Density functional theory in the solid state

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Summary

1. **Density functional theory**
   - Motivation
   - History
   - Kohn-Sham method

2. **Bloch theorem / supercells**

3. **Plane wave basis set**
Motivation: Why use DFT?

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  - Knowledge of the electron structure can be used for the analysis; many observables can be obtained directly

- Preferable scaling compared to many quantum chemistry methods
History of DFT — I

- There were already methods in the early 20th century
  - Thomas-Fermi-method
  - Hartree-Fock-method
Walter Kohn
Inhomogeneous Electron Gas*

P. Hohenberg†
École Normale Superieure, Paris, France

AND

W. Kohn‡
École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France

and

University of California at San Diego, La Jolla, California
(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential \( v(\mathbf{r}) \). It is proved that there exists a universal functional of the density, \( F[n(\mathbf{r})] \), independent of \( v(\mathbf{r}) \), such that the expression \( E = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})] \) has as its minimum value the correct ground-state energy associated with \( v(\mathbf{r}) \). The functional \( F[n(\mathbf{r})] \) is then discussed for two situations: (1) \( n(\mathbf{r}) = n_0 + \bar{n}(\mathbf{r}) \), \( \bar{n}/n_0 < 1 \), and (2) \( n(\mathbf{r}) = \varphi(\mathbf{r}/r_0) \) with \( \varphi \) arbitrary and \( r_0 \to \infty \). In both cases \( F \) can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.
Hohenberg-Kohn theorems: Theorem I

- Given a potential, one obtains the wave functions via Schrödinger equation:

\[ V(r) \Rightarrow \psi_i(r) \]
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The density is the probability distribution of the wave functions:

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\[ n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \]

Thus

\[ V(\mathbf{r}) \Rightarrow \psi_i(\mathbf{r}) \Rightarrow n(\mathbf{r}) \]
The potential, and hence also the total energy, is a unique functional of the electron density $n(r)$.

Theorem

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**Theorem**

*The potential, and hence also the total energy, is a unique functional of the electron density \( n(r) \)*

Thus

\[
V(r) \Rightarrow \psi_i(r) \Rightarrow n(r) \Rightarrow V(r)
\]
Hohenberg-Kohn theorems: Theorem I

The potential, and hence also the total energy, is a unique functional of the electron density $n(r)$

Thus

$$v(r) \Rightarrow \psi_i(r) \Rightarrow n(r) \Rightarrow v(r)$$

The electron density can be used to determine all properties of a system.
The total energy is variational: In the ground state the total energy is minimised
Hohenberg-Kohn theorems: Theorem II

Theorem

*The total energy is variational: In the ground state the total energy is minimised*

Thus

\[ E[n] \geq E[n_{GS}] \]
Self-Consistent Equations Including Exchange and Correlation Effects*

W. Kohn and L. J. Sham

University of California, San Diego, La Jolla, California

(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.
History of DFT — V: The reward

... in 1998:
Let us write the total energy as:

\[ E_{\text{tot}}[n] = E_{\text{kin}}[n] \]

- \( E_{\text{kin}}[n] = QM \) kinetic energy of electrons
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\[ E_{\text{tot}}[n] = E_{\text{kin}}[n] + E_{\text{ext}}[n] + E_{\text{H}}[n] + E_{\text{xc}}[n] \]

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- \( E_{\text{ext}}[n] \) = energy due to external potential (usually ions)
- \( E_{\text{H}}[n] \) = classical Hartree repulsion (\(e^- - e^-\))
- \( E_{\text{xc}}[n] \) = exchange-correlation energy
Kohn-Sham method: Noninteracting electrons

To solve the many-body Schrödinger equation as such is an unformidable task
Kohn-Sham method: Noninteracting electrons

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- Let us write the many-body wave function as a determinant of single-particle equations
Kohn-Sham method: Noninteracting electrons

To solve the many-body Schrödinger equation as such is an unformidable task

Let us write the many-body wave function as a determinant of single-particle equations

