Density functional theory in the solid state

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Summary

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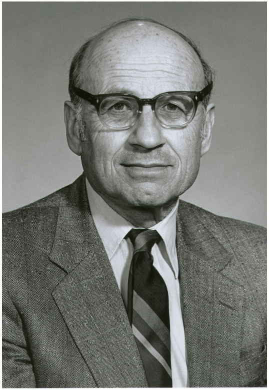
  - Predictable accuracy (unlike fitted/empirical approaches)
  - Knowledge of the electron structure can be used for the analysis; many observables can be obtained directly
- Preferable scaling compared to many quantum chemistry methods

History of DFT — I

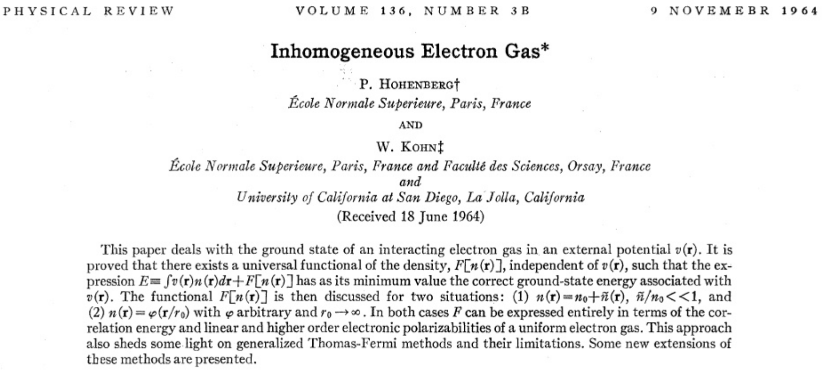
- There were already methods in the early 20th century
    - Thomas-Fermi-method
    - Hartree-Fock-method

History of DFT — II

Walter Kohn



History of DFT — III: Foundations



PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMEBR 1964

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 $E\equiv\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n(\mathbf{r})]$ 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) $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$, $\tilde{n}/n_0<<1$, and (2) $n(\mathbf{r})=\varphi(\mathbf{r}/r_0)$ with φ 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.

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$$V(\mathbf{r}) \Rightarrow \psi_i(\mathbf{r})$$

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  Thus

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$$V(\mathbf{r}) \Rightarrow \psi_i(\mathbf{r}) \Rightarrow n(\mathbf{r}) \Rightarrow V(\mathbf{r})$$

The electron density can be used to determine all properties of a system

Hohenberg-Kohn theorems: Theorem II

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

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Thus

$$E[n] \geq E[n_{\mathrm{GS}}]$$

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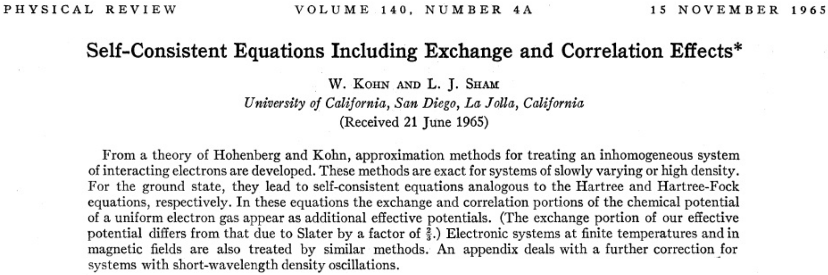

PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

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:

Kohn-Sham method: Total energy

Let us write the total energy as:

$$E_{\mathrm{tot}}[n] = E_{\mathrm{kin}}[n]$$

- $E_{\mathrm{kin}}[n]$ = *QM* kinetic energy of electrons

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- $E_{\mathrm{xc}}[n]$ = exchange-correlation energy

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

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- Let us write the many-body wave function as a determinant of single-particle equations
- Then kinetic energy of electrons becomes

$$E_{\mathrm{kin,s}} = \sum_i -\frac{1}{2} f_i \left\langle \psi_i(\mathbf{r}) \mid \nabla^2 \mid \psi_i(\mathbf{r}) \right\rangle$$

f_i = occupation of orbital i (with spin-degeneracy included)

