

Plane Wave Basis Sets

Kohn–Sham Method

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

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

$$n(\mathbf{r}) = \sum_{i=1}^N f_i |\Phi_i(\mathbf{r})|^2$$

Basis Set Methods

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

Linear expansion of Kohn–Sham orbitals

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

Kohn–Sham Method

$$\min_{\mathbf{c}} E_{\text{KS}}[\mathbf{c}]$$

$$\sum_{\alpha\beta} c_{\alpha i}^* c_{\beta j} \int \varphi_{\alpha}^*(\mathbf{r}) \varphi_{\beta}(\mathbf{r}) d\mathbf{r} = \sum_{\alpha\beta} c_{\alpha i}^* c_{\beta j} \mathbf{S}_{\alpha\beta} = \delta_{ij}$$

$$\mathbf{C}^{\dagger} \mathbf{S} \mathbf{C} = \mathbf{1}$$

$$n(\mathbf{r}) = \sum_{i=1}^N f_i \sum_{\alpha\beta} c_{\beta i}^* c_{\alpha i} \varphi_{\beta}^*(\mathbf{r}) \varphi_{\alpha}(\mathbf{r}) = \sum_{\alpha\beta} \mathbf{P}_{\alpha\beta} \varphi_{\alpha\beta}(\mathbf{r})$$

Atomic Orbital Basis Sets

Philosophy : Molecules are assemblies of slightly distorted atoms

$$\varphi_{\alpha}(\mathbf{r}) = \varphi_{\alpha}(r)Y_{lm}(\Theta, \phi)$$

$$\varphi_{\alpha}(r) = \begin{cases} \exp[-\alpha r^2] & \text{Gaussian} \\ \exp[-\alpha r] & \text{Slater} \end{cases}$$

$\varphi_{\alpha}(\mathbf{r}; \mathbf{R}_I)$: basis functions are attached to nuclear positions

Advantages / Disadvantages AO Basis Sets

- + according to chemical insight
- + small basis sets give already good results
- non-orthogonal
- depend on atomic position
- basis set superposition errors (BSSE)

Plane Waves

Philosophy : Assemblies of atoms are slight distortions to free electrons

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

+ orthogonal

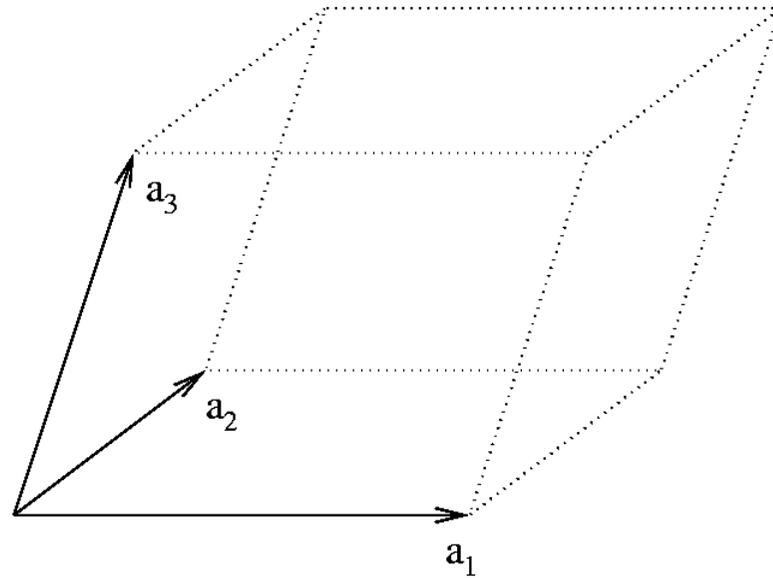
+ independent of atomic positions

+ no BSSE

± naturally periodic

– many functions needed

Computational Box



- Box matrix : $\mathbf{h} = [a_1, a_2, a_3]$
- Box volume : $\Omega = \det \mathbf{h}$