Then kinetic energy of electrons becomes

$$E_{\text{kin},s} = \sum_i -\frac{1}{2} f_i \langle \psi_i(r) | \nabla^2 | \psi_i(r) \rangle$$

$$f_i = \text{occupation of orbital } i \text{ (with spin-degeneracy included)}$$
Energy due to external potential; usually $V_{\text{ext}} = \sum Z_i - \frac{Z_i}{|r - R_i|}$

$$E_{\text{ext}} = \int n(r) V_{\text{ext}}(r) \, dr$$

$$n(r) = \sum_i f_i |\psi_i(r)|^2$$
Kohn-Sham method: Hartree energy

- Classical electron-electron repulsion

\[
E_H = \frac{1}{2} \int \int \frac{n(r) n(r')}{|r - r'|} \, dr' \, dr
\]

\[
= \frac{1}{2} \int n(r) V_H(r) \, dr
\]

\[
V_H(r) = \int |r - r'| n(r') \, dr'
\]
Kohn-Sham method: Exchange-correlation energy

- The remaining component: Many-body complications combined

→ Will be discussed later
Total energy expression

Kohn-Sham (total\(^1\)) energy:

\[
E_{KS}[n] = \sum_i -\frac{1}{2} f_i \langle \psi_i | \nabla^2 | \psi_i \rangle + \int n(r) V_{\text{ext}}(r) \, dr \\
+ \frac{1}{2} \int \int \frac{n(r) n(r')}{|r - r'|} \, dr' \, dr + E_{xc}
\]

\(^1\)without ion-ion interaction
Vary the Kohn-Sham energy $E_{KS}$ with respect to $\psi_j^*(r'')$: $\frac{\delta E_{KS}}{\delta \psi_j^*(r'')}$
Kohn-Sham equations

Vary the Kohn-Sham energy $E_{KS}$ with respect to $\psi_j^*(r'')$: 

$$\frac{\delta E_{KS}}{\delta \psi_j^*(r'')}$$

$$\left\{ \begin{array}{c}
-\frac{1}{2} \nabla^2 + V_{KS}(r) \\
\end{array} \right\} \psi_i(r) = \varepsilon_i \psi_i(r)$$

$$n(r) = \sum_i f_i |\psi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + V_{xc}(r)$$

$$V_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)}$$
Kohn-Sham equations: Notes

\[
\left\{-\frac{1}{2}\nabla^2 + V_{\text{KS}}(\mathbf{r})\right\} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) ; \quad n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2
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- Equation looking like Schrödinger equation
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\[ \left\{ -\frac{1}{2} \nabla^2 + V_{\text{KS}} (r) \right\} \psi_i (r) = \varepsilon_i \psi_i (r) \quad ; \quad n (r) = \sum_i f_i |\psi_i (r)|^2 \]

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- The potential \( V_{\text{KS}} \) is local
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- The Kohn-Sham potential, however, depends on density
- The equations are coupled and highly non-linear
- \( \Rightarrow \) Self-consistent solution required
- \( \varepsilon_i \) and \( \psi_i \) are in principle only help variables (only \( \varepsilon_{\text{HOMO}} \) has a meaning)
- The potential \( V_{\text{KS}} \) is local
- The scheme is in principle exact
1. Generate a starting density \( n^{\text{init}} \)
Kohn-Sham equations: Self-consistency

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2. Generate the Kohn-Sham potential $\Rightarrow V_{\text{KS}}^{\text{init}}$
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1. Generate a starting density $n^\text{init}$
2. Generate the Kohn-Sham potential $\Rightarrow V_{\KS}^\text{init}$
3. Solve the Kohn-Sham equations $\Rightarrow \psi_i^\text{init}$
4. New density $n^1$
Kohn-Sham equations: Self-consistency

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2. Generate the Kohn-Sham potential $\Rightarrow V^{\text{init}}_{\text{KS}}$
3. Solve the Kohn-Sham equations $\Rightarrow \psi^{\text{init}}_i$
4. New density $n^1$
5. Kohn-Sham potential $V^1_{\text{KS}}$
Kohn-Sham equations: Self-consistency