Kohn-Sham method: External energy

- Energy due to external potential; usually $V_{\text{ext}} = \sum_I -\frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}$

$$E_{\text{ext}} = \int_{\mathbf{r}} n(\mathbf{r})\, V_{\text{ext}}(\mathbf{r})\, d\mathbf{r}$$

$$n(\mathbf{r}) = \sum_i f_i \left|\psi_i(\mathbf{r})\right|^2$$

Kohn-Sham method: Hartree energy

- Classical electron-electron repulsion

$$\begin{aligned} E_{\mathrm{H}} &= \frac{1}{2}\int_{\mathbf{r}}\int_{\mathbf{r}'}\frac{n(\mathbf{r})\,n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'\,d\mathbf{r} \\ &= \frac{1}{2}\int_{\mathbf{r}} n(\mathbf{r})\,V_{\mathrm{H}}(\mathbf{r})\,d\mathbf{r} \\ V_{\mathrm{H}}(\mathbf{r}) &= \int_{\mathbf{r}'}\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' \end{aligned}$$

Kohn-Sham method: Exchange-correlation energy

- The remaining component: Many-body complications combined

$\Longrightarrow$ Will be discussed later

Total energy expression

Kohn-Sham (total[1]) energy:

$$\begin{aligned} E_{\mathrm{KS}}[n] &= \sum_i -\frac{1}{2} f_i \left\langle \psi_i \mid \nabla^2 \mid \psi_i \right\rangle + \int_{\mathbf{r}} n(\mathbf{r})\, V_{\mathrm{ext}}(\mathbf{r})\; d\mathbf{r} \\ &+ \frac{1}{2} \int_{\mathbf{r}} \int_{\mathbf{r}'} \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}'\, d\mathbf{r} + E_{\mathrm{xc}} \end{aligned}$$

---

[1] without ion-ion interaction

Kohn-Sham equations

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

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$$\begin{aligned}\left\{-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{r})\right\}\psi_i(\mathbf{r}) &= \varepsilon_i\psi_i(\mathbf{r}) \\ n(\mathbf{r}) &= \sum_i f_i\left|\psi_i(\mathbf{r})\right|^2 \\ V_{\mathrm{KS}}(\mathbf{r}) &= V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})\end{aligned}$$

$V_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r})}$

Kohn-Sham equations: Notes

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- The scheme is in principle exact

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…until self-consistency is achieved (to required precision)

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- 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:

$$-\frac{1}{2} f_i \int_{\mathbf{r}} \psi_i(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r})\ d\mathbf{r} + f_i \int_{\mathbf{r}} V_{\mathrm{KS}}(\mathbf{r}) \left|\psi_i(\mathbf{r})\right|^2 d\mathbf{r} = f_i \varepsilon_i$$

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

$$E_{\mathrm{KS}}[n] \quad = \quad \sum_i f_i \varepsilon_i - E_{\mathrm{H}} + E_{\mathrm{xc}} - \int_{\mathbf{r}} n(\mathbf{r}) \, V_{\mathrm{xc}} d\mathbf{r}$$

Summary

1. Density functional theory
2. Bloch theorem / supercells
3. Plane wave basis set

Periodic systems

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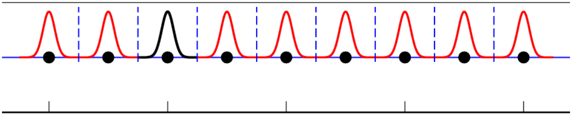
- At this scale the systems are often repeating (crystals)
- . . . or the observable is localised and the system can be made periodic
- Choices: Periodic boundary conditions or isolated (saturated) cluster