Lattice Vectors

- Direct lattice $\mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$
- Direct lattice vectors : $\mathbf{L} = i \cdot \mathbf{a}_1 + j \cdot \mathbf{a}_2 + k \cdot \mathbf{a}_3$
- 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 : $\mathbf{G} = i \cdot \mathbf{b}_1 + j \cdot \mathbf{b}_2 + k \cdot \mathbf{b}_3$

Properties of Plane Waves

$$\varphi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp[i\mathbf{G} \cdot \mathbf{r}]$$

- Plane waves are **periodic** wrt. box \mathbf{h}
- Plane waves are **orthonormal**

$$\langle \varphi_{\mathbf{G}'} | \varphi_{\mathbf{G}} \rangle = \delta_{\mathbf{G}', \mathbf{G}}$$

- Plane waves are **complete**

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{L}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} \psi(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}]$$

Local Functions

$$\begin{aligned}\phi(\mathbf{r}) &= \phi(r) Y_{lm}(\Theta, \Phi) \\ &= \sum_{\mathbf{G}} \phi(G) \exp[iGr] Y_{lm}(\tilde{\Theta}, \tilde{\Phi})\end{aligned}$$

Bessel transform

$$\phi(G) = 4\pi(-i)^l \int_0^\infty dr r^2 \phi(r) j_l(Gr)$$

j_l : Spherical Bessel functions of the first kind

Position Dependence

Translation

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

$$\begin{aligned}\phi(\mathbf{r} - \mathbf{R}_I) &= \sum_{\mathbf{G}} \phi(\mathbf{G}) \exp[i\mathbf{G} \cdot (\mathbf{r} - \mathbf{R}_I)] \\ &= \sum_{\mathbf{G}} \phi(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}] \exp[-i\mathbf{G} \cdot \mathbf{R}_I]\end{aligned}$$

Structure Factor

$$S_I(\mathbf{G}) = \exp[-i\mathbf{G} \cdot \mathbf{R}_I]$$

Derivatives

$$\frac{\partial \phi(\mathbf{r}; \mathbf{R}_I)}{\partial \mathbf{R}_{I,s}} = -i \sum_{\mathbf{G}} \mathbf{G}_s \phi(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}] S_I(\mathbf{G})$$

Kinetic Energy

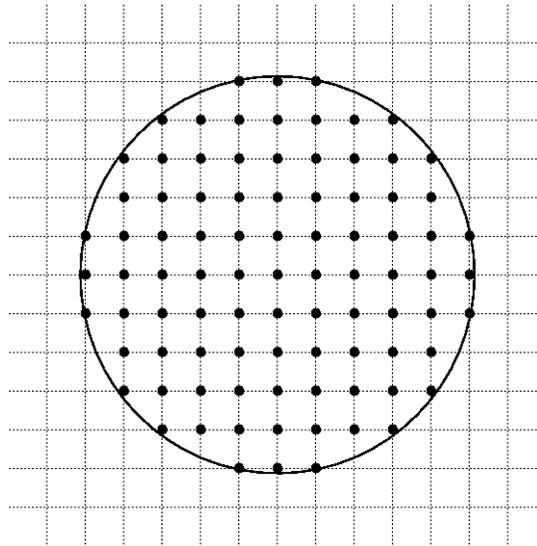
Kinetic energy operator is diagonal in the plane wave basis

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

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

Cutoff: Finite Basis Set

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



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

Basis set size depends on volume of box and cutoff only

Real Space Grid

Sampling Theorem

- Sampling interval $\Delta = \frac{L}{N}$
- Nyquist critical frequency $f_c = \frac{1}{2\Delta}$

For a given plane wave cutoff (frequency) there is a minimum number of equidistant real space grid points needed for the same accuracy.

$$\text{Real space grid: } \mathbf{R}_i = (i - 1)\Delta$$

Fast Fourier Transform

$$\psi(\mathbf{G}) \longleftrightarrow \psi(\mathbf{R})$$

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

Transform from $\psi(\mathbf{G})$ to $\psi(\mathbf{R})$ and back is done using Fourier methods. If the number of grid points can be decomposed into small prime numbers fast Fourier transform techniques can be used.