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2. Generate the Kohn-Sham potential $\Rightarrow V_{\text{KS}}^{\text{init}}$
3. Solve the Kohn-Sham equations $\Rightarrow \psi^{\text{init}}_i$
4. New density $n^1$
5. Kohn-Sham potential $V_{\text{KS}}^1$
6. Kohn-Sham orbitals $\Rightarrow \psi^1_i$
Kohn-Sham equations: Self-consistency

1. Generate a starting density $n_{\text{init}}$
2. Generate the Kohn-Sham potential $\Rightarrow V_{\text{KS}}^{\text{init}}$
3. Solve the Kohn-Sham equations $\Rightarrow \psi_{i}^{\text{init}}$
4. New density $n^{1}$
5. Kohn-Sham potential $V_{\text{KS}}^{1}$
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7. Density $n^{2}$
Kohn-Sham equations: Self-consistency

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2. Generate the Kohn-Sham potential $V^{\text{init}}_{\text{KS}}$
3. Solve the Kohn-Sham equations $\Rightarrow \psi^{\text{init}}_{i}$
4. New density $n^{1}$
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Kohn-Sham equations: Self-consistency

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Kohn-Sham equations: Self-consistency

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4. New density \( n^1 \)
5. Kohn-Sham potential \( V_{\text{KS}}^1 \)
6. Kohn-Sham orbitals \( \Rightarrow \psi_i^1 \)
7. Density \( n^2 \)
8. . .

. . . until self-consistency is achieved (to required precision)
Kohn-Sham equations: Self-consistency

- Usually the density coming out from the wave functions is **mixed** with the previous ones, in order to improve convergence.
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- In metals *fractional occupations numbers* are necessary.
Kohn-Sham equations: Self-consistency

- Usually the density coming out from the wave functions is mixed with the previous ones, in order to improve convergence.
- In metals fractional occupations numbers are necessary.
- The required accuracy in self-consistency depends on the observable and the expected.
Kohn-Sham energy: Alternative expression

- Take the Kohn-Sham equation, multiply from the left with $f_i \psi_i^*$ and integrate:

$$
-\frac{1}{2} f_i \int \nabla^2 \psi_i (r) \; dr + f_i \int V_{KS} (r) |\psi_i (r)|^2 \; dr = f_i \varepsilon_i
$$
Kohn-Sham energy: Alternative expression

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- Sum over $i$ and substitute into the expression for Kohn-Sham energy:

$$E_{KS}[n] = \sum_i f_i \epsilon_i - E_H + E_{xc} - \int n(r) V_{xc} \, dr$$
Summary

1. Density functional theory
2. Bloch theorem / supercells
3. Plane wave basis set
In realistic systems there are \( \approx 10^{20} \) atoms in cubic millimetre — formidable to treat by any numerical method.
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At this scale the systems are often repeating (crystals).

... or the observable is localised and the system can be made periodic.

Choices: Periodic boundary conditions or isolated (saturated) cluster.
Periodic systems
Periodic systems
Periodic systems
Periodic systems

DFT in the solid state
Periodic systems

Is it possible to replace the summation over translations $L$ with a modulation?
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**Bloch’s theorem**

For a periodic potential $V(\mathbf{r} + \mathbf{L}) = V(\mathbf{r})$ the eigenfunctions can be written in the form

$$
\psi_i(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{ik}(\mathbf{r}) ,
$$

$$
u_{ik}(\mathbf{r} + \mathbf{L}) = u_{ik}(\mathbf{r})$$
Reciprocal lattice vectors:

\[
\begin{align*}
\mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \\
\mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot \mathbf{a}_3 \times \mathbf{a}_1} \\
\mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot \mathbf{a}_1 \times \mathbf{a}_2}
\end{align*}
\]
First Brillouin zone: Part of space closer to the origin than to any integer multiple of the reciprocal lattice vectors,
\[ \mathbf{K}' = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3 \]
Thus the summation over infinite number of translations becomes an integral over the first Brillouin zone:

\[ \sum_{L}^{\infty} \Rightarrow \int_{\mathbf{k} \in 1.BZ} d\mathbf{k} \]
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\[ \sum_{L} \Rightarrow \int_{k \in 1.BZ} dk \]