Periodic systems



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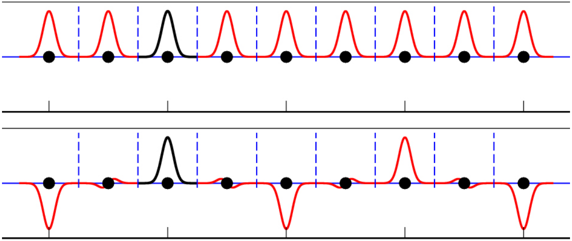

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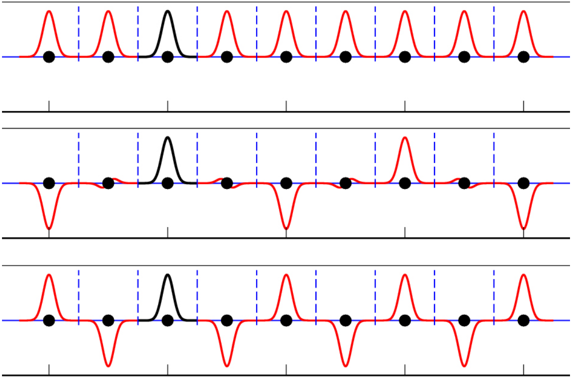

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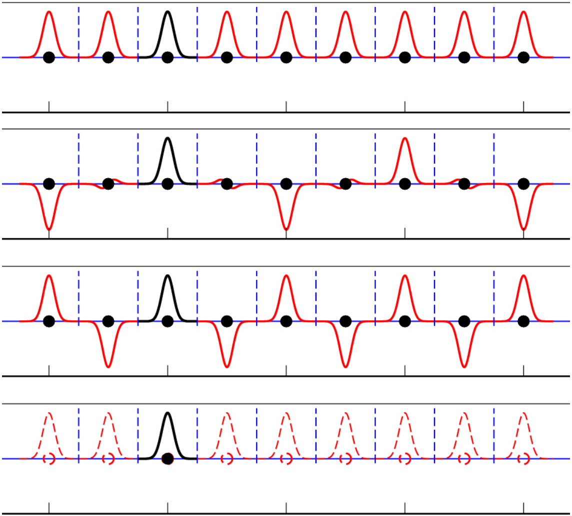

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Bloch's theorem

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

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

$$u_{i\mathbf{k}}(\mathbf{r}+\mathbf{L}) = u_{i\mathbf{k}}(\mathbf{r})$$

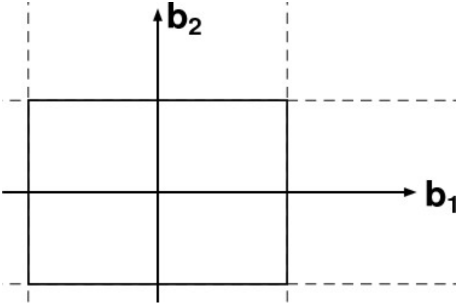
Periodic systems: Reciprocal space

Reciprocal lattice vectors:

$$\begin{aligned}
\mathbf{b}_1 &= 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \\
\mathbf{b}_2 &= 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot \mathbf{a}_3 \times \mathbf{a}_1} \\
\mathbf{b}_3 &= 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot \mathbf{a}_1 \times \mathbf{a}_2}
\end{aligned}$$

Periodic systems: Brillouin zone

- First Brillouin zone: Part of space closer to the origin than to any integer multiple of the reciprocal lattice vectors, $\mathbf{K}' = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$



Integration over reciprocal space

- Thus the summation over infinite number of translations becomes an integral over the first Brillouin zone:

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$$\int_{\mathbf{k}} d\mathbf{k} \approx \sum_{\mathbf{k}} w_{\mathbf{k}}$$

