Plane-Wave Density Functional Theory

A Primer for Computational Chemists

Ivo A.W. Filot | Han-sur-Lesse Winterschool 2026 | November 2026



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Outline

1 Introduction

2 Plane waves and unit cells

3 Potentials

4 Ewald summation

5 Self-consistent field procedure

6 Example calculations

7 Pseudopotentials

1

Introduction

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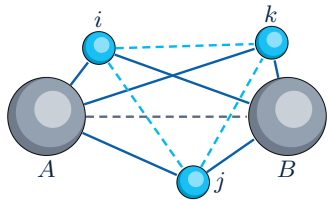
Where it all starts

$$\hat{\mathcal{H}}\,\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = E\,\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

time-independent · non-relativistic · atomic units · spin not written

The molecular Hamiltonian

$$\hat{\mathcal{H}} = \underbrace{-\frac{1}{2}\sum_{i}^{N}\nabla_i^2}_{\text{electron kinetic}} \underbrace{-\sum_{A}^{M}\frac{1}{2M_A}\nabla_A^2}_{\text{nuclear kinetic}} \underbrace{-\sum_{i}^{N}\sum_{A}^{M}\frac{Z_A}{|\vec{r}_i - \vec{R}_A|}}_{\text{e–n attraction}} + \underbrace{\sum_{i<j}^{N}\frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\text{e–e repulsion}} + \underbrace{\sum_{A<B}^{M}\frac{Z_A Z_B}{|\vec{R}_A - \vec{R}_B|}}_{\text{n–n repulsion}}$$



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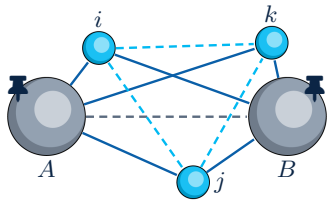


Born–Oppenheimer: nuclei are heavy ($M_{\mathrm{H}} \approx 1836$), so we fix them at $\vec{R}_A$

the n–n repulsion becomes a constant, added to the energy (Section 4)

The electronic Hamiltonian

$$\hat{\mathcal{H}} = \underbrace{-\frac{1}{2}\sum_{i}^{N}\nabla_i^2}_{\text{kinetic energy}} \underbrace{-\sum_{i}^{N}\sum_{A}^{M}\frac{Z_A}{|\vec{r}_i - \vec{R}_A|}}_{\text{attraction to the nuclei}} + \underbrace{\sum_{i<j}^{N}\frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\text{electron–electron repulsion}}$$

The last term couples **every electron to every other**.

The wave function is too big

$$\Psi(\underbrace{\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N}_{3N \text{ variables}})$$

H_2O: 10 electrons, 10 grid points per coordinate

$$10^{3 \cdot 10} = 10^{30} \text{ numbers}$$

The electron density

$$\underbrace{\rho(\vec{r})}_{\text{3 variables}} = N \int |\Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)|^2 \, d\vec{r}_2 \cdots d\vec{r}_N$$

H_2O: 10^3 numbers, for any number of electrons

Is $\rho(\vec{r})$ enough?

The density is enough

> It is proved that there exists a universal functional of the density, $F[n(\vec{r})]$, independent of $v(\vec{r})$, such that the expression $E \equiv \int v(\vec{r}) n(\vec{r})\, d\vec{r} + F[n(\vec{r})]$ has as its minimum value the correct ground-state energy associated with $v(\vec{r})$.
>
> — P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)

$n = \rho, v = \nu_{\text{ext}}$

proof: if $v \neq v' +$ const gave the same ground-state n, use each ground state as trial function for the other, and add

$$E_0 < E_0' + \int (v - v')\, n\, d\vec{r} \qquad E_0' < E_0 + \int (v' - v)\, n\, d\vec{r} \qquad \Longrightarrow \qquad E_0 + E_0' < E_0 + E_0'$$