In practise the integral is replaced by a weighted sum of discrete points:

\[ \int_{k} dk \approx \sum_{k} w_{k} \]
Thus the summation over infinite number of translations becomes an integral over the first Brillouin zone:

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In practise the integral is replaced by a weighted sum of discrete points:

$$\int_{k} dk \approx \sum_{k} w_{k}$$

Thus eg.

$$n(r) = \sum_{k} w_{k} \sum_{i} f_{ik} |\psi_{ik}(r)|^2$$
Periodic systems: Dispersion
Band structure: Example Pb/Cu(111)

Photoemission vs DFT calculations for a free-standing layer

Felix Baumberger, Anna Tamai, Matthias Muntwiler, Thomas Greber and Jürg Osterwalder; Surface Science 532-535 (2003) 82-86

DFT in the solid state
Monkhorst-Pack algorithm

- Approximate the integral with an equidistance grid of \( k \) vectors with identical weight:
Approximate the integral with an equidistance grid of $k$ vectors with identical weight:

$$n = \frac{2p - q - 1}{2q}, \quad p = 1 \ldots q$$

$$k_{ijk} = n_1 b_1 + n_2 b_2 + n_3 b_3$$
Symmetry operations

- If the atoms are related by symmetry operation $S$ ($S\psi (r) = \psi (Sr)$) the integration over the whole 1st Brillouin zone can be reduced into the *irreducible Brillouin zone*, IBZ.
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$$S \psi_{ik} (r) = \psi_{ik} (Sr) = e^{ik \cdot Sr} u_{ik} (Sr) = e^{ik' \cdot r} u_{ik'} (r), \quad k' = S^{-1} k$$
Symmetry operations

If the atoms are related by symmetry operation $S$ 
$(S\psi (r) = \psi (Sr))$ the integration over the whole 1st 
Brillouin zone can be reduced into the *irreducible Brillouin zone*, IBZ

$$S\psi_{ik} (r) = \psi_{ik} (Sr) = e^{i k \cdot Sr} u_{ik} (Sr) = e^{i k' \cdot r} u_{ik'} (r) , \; k' = S^{-1} k$$

$$\int d\mathbf{k} \approx \sum_{\mathbf{k} \in BZ} w_{\mathbf{k}} = \sum_{\mathbf{k} \in IBZ} \sum_{S} w'_{Sk}$$
Irreducible Brillouin zone: Examples
Doubling the unit cell
If one doubles the unit cell in one direction, it is enough to take only half of the $k$ points in the corresponding direction in the reciprocal space.
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And has to be careful when comparing energies in cells with different size unless either equivalent sampling of $k$ points is used.
Doubling the unit cell (super-cells)

- If one doubles the unit cell in one direction, it is enough to take only half of the $k$ points in the corresponding direction in the reciprocal space.
- And has to be careful when comparing energies in cells with different size unless either equivalent sampling of $k$ points is used or one is converged in the total energy in both cases.
Summary

1. Density functional theory
2. Bloch theorem / supercells
3. Plane wave basis set
   - Basics of plane wave basis set
   - Operators
   - Energy terms in plane wave basis set
   - Introduction to pseudo potentials
Kohn–Sham method