Fourier transform	N^2 operations
fast Fourier transform	$N \log[N]$ operations

Integrals

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

Parseval's theorem

$$\Omega \sum_{\mathbf{G}} A^*(\mathbf{G})B(\mathbf{G}) = \frac{\Omega}{N} \sum_i A^*(\mathbf{R}_i)B(\mathbf{R}_i)$$

Electron density

$$n(\mathbf{r}) = \sum_i f_i |\Phi_i(\mathbf{r})|^2 = \frac{1}{\Omega} \sum_i f_i \sum_{\mathbf{G}, \mathbf{G}'} c_i^*(\mathbf{G}) c_i(\mathbf{G}') \exp[i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{r}]$$

$$n(\mathbf{r}) = \sum_{\mathbf{G}=-2G_{\max}}^{2G_{\max}} n(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}]$$

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

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

Comparison to AO Basis Set

Plane Waves:

$$\frac{1}{2}G^2 < E_{\text{cut}}$$

$$\frac{1}{2}G'^2 < E_{\text{cut}}$$

$$\frac{1}{2}(G + G')^2 < \left(\sqrt{E_{\text{cut}}} + \sqrt{E_{\text{cut}}}\right)^2 = 4E_{\text{cut}}$$

Atomic orbitals: every product results in a new function

$$\varphi_{\alpha}(\mathbf{r} - \mathbf{A})\varphi_{\beta}(\mathbf{r} - \mathbf{B}) = \varphi_{\gamma}(\mathbf{r} - \mathbf{C})$$

Linear dependence for plane waves vs. quadratic dependence for AO basis sets.

Operators

Matrix representation of operators in Kohn–Sham theory

$$O(\mathbf{G}, \mathbf{G}') = \langle \mathbf{G} | \mathcal{O} | \mathbf{G}' \rangle$$

Kinetic Energy Operator

$$T_{\mathbf{G}, \mathbf{G}'} = \langle \mathbf{G} | -\frac{1}{2} \nabla^2 | \mathbf{G}' \rangle = \frac{1}{2} G^2 \delta_{\mathbf{G}, \mathbf{G}'}$$

Local Operators

$$\begin{aligned}\langle \mathbf{G}' | \mathcal{O}(\mathbf{r}) | \mathbf{G}'' \rangle &= \frac{1}{\Omega} \sum_{\mathbf{G}} \mathcal{O}(\mathbf{G}) \int e^{-i\mathbf{G}' \cdot \mathbf{r}} e^{i\mathbf{G} \cdot \mathbf{r}} e^{i\mathbf{G}'' \cdot \mathbf{r}} d\mathbf{r} \\ &= \frac{1}{\Omega} \sum_{\mathbf{G}} \mathcal{O}(\mathbf{G}) \int e^{i(\mathbf{G} - \mathbf{G}' + \mathbf{G}'') \cdot \mathbf{r}} d\mathbf{r} \\ &= \frac{1}{\Omega} \mathcal{O}(\mathbf{G}' - \mathbf{G}'')\end{aligned}$$

Local operators can be expanded in plane waves with a cutoff four times the basis set cutoff.

Applying Operators

$$B(\mathbf{G}) = \sum_{\mathbf{G}'} \mathbf{O}(\mathbf{G}, \mathbf{G}') A(\mathbf{G}')$$

Local Operators: Convolution

$$B(\mathbf{G}) = \sum_{\mathbf{G}'} \frac{1}{\Omega} \mathbf{O}(\mathbf{G} - \mathbf{G}') A(\mathbf{G}') = (\mathbf{O} * A)(\mathbf{G})$$

Convolution in frequency space transforms to product in real space

$$B(\mathbf{R}_i) = \mathbf{O}(\mathbf{R}_i) A(\mathbf{R}_i)$$

Kohn–Sham Orbitals

- KS–orbitals (for periodic system)

Bloch theorem

$$\Phi_i(\mathbf{r}, \mathbf{k}) = \exp[i\mathbf{k} \cdot \mathbf{r}] u_i(\mathbf{r}, \mathbf{k})$$

$$u_i(\mathbf{r}, \mathbf{k}) = u_i(\mathbf{r} + \mathbf{L}, \mathbf{k})$$

- Γ - point approximation:
 $\mathbf{k} = \mathbf{0}$ only point considered in the Brillouin zone.