Finding the ground-state density

$$E_0 \leq \langle \tilde{\Psi} | \hat{\mathcal{H}} | \tilde{\Psi} \rangle \qquad \text{any normalised trial wave function}$$

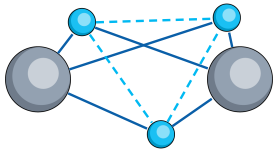
$$E_0 \leq E[\tilde{\rho}] \qquad \text{any trial density with } \int \tilde{\rho}\, d\vec{r} = N$$

Find ρ_0 by **minimising** $E[\rho]$

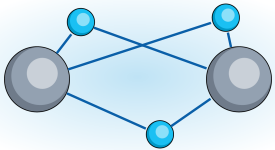
Energy as a functional of the density

$$E[\rho] = \underbrace{T[\rho]}_{\substack{\text{kinetic}\\ \text{unknown}}} + \underbrace{\int \nu_{\text{ext}}(\vec{r})\rho(\vec{r})\, d\vec{r}}_{\substack{\text{nuclear attraction}\\ \text{known}}} + \underbrace{V_{\text{ee}}[\rho]}_{\substack{\text{e–e repulsion}\\ \text{unknown}}}$$

Kohn–Sham: a non-interacting stand-in



same $\rho(\vec{r})$



interacting electrons in ν_{ext}

non-interacting electrons in ν_{eff}

$$\Psi_{\text{s}} = (N!)^{-1/2} \det\left[\psi_1\alpha \;\; \psi_1\beta \;\; \cdots \;\; \psi_{N/2}\beta\right]$$

$$\rho(\vec{r}) = 2\sum_{i=1}^{N/2} |\psi_i(\vec{r})|^2 \qquad T_{\text{s}}[\rho] = 2\sum_{i=1}^{N/2} \left\langle \psi_i \left| -\frac{1}{2}\nabla^2 \right| \psi_i \right\rangle$$

W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)

One term for everything unknown

$$E[\rho] = \underbrace{T_\mathrm{s}[\rho]}_{\text{non-interacting}} + \underbrace{\int \nu_\mathrm{ext}(\vec{r})\rho(\vec{r})\,d\vec{r}}_{\text{nuclear attraction}} + \underbrace{J[\rho]}_{\text{classical repulsion}} + \underbrace{E_\mathrm{xc}[\rho]}_{\text{everything else}}$$

$$J[\rho] = \frac{1}{2}\iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d\vec{r}\,d\vec{r}'$$

$$E_\mathrm{xc}[\rho] = \big(T[\rho] - T_\mathrm{s}[\rho]\big) + \big(V_\mathrm{ee}[\rho] - J[\rho]\big)$$

Key idea

All that is unknown now sits in E_xc, the only term we need to approximate.

From energy to equations

minimise $E[\rho]$ while keeping every ψ_i normalised

$$\mathcal{L} = E[\rho] - 2\sum_{i=1}^{N/2} \epsilon_i \Big(\langle \psi_i | \psi_i \rangle - 1 \Big) \qquad \frac{1}{2}\frac{\delta \mathcal{L}}{\delta \psi_i^*} = 0 \;\Leftrightarrow\; \frac{1}{2}\frac{\delta E}{\delta \psi_i^*} = \epsilon_i \psi_i$$

$$E[\rho] = \quad T_\mathsf{s}[\rho] \quad + \int \nu_\mathsf{ext}\rho \, d\vec{r} \; + \; J[\rho] \; + \; E_\mathsf{xc}[\rho]$$

From energy to equations

minimise $E[\rho]$ while keeping every ψ_i normalised

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$$E[\rho] = \quad T_\mathsf{s}[\rho] \quad + \int \nu_\mathsf{ext}\rho \, d\vec{r} \; + \; J[\rho] \; + \; E_\mathsf{xc}[\rho]$$

$$\frac{1}{2}\frac{\delta E}{\delta \psi_i^*} = \; -\frac{1}{2}\nabla^2\psi_i \; + \quad \nu_\mathsf{ext}\psi_i \quad + \; \nu_\mathsf{H}\psi_i \; + \; \nu_\mathsf{xc}\psi_i \; = \epsilon_i \psi_i$$