The ground state energy is obtained as the solution of a constrained minimisation of the Kohn-Sham energy:

$$\min_{\{\Phi\}} E_{KS}[\{\Phi_i(r)\}]$$
Kohn–Sham method

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\[
\min_{\{\Phi\}} E_{KS}[\{\Phi_i(r)\}]
\]

\[
\int \Phi_i^*(r) \Phi_j(r) \, dr = \delta_{ij}
\]
For practical purposes it is necessary to expand the Kohn-Sham orbitals using a set of basis functions. Let the basis set be:

$$\{ \varphi_\alpha (\mathbf{r}) \}^{M}_{\alpha=1}$$

Usually a linear expansion:

$$\psi_i (\mathbf{r}) = \sum_{\alpha=1}^{M} c_\alpha i \varphi_\alpha (\mathbf{r})$$
Assemblies of atoms are slight distortions to free electrons

\[ \varphi_\alpha(r) = \frac{1}{\sqrt{\Omega}} e^{i \mathbf{G}_\alpha \cdot r} \]

\[ \ldots = \cos(\mathbf{G}_\alpha \cdot \mathbf{r}) + i \sin(\mathbf{G}_\alpha \cdot \mathbf{r}) \]
Plane waves

Philosophy
Assemblies of atoms are slight distortions to free electrons

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+ orthogonal
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+ independent of atomic positions
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+ no BSSE
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+ orthogonal
+ independent of atomic positions
+ no BSSE
± naturally periodic
Plane waves

Philosophy

Assemblies of atoms are slight distortions to free electrons

\[ \varphi_\alpha(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{iG_\alpha \cdot \mathbf{r}} \]

+ orthogonal
+ independent of atomic positions
+ no BSSE
± naturally periodic
– many functions needed
Computational box

- Box matrix: \( \mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3] \)
- Box volume: \( \Omega = \det \mathbf{h} \)
Lattice vectors

- **Direct lattice** \( \mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3] \)
- Translations in direct lattice: \( \mathbf{L} = i \cdot \mathbf{a}_1 + j \cdot \mathbf{a}_2 + k \cdot \mathbf{a}_3 \)
Lattice vectors

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- Translations in direct lattice: \( \mathbf{L} = i \cdot \mathbf{a}_1 + j \cdot \mathbf{a}_2 + k \cdot \mathbf{a}_3 \)
- **Reciprocal lattice** \( 2\pi(\mathbf{h}^t)^{-1} = [\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3] \)
  \[
  \mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}
  \]
- Reciprocal lattice vectors: \( \mathbf{G} = i \cdot \mathbf{b}_1 + j \cdot \mathbf{b}_2 + k \cdot \mathbf{b}_3 \)
Expansion of Kohn-Sham orbitals

Plane wave expansion

\[ \psi_{ik}(r) = \sum_{G} c_{ik}(G) e^{i(k+G) \cdot r} \]

To be solved: Coefficients \( c_{ik}(G) \)
Expansion of Kohn-Sham orbitals

Plane wave expansion

$$
\psi_{ik}(r) = \sum_{G} c_{ik}(G) e^{i(k+G) \cdot r}
$$

To be solved: Coefficients $c_{ik}(G)$

Different routes:
- Direct optimisation of total energy
- Iterative diagonalisation/minimisation
Dependence on position

Translation:

$$\phi(r) \rightarrow \phi(r - R_i)$$

$$\phi(r - R_i) = \sum_G \phi(G) e^{iG \cdot (r - R_i)}$$

$$= \sum_G \left( \phi(G) e^{iG \cdot r} \right) e^{-iG \cdot R_i}$$
**Translation:**

\[
\phi(r) \rightarrow \phi(r - R_I)
\]

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\]

**Structure Factor:**

\[
S_I(G) = e^{-iG \cdot R_I}
\]
Dependence on position

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\]

- **Structure Factor:**

\[
S_I(G) = e^{-iG \cdot R_l}
\]

- **Derivatives:**

\[
\frac{\partial \phi(r - R_l)}{\partial R_{l,s}} = -i \sum_G G_s \left( \phi(G)e^{iG \cdot r} \right) S_I(G)
\]
Plane waves: Kinetic energy

- Kinetic energy operator in the plane wave basis:

\[-\frac{1}{2} \nabla^2 \varphi_G(r) = -\frac{1}{2} (iG)^2 \frac{1}{\sqrt{\Omega}} e^{iG \cdot r} = \frac{1}{2} G^2 \varphi_G(r)\]
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- Thus the operator is diagonal in the plane wave basis set

\[ E_{\text{kin}}(G) = \frac{1}{2} G^2 \]
Density functional theory
Bloch theorem / supercells
Plane wave basis set