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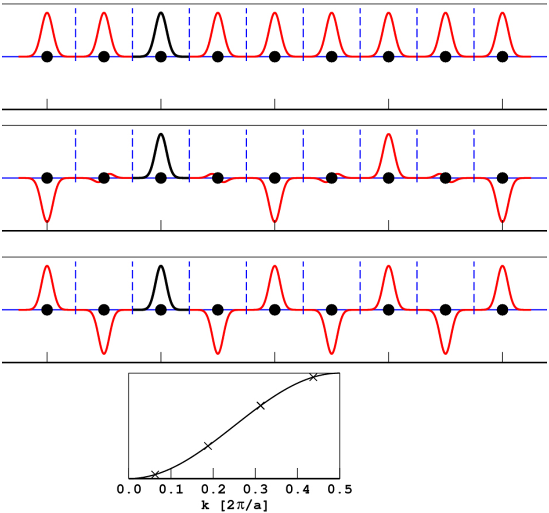
- Thus *eg.*

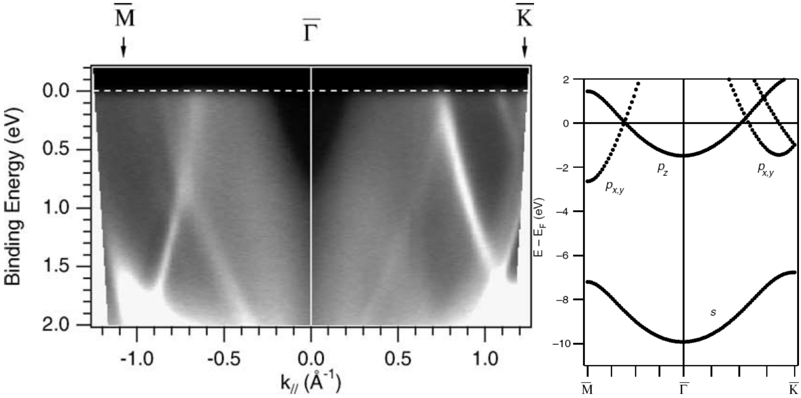
$$n(\mathbf{r}) = \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{i} f_{i\mathbf{k}} \left|\psi_{i\mathbf{k}}(\mathbf{r})\right|^2$$

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

Monkhorst-Pack algorithm

- Approximate the integral with an equidistance grid of k vectors with identical weight:

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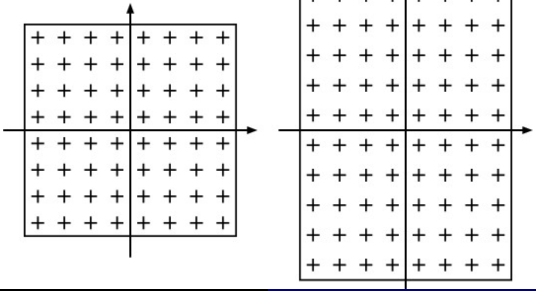
$$n = \frac{2p - q - 1}{2q}\ ,\ p = 1 \dots q$$