- Γ - point KS–orbitals

$$\begin{aligned}\Phi_i(\mathbf{r}) &= u_i(\mathbf{r}) \\ &= \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_i(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}]\end{aligned}$$

Kohn–Sham Energy

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

E_{kin} Kinetic energy

E_{PP} Pseudopotential energy

E_{ES} Electrostatic energy (sum of electron-electron interaction + nuclear core-electron interaction + ion-ion interaction)

E_{xc} Exchange–correlation energy

Kinetic Energy

$$\begin{aligned} E_{\text{kin}} &= \sum_i f_i \langle \Phi_i | -\frac{1}{2} \nabla^2 | \Phi_i \rangle \\ &= \sum_i \sum_{\mathbf{G} \mathbf{G}'} c_i^*(\mathbf{G}) c_i(\mathbf{G}') \langle \mathbf{G} | -\frac{1}{2} \nabla^2 | \mathbf{G}' \rangle \\ &= \sum_i \sum_{\mathbf{G} \mathbf{G}'} c_i^*(\mathbf{G}) c_i(\mathbf{G}') \Omega \frac{1}{2} \mathbf{G}^2 \delta_{\mathbf{G}, \mathbf{G}'} \\ &= \boxed{\frac{\Omega}{2} \sum_i \sum_{\mathbf{G}} \mathbf{G}^2 |c_i(\mathbf{G})|^2} \end{aligned}$$

Electrostatic Energy

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

Gaussian charge distributions

$$n_{\text{C}}^I(\mathbf{r}) = -\frac{Z_I}{(R_I^{\text{C}})^3} \pi^{-3/2} \exp\left[-\left(\frac{\mathbf{r} - \mathbf{R}_I}{R_I^{\text{C}}}\right)^2\right]$$

Electrostatic potential of n_{C}^I

$$V_{\text{core}}^I(\mathbf{r}) = \int d\mathbf{r}' \frac{n_{\text{C}}^I(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = -\frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \text{erf}\left[\frac{|\mathbf{r} - \mathbf{R}_I|}{R_I^{\text{C}}}\right]$$

Electrostatic Energy

$$E_{\text{ES}} = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n_c(\mathbf{r})n_c(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ + \iint d\mathbf{r} d\mathbf{r}' \frac{n_c(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n_c(\mathbf{r})n_c(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

where $n_c(\mathbf{r}) = \sum_I n_c^I(\mathbf{r})$.

The first three terms can be combined to the electrostatic energy of a total charge distribution

$$n_{\text{tot}}(\mathbf{r}) = n(\mathbf{r}) + n_c(\mathbf{r})$$

and the other two terms calculated analytically.

Electrostatic Energy

$$E_{\text{ES}} = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{n_{\text{tot}}(\mathbf{r})n_{\text{tot}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \operatorname{erfc} \left[\frac{|\mathbf{R}_I - \mathbf{R}_J|}{\sqrt{R_I^c{}^2 + R_J^c{}^2}} \right] - \sum_I \frac{1}{\sqrt{2\pi}} \frac{Z_I^2}{R_I^c}$$

- 1. Term: Long-ranged forces
- 2. Term: Short-ranged two-center terms
- 3. Term: One-center term

Periodic Systems

Plane wave expansion of n_{tot}

$$\begin{aligned} n_{\text{tot}}(\mathbf{G}) &= n(\mathbf{G}) + \sum_I n_{\text{C}}^I(\mathbf{G}) S_I(\mathbf{G}) \\ &= n(\mathbf{G}) - \frac{1}{\Omega} \sum_I \frac{Z_I}{\sqrt{4\pi}} \exp\left[-\frac{1}{2} G^2 R_I^{\text{C}2}\right] S_I(\mathbf{G}) \end{aligned}$$

Criteria for parameter R_I^{C} : PW expansion of n_{C}^I has to be converged with density cutoff.