Cutoff: Finite basis set

Choose all basis functions into the basis set that fulfill

\[ \frac{1}{2} G^2 \leq E_{\text{cut}} \]

— a cut-off sphere
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\[ N_{\text{PW}} \approx \frac{1}{2\pi^2} \Omega E_{\text{cut}}^{3/2} [\text{a.u.}] \]

Basis set size depends on volume of box and cutoff only
Choose all basis functions into the basis set that fulfill

\[ \frac{1}{2} G^2 \leq E_{\text{cut}} \]

— a cut-off sphere

Basis set size depends on volume of box and cutoff only — and is \textit{variational}!
The information contained in $\psi(G)$ and $\psi(r)$ are equivalent:

$$\psi(G) \leftrightarrow \psi(r)$$
Plane waves: Fast Fourier Transform

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  \[ \psi(G) \leftrightarrow \psi(r) \]

- Transform from $\psi(G)$ to $\psi(r)$ and back is done using fast Fourier transforms (FFT’s)

- Along one direction the number of operations $\propto N \log[N]$
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3D-transform = three subsequent 1D-transforms

Information can be handled always in the most appropriate space
Parseval’s theorem

\[ \Omega \sum_{\mathbf{G}} A^*(\mathbf{G}) B(\mathbf{G}) = \frac{\Omega}{N} \sum_i A^*(\mathbf{r}_i) B(\mathbf{r}_i) \]
Parseval’s theorem

$$\Omega \sum_G A^\ast(G)B(G) = \frac{\Omega}{N} \sum_i A^\ast(r_i)B(r_i)$$

Proof.

$$I = \int_\Omega A^\ast(r)B(r)dr$$

$$= \sum_{GG'} A^\ast(G)B(G) \int \exp[-iG \cdot r] \exp[iG' \cdot r]dr$$

$$= \sum_{GG'} A^\ast(G)B(G) \Omega \delta_{GG'} = \Omega \sum_G A^\ast(G)B(G)$$
Plane waves: Electron density

\[ n(r) = \sum_{i,k} w_k f_{ik} |\psi_{ik}(r)|^2 = \frac{1}{\Omega} \sum_{i,k} w_k f_{ik} \sum_{G,G'} c^*_{ik}(G) c_{ik}(G') e^{i(G-G') \cdot r} \]

\[ n(r) = \sum_{G=-2G_{\text{max}}}^{2G_{\text{max}}} n(G) e^{iG \cdot r} \]
The electron density can be expanded exactly in a plane wave basis with a cut-off four times the basis set cutoff.

\[ N_{PW}(4E_{cut}) = 8N_{PW}(E_{cut}) \]
The Kohn-Sham equations written in reciprocal space:

\[
\begin{align*}
\left\{ -\frac{1}{2} \nabla^2 + V_{KS}(G, G') \right\} \psi_{ik}(G) &= \varepsilon_i \psi_{ik}(G)
\end{align*}
\]
Density functional theory
Bloch theorem / supercells
Plane wave basis set

Basics of plane wave basis set
Operators
Energy terms in plane wave basis set
Introduction to pseudo potentials

Plane waves: Operators

- The Kohn-Sham equations written in reciprocal space:
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\begin{aligned}
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- However, it is better to do it like Car and Parrinello (1985) suggested: Always use the appropriate space (via FFT)
Plane waves: Operators

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- There one needs to apply an operator on a wave function:

  \[
  \sum_{G'} O(G, G') \psi(G') = \sum_{G'} c(G') \langle G | O | G' \rangle
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Matrix representation of operators in: \( O(G, G') = \langle G | O | G' \rangle \)
Plane waves: Operators

