} C_{\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

# FROM 1-D TO 3-D

1-D

 $\psi_k(x) = \frac{1}{\sqrt{Na}} e^{ikx} u_k(x)$  where  $u_k(x+a) = u_k(x)$ 

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3-D 
$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{NV}} e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r})$$

where 
$$u_k(\mathbf{r}+\mathbf{R})=u_k(\mathbf{r})$$

Fourier series in 3-D:

$$\boldsymbol{u}_{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{|\boldsymbol{G}| < G_{\text{max}}} C_{\boldsymbol{k}}(\boldsymbol{G}) e^{i\boldsymbol{G}\cdot\boldsymbol{r}}$$



Final expression:

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{NV}} \sum_{\mathbf{G} < G_{\text{max}}} C_k(\mathbf{G}) e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}} u_k(\mathbf{r})$$

G<sub>max</sub>

# **HOW MANY PLANE-WAVES = CUTOFF ENERGY**

# Reciprocal lattice: $\boldsymbol{G} = h \boldsymbol{b}_1 + k \boldsymbol{b}_2 + l \boldsymbol{b}_3$

Volume of the sphere containing all the PW:

$$V_{\text{sphere}} = \frac{4 \pi}{3} G_{max}^3$$

Volume of occupied by 1 single PW:

$$V_{\rm PW} = b_1 \cdot (b_2 \times b_3) = \frac{(2\pi)^3}{V}$$

G<sub>max</sub>

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Number of PW:  

$$N_{PW} = \frac{V_{sphere}}{V_{PW}} = \frac{V}{6 \pi^2} G_{max}^3$$
Cutoff energy:  

$$E_{cutoff} = \frac{\hbar^2 G_{max}^2}{2 m}$$
And finally  

$$N_{PW} \propto V E_{cutoff}^{3/2}$$

# LINK WITH DFT CODES



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model = model\_LDA(lattice, atoms, positions)
kgrid = [4, 4, 4] # k-point grid (Regular Monkhorst-Pack grid)
Ecut = 7 # kinetic energy cutoff
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basis = PlaneWaveBasis(model; Ecut, kgrid)

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V N_1 N_2 N_3}} e^{i(\frac{n_1}{N_1} b_1 + \frac{n_2}{N_2} b_2 + \frac{n_3}{N_3} b_3) \cdot \mathbf{r}} \sum_{|\mathbf{G}|^2/2 \le \mathbf{E}_{\text{cutoff}}} C_{n_1, n_2, n_3}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}$$

 $n_{1} \in \left[-\frac{N_{1}}{2} + 1, \frac{N_{1}}{2}\right]$ where  $n_{2} \in \left[-\frac{N_{2}}{2} + 1, \frac{N_{2}}{2}\right]$  $n_{3} \in \left[-\frac{N_{3}}{2} + 1, \frac{N_{3}}{2}\right]$ 

Regular sampling of the 1<sup>st</sup> Brillouin zone



PW basis functions are orthogonal + quantum-mechanics variational principle



Adding more PW or increasing the cutoff energy makes ALWAYS the result more accurate

# **EXAMPLE: BAND STRUCTURE**





- 1. Plane-wave basis in 1D
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Why should we treat the core electrons?

Si: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>2</sup>

- 1. They do not participate to the chemical bonds
- 2. They converge very slowly with respect to the PW basis



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First, frozen-core approximation:

The core electron do not change with the environment

same in the isolated atom, a molecule, an ion, a crystal



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The core electron do not change with the environment

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Second, pseudopotential:

Create an effective potential that simulates the sum of the nucleus attraction and core electron repulsion



# FICTIOUS EXAMPLE

# All electron



# FICTIOUS EXAMPLE

# All electron

# **Pseudopotentials**





# **Pseudopotentials**





# LINK WITH DFT CODES



# Load HGH pseudopotential for Silicon
Si = ElementPsp(:Si, psp=load\_psp("hgh/lda/Si-q4"))

pseudopotentials are

- element-specific
- generated for an isolated spherical atom (with another code)
- read from a file shipped with the code or obtained somewhere else