Poisson equation

$$\nabla^2 V_{\text{H}}(\mathbf{r}) = -4\pi n_{\text{tot}}(\mathbf{r})$$

for periodic boundary conditions

$$V_{\text{H}}(\mathbf{G}) = 4\pi \frac{n_{\text{tot}}(\mathbf{G})}{G^2}$$

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

Periodic Systems

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

where

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

and

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

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

Exchange and Correlation Energy

$$E_{xc} = \int d\mathbf{r} \varepsilon_{xc}(\mathbf{r}) n(\mathbf{r}) = \Omega \sum_{\mathbf{G}} \varepsilon_{xc}(\mathbf{G}) n^*(\mathbf{G})$$

$\varepsilon_{xc}(\mathbf{G})$ is not local in \mathbf{G} space. Calculation in real space requires very accurate integration scheme.

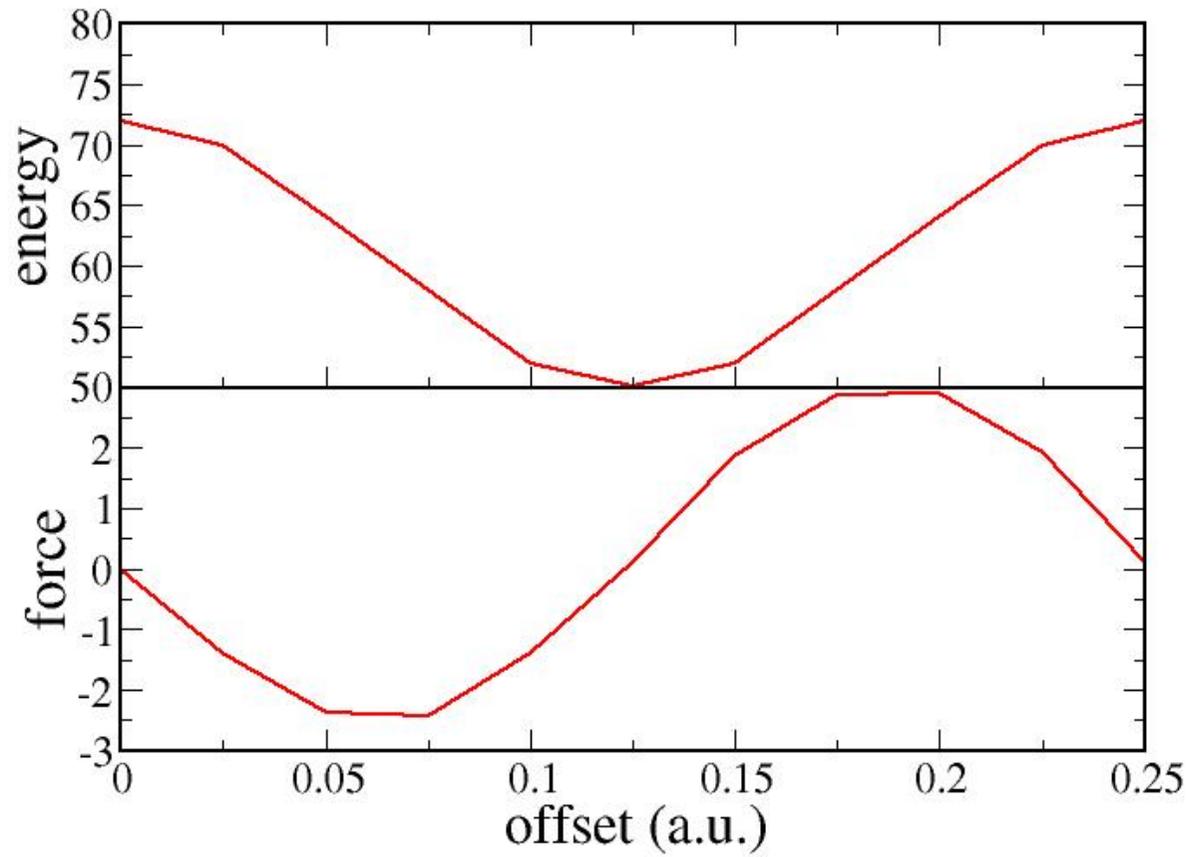
New definition of E_{xc}

$$E_{xc} = \frac{\Omega}{N_x N_y N_z} \sum_{\mathbf{R}} \varepsilon_{xc}(\mathbf{R}) n(\mathbf{R}) = \Omega \sum_{\mathbf{G}} \tilde{\varepsilon}_{xc}(\mathbf{G}) n(\mathbf{G})$$

where $\tilde{\varepsilon}_{xc}(\mathbf{G})$ is the finite Fourier transform of $\varepsilon_{xc}(\mathbf{R})$.