- The Kohn-Sham equations written in reciprocal space:
  \[
  \left\{ -\frac{1}{2} \nabla^2 + V_{KS}(\mathbf{G}, \mathbf{G}') \right\} \psi_{ik}(\mathbf{G}) = \varepsilon_i \psi_{ik}(\mathbf{G})
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  \sum_{\mathbf{G}'} O(\mathbf{G}, \mathbf{G}') \psi(\mathbf{G}') = \sum_{\mathbf{G}'} c(\mathbf{G}') \langle \mathbf{G} | O | \mathbf{G}' \rangle
  \]

- Matrix representation of operators in: \(O(\mathbf{G}, \mathbf{G}') = \langle \mathbf{G} | O | \mathbf{G}' \rangle\)

- Eg. Kinetic energy operator
  \[
  T_{\mathbf{G}, \mathbf{G}'} = \langle \mathbf{G} | -\frac{1}{2} \nabla^2 | \mathbf{G}' \rangle = \frac{1}{2} G^2 \delta_{\mathbf{G}, \mathbf{G}'}
  \]
Kohn–Sham energy

$$E_{KS} = E_{\text{kin}} + E_{ES} + E_{pp} + E_{xc}$$

- \(E_{\text{kin}}\): Kinetic energy
- \(E_{ES}\): Electrostatic energy (sum of electron-electron interaction + nuclear core-electron interaction + ion-ion interaction)
- \(E_{pp}\): Pseudo potential energy not included in \(E_{ES}\)
- \(E_{xc}\): Exchange–correlation energy
Kinetic energy

\[ E_{\text{kin}} = \sum_{i,k} w_{k} f_{ik} \langle \psi_{ik} | -\frac{1}{2} \nabla^2 | \psi_{ik} \rangle \]

\[ = \sum_{i,k} w_{k} f_{ik} \sum_{GG'} c_{ik}(G)c_{ik}(G') \langle k + G | -\frac{1}{2} \nabla^2 | k + G' \rangle \]

\[ = \sum_{i,k} w_{k} f_{ik} \sum_{GG'} c_{ik}^*(G)c_{ik}(G') \Omega \frac{1}{2} | k + G |^2 \delta_{G,G'} \]

\[ = \Omega \sum_{i,k} w_{k} f_{ik} \sum_{G} \frac{1}{2} | k + G |^2 | c_{ik}(G) |^2 \]
Periodic Systems

- Hartree-like terms are most efficiently evaluated in reciprocal space via the

<table>
<thead>
<tr>
<th>Poisson equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nabla^2 V_H(r) = -4\pi n_{\text{tot}}(r) )</td>
</tr>
<tr>
<td>( V_H(G) = 4\pi \frac{n(G)}{G^2} )</td>
</tr>
</tbody>
</table>

- \( V_H(G) \) is a local operator with same cutoff as \( n_{\text{tot}} \)
Electrostatic energy

\[ E_{ES} = \frac{1}{2} \int \int \frac{n(r)n(r')}{|r - r'|} \, dr' \, dr + \sum \int n(r)V_{\text{core}}^I(r) \, dr + \frac{1}{2} \sum_{l \neq J} \frac{Z_l Z_J}{|R_l - r_J|} \]
Electrostatic energy

\[ E_{\text{ES}} = \frac{1}{2} \iiint \frac{n(r)n(r')}{|r - r'|} \, dr' \, dr + \sum_I \int n(r) V_{\text{core}}^I(r) \, dr + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - r_J|} \]

- The isolated terms do not converge; the sum only for neutral systems
- Gaussian charge distributions à la Ewald summation:
  \[ n^I_c(r) = - \frac{Z_I}{(R^c_I)^3} \pi^{-3/2} \exp \left[ - \left( \frac{r - R_I}{R^c_I} \right)^2 \right] \]
  \[ V_{\text{core}}^I(r) = \int \frac{n^I_c(r')}{|r - r'|} \, dr' = - \frac{Z_I}{|r - R_I|} \text{erf} \left[ \frac{|r - R_I|}{R^c_I} \right] \]