Example:	Help me		PSEL DOJO	<b>5</b> <b>1</b> <b>1</b> <b>1</b> <b>1</b> <b>1</b> <b>1</b> <b>1</b> <b>1</b> <b>1</b> <b>1</b>	F.A.Q. Contr Select the flavor and to get the complete te specific element. "HT 5 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	ibute Papers format, then click "Dor ble of pseudos or chc ML" gives full test rest 7 7 2 3 4 4 0 2 3 0 0 2 9 0 0 9 0 0 9 0 0 0 0 0 9 0 0 0 1 0 1 0	About wmload" 2 1 35 He co 42 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4
	11 3 <sup>38</sup> Na <sub>0.4</sub> <sup>44</sup> 4.000 Sodium 12 3 <sup>38</sup> Mg <sub>0.4</sub> <sup>45</sup> 4.5 <sup>46</sup> 4.8 <sup>46</sup> 0.00 Magnesium	Type NC SR (ONCVPSP v0.4.1)   ◆	XC Acc PBE < stand	ard <b>¢</b> psp8 <b>¢</b>	13 2 14 5 0.1 14 0.2 20 1.5 0.1 14 0.2 15 0.1 16	15 2 16 2 18 P 16 2 18 0.3 20 0.0 22 0.3 20 0.0 28 -0.50 Sulphur	17 2 25 Cl 08 29 Ar 00 12 31 030 Chlorine
	19 3 20 3 21 33 K 22 28 Ca <sub>0.1</sub> 35 37 2.0 34 0.3 9 Potassium 26 Calcium 5	$ \begin{array}{c c} 1 & 4 \\ Sc_{1,3} \\ 0,00 \\ candhum \\ \end{array} \begin{array}{c} 22 & 4 \\ Ti \\ \frac{3}{42} \\ 184 \\ \frac{4}{40} \\ 174nium \\ \end{array} \begin{array}{c} 23 & 4 \\ V \\ \frac{3}{42} \\ 44 \\ 44 \\ 186 \\ 75 \\ 100 \\ Vanadium \\ Vanadium \\ Chromium \\ Ch$	25 4 42 Mn 46 16.9 54 -0.10 Manganese 26 4 41 Fe 5.6 5.2 5.2 5.2 5.4 42 Co 1.0 5.4 5.4 5.5 5.4 5.5 5.4 5.5 5.5	28 4 45 NI 11 55 -0.10 Nickel 29 4 30 4 30 4 30 4 30 4 30 4 30 4 30 4 30	$\begin{array}{c} 31 & 3 \\ 36 & Ga_{0.5} \\ 40 & 1.5 \\ 46 & -0.00 \\ Gallium \end{array} \begin{array}{c} 32 & 3 \\ 35 & Ge_{0.5} \\ 35 & -0.00 \\ Germanium \end{array}$	33 3 34 3 38 AS 0.4 39 Se 0.2 42 0.7 49 -0.10 Arsenic Selenium	35 2 19 Br 00 23 002 Bromine 36 2 22 Kr 00 23 36 2 22 Kr 00 23 34 ma Krypton
	37 3 38 3 3 19 Rb 0 2 28 Sr 1 3 20 29 0.40 Strontlum	9 4 40 4 41 4 42 4 Y 10 23 33 11 41 41 4 42 4 0.010 33 49 0.000 40 0.0000 40 0.000 40 0.0	43 4 44 4 45 4 38 TC 16 38 RU 21 40 Rh 26 448 -0.000 550 -0.005 550 -0.00	$\begin{smallmatrix} 46 & 3 \\ _{37}^{7} Pd \\ _{49}^{1} & _{-0,10}^{13} \\ Palladium \end{smallmatrix} \begin{smallmatrix} 47 & 4 \\ _{37}^{7} Ag \\ _{0,6}^{0,3} \\ _{47}^{0,10} \\ _{-0,10}^{0,6} \\ \\ Silver \end{smallmatrix} \begin{smallmatrix} 48 & 4 \\ _{47}^{7} Cd \\ _{57}^{1} \\ _{-0,00}^{3} \\ \\ Cadmium \end{smallmatrix}$	$\begin{smallmatrix} 49 & 3 \\ 31 & In \\ 35 & 0.12 \\ 41 & 0.10 \\ Indium & Indium \\ Indium & Indiu \\ Indium & Indium \\ Indium & Indium \\ Indium & Indium \\ In$	51 3 52 3 36 Sb 05 34 Te 08 40 1.0 46 0.10 Antimony Tellurium	53 2 31 04 35 11 1000 1000 1000 25 4 2 28 Xe <sub>00</sub> 25 4 28 Xe <sub>00</sub> 25 4 28 Xe <sub>00</sub> 25 4 28 Xe <sub>00</sub> 25 4 28 Xe <sub>00</sub>
	55 3 56 3 19 CS 01 18 Ba 09 25 0.040 22 -010 Caesium Barium	72 4 73 4 74 4 55 0,00 5 0,00 5 0,00 0 0,00 0,00 0,00	75 4 30 Re 0.7 42 -0.10 Rhenium 75 4 76 4 77 4 77 4 17 15 20 40 00 17 16 17 17 15 20 0 17 17 17 17 17 17 17 17 17 17 17 17 17	78 4 79 4 80 4 <sup>38</sup> Pt 32 AU 13 <sup>50</sup> -0.20 4 10 Platinum Gold AU 33 <sup>30</sup> AU 13 <sup>31</sup> 10 <sup>32</sup> AU 33 <sup>33</sup> AU 33 <sup>34</sup> AU 33 <sup>35</sup> AU 3	81 3 TI 01 27 -0.0 Thallum 24 Pb 01 37 -0.0 Lead	83 3 BI 0.4 33 0.4 37 -0.00 Bismuth Polonium	At na na na na na Astatine
	87 88 Ra Francium Radium	104 Rf Db Sg Ruther- fordium Dubnium Seaborgium	107 Bh Hs 109 Mt Bohrium Hassium Meitnerium	110         111         112           Ds         Rg         Cn           Darm- stadtium         Roent- genium         Coper- nicium	113 Nh Fl Nihonium Flerovium	115 Mc Lv Moscovium Livermorium	117 Ts Og Tennessine Oganesson
		$\begin{bmatrix} 57 & 4 \\ 50 & La \\ \frac{59}{50} & a^{na} \end{bmatrix} \xrightarrow{58} \begin{bmatrix} na \\ na$	$\begin{array}{c} 60 & na \\ na$	63 na 64 na 65 na na Eu na na Gd na na Tb na na na na na na na na	66 na 67 na na na na na na	68 na 69 na na Er na na TM na na na na na	70 na Yb na na na na na na 50 22 50 22