$$\mathbf{k}_{ijk} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3$$



Symmetry operations

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

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

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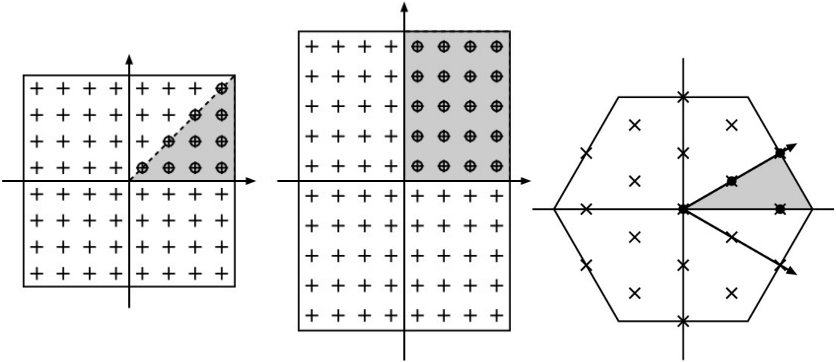
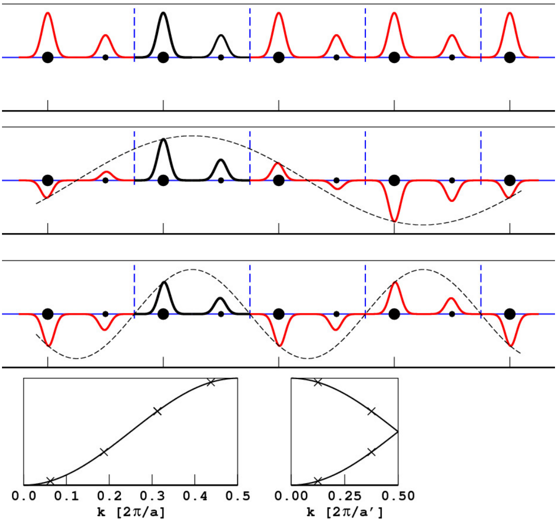
$$\int_{\mathbf{k}} d\mathbf{k} \approx \sum_{\mathbf{k}\in\mathrm{BZ}} w_{\mathbf{k}} = \sum_{\mathbf{k}\in\mathrm{IBZ}} \sum_{S} w'_{S\mathbf{k}}$$

Irreducible Brillouin zone: Examples



Doubling the unit cell



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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:

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$$\int \Phi_i^\star(\mathbf{r})\Phi_j(\mathbf{r})d\mathbf{r} = \delta_{ij}$$

Expansion using a basis set

- For practical purposes it is necessary to expand the Kohn-Sham orbitals using a set of basis functions
- Basis set $\{\varphi_\alpha(\mathbf{r})\}_{\alpha=1}^{M}$
- Usually a linear expansion

$$\boxed{\psi_i(\mathbf{r}) = \sum_{\alpha=1}^{M} c_{\alpha i}\varphi_\alpha(\mathbf{r})}$$

Plane waves

Philosophy

Assemblies of atoms are slight distortions to free electrons

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

$$(\ldots = \cos(\mathbf{G}_\alpha \cdot \mathbf{r}) + i \sin(\mathbf{G}_\alpha \cdot \mathbf{r}))$$

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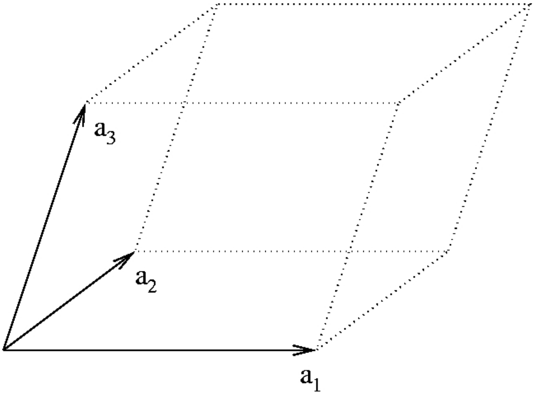
- + no BSSE
- ± naturally periodic
- – many functions needed

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: $\mathbf{L} = i \cdot \mathbf{a}_1 + j \cdot \mathbf{a}_2 + k \cdot \mathbf{a}_3$

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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

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

To be solved: Coefficients $c_{i\mathbf{k}}(\mathbf{G})$

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To be solved: Coefficients $c_{i\mathbf{k}}(\mathbf{G})$

Different routes:

- Direct optimisation of total energy
- Iterative diagonalisation/minimisation

Dependence on position

- Translation:

$$\phi(\mathbf{r}) \longrightarrow \phi(\mathbf{r} - \mathbf{R}_l)$$

$$\begin{aligned} \phi(\mathbf{r} - \mathbf{R}_l) &= \sum_{\mathbf{G}} \phi(\mathbf{G}) e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{R}_l)} \\ &= \sum_{\mathbf{G}} \left(\phi(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}\right) e^{-i\mathbf{G}\cdot\mathbf{R}_l} \end{aligned}$$