Electrostatic potential due to \( n^I_c \):
Electrostatic energy

\[
E_{ES} = 2\pi \Omega \sum_{\mathbf{G} \neq 0} \left\{ \frac{|n_{\text{tot}}(\mathbf{G})|^2}{G^2} \right\} + E_{\text{ovrl}} - E_{\text{self}}
\]

\[
E_{\text{ovrl}} = \sum_i' \sum_{J} \sum_{L} \frac{Z_i Z_J}{|\mathbf{R}_i - \mathbf{r}_J - \mathbf{L}|} \text{erfc} \left[ \frac{|\mathbf{R}_i - \mathbf{r}_J - \mathbf{L}|}{\sqrt{R_i^c R_j^c}} \frac{Z_i^2}{R_i^c} \right]
\]

\[
E_{\text{self}} = \sum_i \frac{1}{\sqrt{2\pi}} \frac{Z_i^2}{R_i^c}
\]

- Sums expand over all atoms in the simulation cell, all direct lattice vectors \( \mathbf{L} \); the prime in the first sum indicates that \( I < J \) is imposed for \( \mathbf{L} = 0 \).
Exchange-correlation energy

\[ \int \! n(r) \varepsilon_{xc}(r) \, dr = \Omega \sum_{G} \varepsilon_{xc}(G) n^*(G) \]

- \( \varepsilon_{xc}(G) \) is not local in G space; the calculation in real space requires very accurate integration scheme.

- If the function \( \varepsilon_{xc}(r) \) requires the gradients of the density, they are calculated using reciprocal space, otherwise the calculation is done in real space (for LDA and GGA; hybrid functionals are more intensive)
Plane waves: Basic self-consistent cycle

\[ n(r) \]
\[ V_{xc}[n](r) \]
\[ V_{KS}(r) = V_{xc}[n](r) + V_{ES}(r) \]
\[ \psi_{ik}(r) \]
\[ V_{KS}(r)\psi_{ik}(r) \]
\[ \psi'_{ik}(r) \]
\[ n'(r) = \sum_{ik} w_k f_{ik} |\psi'_{ik}(r)|^2 \]
With the plane wave basis set one can apply the Hellmann-Feynman theorem:

\[
\langle F_i = \rangle = - \frac{d}{dR_i} \langle \psi \mid H_{KS} \mid \psi \rangle = - \langle \psi \mid \frac{\partial}{\partial R_i} H_{KS} \mid \psi \rangle
\]
With the plane wave basis set one can apply the Hellmann-Feynman theorem:

\[
\left( \mathbf{F}_I = \right) - \frac{d}{d \mathbf{R}_I} \langle \psi | H_{KS} | \psi \rangle = -\langle \psi | \frac{\partial}{\partial \mathbf{R}_I} H_{KS} | \psi \rangle
\]

All the terms where \( \mathbf{R}_I \) appear explicitly are in reciprocal space, and are thus very simple to evaluate:

\[
\frac{\partial}{\partial \mathbf{R}_I} e^{-i \mathbf{G} \cdot \mathbf{R}_I} = -i \mathbf{G} e^{-i \mathbf{G} \cdot \mathbf{R}_I}
\]
Plane waves: Summary

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- Plane waves are delocalised, periodic basis functions
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- The quality of basis set adjusted using a *single* parameter, the cut-off energy
- Fast Fourier-transform used to efficiently switch between real and reciprocal space
Plane waves: Summary

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- Forces and Hartree term/Poisson equation are trivial.
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- The system has to be neutral! Usual approach for charged states: Homogeneous neutralising background
- The energies must only be compared with the same $E_{\text{cut}}$
Why use pseudo potentials?

- **Reduction of basis set size**
  effective speedup of calculation

- **Reduction of number of electrons**
  reduces the number of degrees of freedom
  For example in Pt: 10 instead of 78

- **Unnecessary** “Why bother? They are inert anyway...”

- **Inclusion of relativistic effects**
  relativistic effects can be included "partially" into effective potentials
Pseudo potential

What is it?

Replacement of the all-electron, \(-Z/r\) problem with a Hamiltonian containing an effective potential
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The construction consists of two steps of approximations

- Frozen core approximation
- Pseudisation