Techniques: norm-conserving pseudos, ultra-soft pseudos, PAW



- 1. Plane-wave basis in 1D
- 2. Plane-wave basis in 3D
- 3. Pseudopotentials
- 4. Kohn-Sham hamiltonian and self-consistency

5. Further reading tips

**NON-LINEAR SCHRODINGER EQUATION** 



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# **NON-LINEAR SCHRODINGER EQUATION**



# **NON-LINEAR SCHRODINGER EQUATION**





In practice, it is a slightly more complicated Instabilities, slow convergence happen

$$\rho^{(n)\text{in}} = F[\rho^{(n)\text{out}}, \rho^{(n-1)\text{out}}, \rho^{(n-2)\text{out}}, \dots]$$
simple mixing
Pulay
Kerker preconditionning
$$\rho^{(n)\text{out}}(\mathbf{r}) = \sum_{\mathbf{k}, i \text{ occ}} |\psi_{\mathbf{k}i}(\mathbf{r})|^2$$



- 1. Plane-wave basis in 1D
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**5.** Further reading tips



# **TO KNOW MORE**

• Book: Parr & Yang (1989)

- Online: ABC of DFT of Burke http://dft.uci.edu/research.php#theabcofdft
- Book: Ashcroft & Mermin (1976)

• Book: R. Martin (2004)





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