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- Derivatives:

$$\frac{\partial \phi(\mathbf{r} - \mathbf{R}_I)}{\partial \mathbf{R}_{I,s}} = -i \sum_{\mathbf{G}} \mathbf{G}_s \left(\phi(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \right) S_I(\mathbf{G})$$

Plane waves: Kinetic energy

- Kinetic energy operator in the plane wave basis:

$$-\frac{1}{2}\nabla^2\varphi_{\mathbf{G}}(\mathbf{r}) = -\frac{1}{2}(iG)^2\frac{1}{\sqrt{\Omega}}e^{i\mathbf{G}\cdot\mathbf{r}} = \frac{1}{2}\ G^2\varphi_{\mathbf{G}}(\mathbf{r})$$

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- Thus the operator is diagonal in the plane wave basis set

$$\boxed{E_{\mathrm{kin}}(\mathbf{G}) = \frac{1}{2}\ G^2}$$

Cutoff: Finite basis set

Choose all basis functions into the basis set that fulfill

$$\frac{1}{2}G^2 \leq E_{\mathrm{cut}}$$

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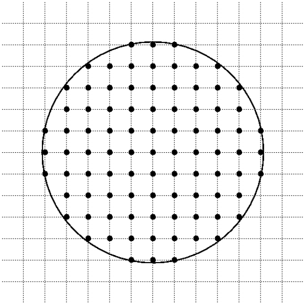

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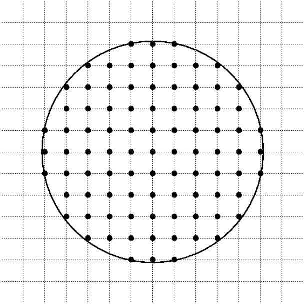

$$N_{\mathrm{PW}} \approx \frac{1}{2\pi^2}\Omega E_{\mathrm{cut}}^{3/2}[a.u.]$$

Basis set size depends on volume of box and cutoff only

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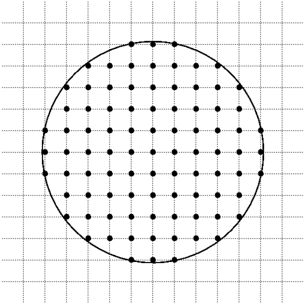

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Plane waves: Fast Fourier Transform

- The information contained in $\psi(\mathbf{G})$ and $\psi(\mathbf{r})$ are equivalent

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- 3D-transform = three subsequent 1D-transforms
- Information can be handled always in the most appropriate space

Plane waves: Integrals

Parseval's theorem

$$\Omega \sum_{\mathbf{G}} A^\star(\mathbf{G}) B(\mathbf{G}) = \frac{\Omega}{N} \sum_{i} A^\star(\mathbf{r}_i) B(\mathbf{r}_i)$$

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Proof.

$$\begin{aligned} I &= \int_\Omega A^\star(\mathbf{r}) B(\mathbf{r}) d\mathbf{r} \\ &= \sum_{\mathbf{G}\mathbf{G}'} A^\star(\mathbf{G}) B(\mathbf{G}) \int \exp[-i\mathbf{G}\cdot\mathbf{r}] \exp[i\mathbf{G}'\cdot\mathbf{r}] d\mathbf{r} \\ &= \sum_{\mathbf{G}\mathbf{G}'} A^\star(\mathbf{G}) B(\mathbf{G})\, \Omega\, \delta_{\mathbf{G}\mathbf{G}'} = \Omega \sum_{\mathbf{G}} A^\star(\mathbf{G}) B(\mathbf{G}) \end{aligned}$$

☐

Plane waves: Electron density

$$n(\mathbf{r}) = \sum_{i\mathbf{k}} w_{\mathbf{k}} f_{i\mathbf{k}} |\psi_{i\mathbf{k}}(\mathbf{r})|^2 = \frac{1}{\Omega} \sum_{i\mathbf{k}} w_{\mathbf{k}} f_{i\mathbf{k}} \sum_{\mathbf{G},\mathbf{G}'} c^{\star}_{i\mathbf{k}}(\mathbf{G}) c_{i\mathbf{k}}(\mathbf{G}') e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}$$