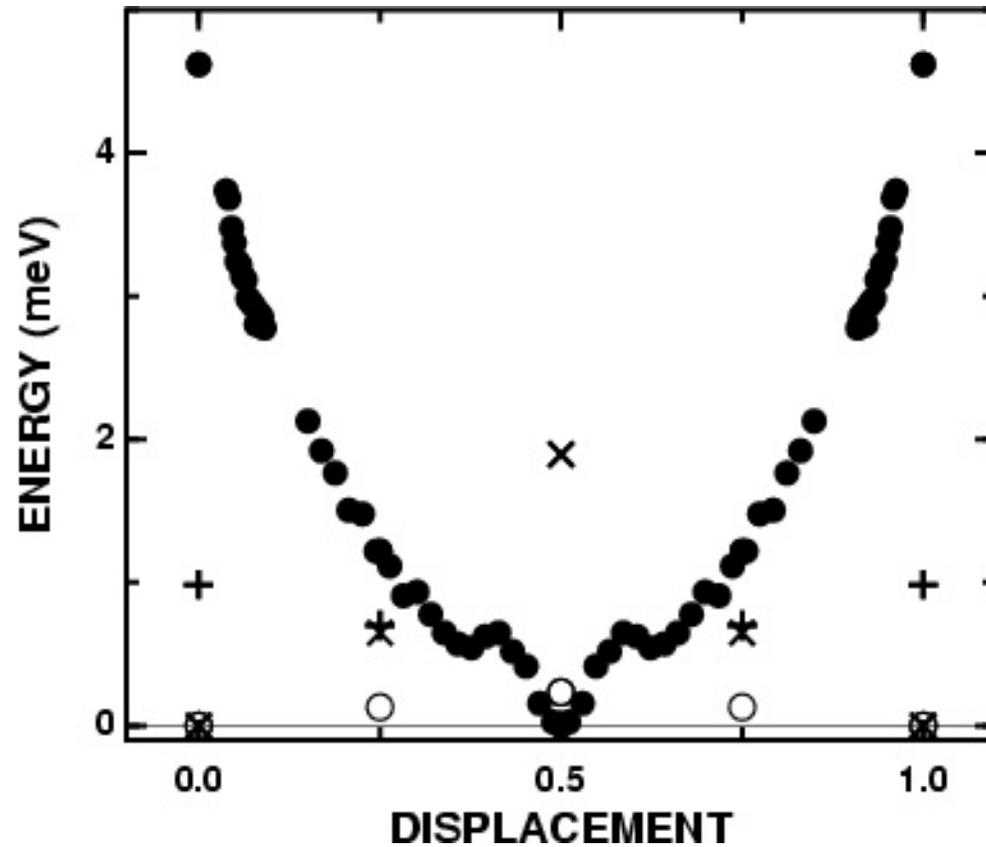
Only translations by a multiple of the grid spacing do not change the total energy. This introduces a small modulation of the energy hyper surface, known as "ripples".

Energy and Force of He Atom



Energy and Force of He Atom

Oxygen atom



PW'91: 40 / 3.2 Ry ●

PW'91: 70 / 4.0 Ry +

PW'91: 50 / 3.85 Ry ×

PBE: 50 / 3.85 ○

Plane waves: Summary

- Plane waves are delocalised, periodic basis functions
- Plenty of them are needed, however the operations are simple
- The quality of basis set adjusted using a *single* parametre, the cut-off energy
- Fast Fourier-transform used to efficiently switch between real and reciprocal space