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$$n(\mathbf{r}) = \sum_{\mathbf{G}=-2G_{\text{max}}}^{2G_{\text{max}}} n(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

The electron density can be expanded *exactly* in a plane wave basis with a cut-off four times the basis set cutoff.

$$N_{\mathrm{PW}}(4E_{\mathrm{cut}}) = 8N_{\mathrm{PW}}(E_{\mathrm{cut}})$$

Plane waves: Operators

- The Kohn-Sham equations written in reciprocal space:

$$\left\{-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{G},\mathbf{G}')\right\}\psi_{i\mathbf{k}}(\mathbf{G}) = \varepsilon_i \psi_{i\mathbf{k}}(\mathbf{G})$$

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- *Eg.* Kinetic energy operator

$$\boxed{\mathbf{T}_{\mathbf{G},\mathbf{G}'} = \langle \mathbf{G}| -\frac{1}{2}\nabla^2|\mathbf{G}'\rangle = \frac{1}{2}G^2\delta_{\mathbf{G},\mathbf{G}'}}$$

Kohn–Sham energy

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

E_{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

$$
\begin{aligned}
E_{\mathrm{kin}} &= \sum_{i\mathbf{k}} w_{\mathbf{k}} f_{i\mathbf{k}} \langle \psi_{i\mathbf{k}} | -\frac{1}{2}\nabla^2 | \psi_{i\mathbf{k}} \rangle \\
&= \sum_{i\mathbf{k}} w_{\mathbf{k}} f_{i\mathbf{k}} \sum_{\mathbf{G}\mathbf{G}'} c^*_{i\mathbf{k}}(\mathbf{G}) c_{i\mathbf{k}}(\mathbf{G}') \langle \mathbf{k}+\mathbf{G} | -\frac{1}{2}\nabla^2 | \mathbf{k}+\mathbf{G}' \rangle \\
&= \sum_{i\mathbf{k}} w_{\mathbf{k}} f_{i\mathbf{k}} \sum_{\mathbf{G}\mathbf{G}'} c^*_{i\mathbf{k}}(\mathbf{G}) c_{i\mathbf{k}}(\mathbf{G}')\ \Omega \frac{1}{2} \left| \mathbf{k}+\mathbf{G} \right|^2 \delta_{\mathbf{G},\mathbf{G}'} \\
&= \boxed{\Omega \sum_{i\mathbf{k}} w_{\mathbf{k}} f_{i\mathbf{k}} \sum_{\mathbf{G}} \frac{1}{2} \left| \mathbf{k}+\mathbf{G} \right|^2 \left| c_{i\mathbf{k}}(\mathbf{G}) \right|^2}
\end{aligned}
$$

Periodic Systems

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

Poisson equation

$$\begin{aligned} \nabla^2 V_{\mathrm{H}}(\mathbf{r}) &= -4\pi n_{\mathrm{tot}}(\mathbf{r}) \\ V_{\mathrm{H}}(\mathbf{G}) &= 4\pi \frac{n(\mathbf{G})}{G^2} \end{aligned}$$

- $V_{\mathrm{H}}(\mathbf{G})$ is a local operator with same cutoff as n_{tot}

Electrostatic energy

$$E_{\mathrm{ES}} = \frac{1}{2}\int\!\!\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'d\mathbf{r} + \sum_I \int n(\mathbf{r})\,V^I_{\mathrm{core}}(\mathbf{r})d\mathbf{r} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{r}_J|}$$

Electrostatic energy

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- The isolated terms do not converge; the sum only for neutral systems
- Gaussian charge distributions a'la Ewald summation:

$$n^I_{\mathrm{c}}(\mathbf{r}) = -\frac{Z_I}{\left(\mathrm{R}^{\mathrm{c}}_I\right)^3}\pi^{-3/2}\exp\left[-\left(\frac{\mathbf{r}-\mathbf{R}_I}{\mathrm{R}^{\mathrm{c}}_I}\right)^2\right]$$

- Electrostatic potential due to n^I_{c}:

$$V^I_{\mathrm{core}}(\mathbf{r}) = \int \frac{n^I_{\mathrm{c}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' = -\frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}\mathrm{erf}\left[\frac{|\mathbf{r}-\mathbf{R}_I|}{\mathrm{R}^{\mathrm{c}}_I}\right]$$

Electrostatic energy

Electrostatic energy

$$E_{\mathrm{ES}} = 2\pi\,\Omega \sum_{\mathbf{G}\neq 0} \frac{|n_{\mathrm{tot}}(\mathbf{G})|^2}{G^2} + E_{\mathrm{ovrl}} - E_{\mathrm{self}}$$

$$E_{\mathrm{ovrl}} = {\sum_{I,J}}' \sum_{\mathbf{L}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{r}_J - \mathbf{L}|} \mathrm{erfc}\left[\frac{|\mathbf{R}_I - \mathbf{r}_J - \mathbf{L}|}{\sqrt{\mathrm{R}_I^{c\,2} + \mathrm{R}_J^{c\,2}}}\right]$$

$$E_{\mathrm{self}} = \sum_I \frac{1}{\sqrt{2\pi}} \frac{Z_I^2}{R_I^{\mathrm{c}}}$$

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

Exchange-correlation energy

$$E_{\mathrm{xc}} = \int_{\mathbf{r}} n(\mathbf{r})\varepsilon_{\mathrm{xc}}(\mathbf{r})d\mathbf{r} = \Omega \sum_{\mathbf{G}} \varepsilon_{\mathrm{xc}}(\mathbf{G})n^{\star}(\mathbf{G})$$

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

$$
\begin{array}{ccc}
n(\mathbf{r}) & \xrightarrow{FFT} & n(\mathbf{G}) \\
V_{\mathrm{xc}}[n](\mathbf{r}) & & \\
 & & V_{\mathrm{ES}}(\mathbf{G}) \\
V_{\mathrm{KS}}(\mathbf{r}) = V_{\mathrm{xc}}[n](\mathbf{r}) + V_{\mathrm{ES}}(\mathbf{r}) & \xleftarrow{FFT} & V_{\mathrm{ES}}(\mathbf{G}) \\
\psi_{i\mathbf{k}}(\mathbf{r}) & \xleftarrow{N_i \times FFT} & \psi_{i\mathbf{k}}(\mathbf{G}) \\
V_{\mathrm{KS}}(\mathbf{r})\psi_{i\mathbf{k}}(\mathbf{r}) & \xrightarrow{N_i \times FFT} & \left[V_{\mathrm{KS}}\psi_{i\mathbf{k}}\right](\mathbf{G}) \\
 & & \text{update } \psi_{i\mathbf{k}}(\mathbf{G}) \\
\psi'_{i\mathbf{k}}(\mathbf{r}) & \xleftarrow{N_i \times FFT} & \psi'_{i\mathbf{k}}(\mathbf{G}) \\
n'(\mathbf{r}) = \sum_{i\mathbf{k}} w_{\mathbf{k}} f_{i\mathbf{k}} \left|\psi'_{i\mathbf{k}}(\mathbf{r})\right|^2 & &
\end{array}
$$

Plane waves: Calculation of forces

- With the plane wave basis set one can apply the

Hellmann-Feynman theorem

$$(\mathbf{F}_I =) -\frac{d}{d\mathbf{R}_I}\langle\Psi \mid H_{\mathrm{KS}} \mid \Psi\rangle = -\langle\Psi \mid \frac{\partial}{\partial\mathbf{R}_I}H_{\mathrm{KS}} \mid \Psi\rangle$$

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- 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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- The energies must only be compared with the same E_{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

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The construction consists of two steps of approximations

- Frozen core approximation
- Pseudisation