From energy to equations

minimise $E[\rho]$ while keeping every ψ_i normalised

$$\mathcal{L} = E[\rho] - 2\sum_{i=1}^{N/2} \epsilon_i \Big(\langle \psi_i | \psi_i \rangle - 1 \Big) \qquad \frac{1}{2}\frac{\delta \mathcal{L}}{\delta \psi_i^*} = 0 \;\Leftrightarrow\; \frac{1}{2}\frac{\delta E}{\delta \psi_i^*} = \epsilon_i \psi_i$$

$$E[\rho] = \quad T_\mathsf{s}[\rho] \quad + \int \nu_\mathsf{ext}\rho \, d\vec{r} \; + \; J[\rho] \; + \; E_\mathsf{xc}[\rho]$$

$$\frac{1}{2}\frac{\delta E}{\delta \psi_i^*} = \; -\frac{1}{2}\nabla^2\psi_i \; + \quad \nu_\mathsf{ext}\psi_i \quad + \nu_\mathsf{H}\psi_i \; + \; \nu_\mathsf{xc}\psi_i \; = \epsilon_i \psi_i$$

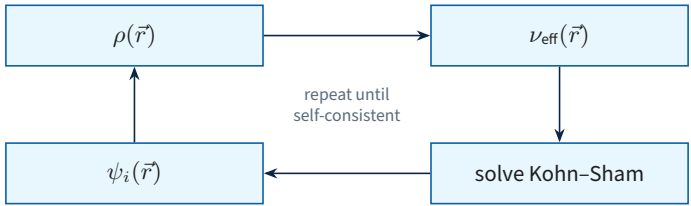
chain rule: for terms that depend on ψ_i only through ρ, $\quad \frac{1}{2}\frac{\delta}{\delta \psi_i^*} = \frac{\delta}{\delta \rho}\,\psi_i$

The Kohn–Sham equations

$$\left(-\frac{1}{2}\nabla^2 + \nu_{\text{eff}}(\vec{r})\right)\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r})$$

$$\nu_{\text{eff}}(\vec{r}) = \underbrace{\nu_{\text{ext}}(\vec{r})}_{\text{nuclei}} + \underbrace{\int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d\vec{r}'}_{\text{Hartree, } \nu_{\text{H}}} + \underbrace{\frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\vec{r})}}_{\text{exchange–correlation, } \nu_{\text{xc}}}$$

A chicken-and-egg problem



The road ahead

2	How do we represent $\psi_i(\vec{r})$?	plane waves
3	How do we build $\nu_{\text{eff}}(\vec{r})$?	potentials
4	How do we add the nuclear repulsion?	Ewald summation
5	How do we reach self-consistency?	self-consistent field

Build it yourself

Python exercises accompany Sections 2–7 of the primer. Step by step, you write a small plane-wave DFT code, **`pwlib`**, until it can run a complete self-consistent field calculation.

Exercise
20–40 min; a skeleton script with built-in checks

Challenge
1.5–3 h; an outline only

every check prints PASS or FAIL; reference solutions are included



github.com/ifilot/pwdft-primer-exercises

2

Plane waves and unit cells

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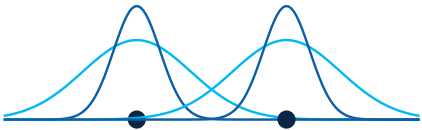
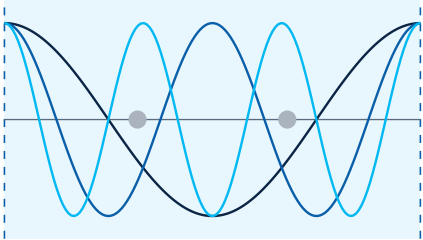
A different starting point

$$e^{-\alpha|\vec{r}-\vec{R}_A|^2}$$



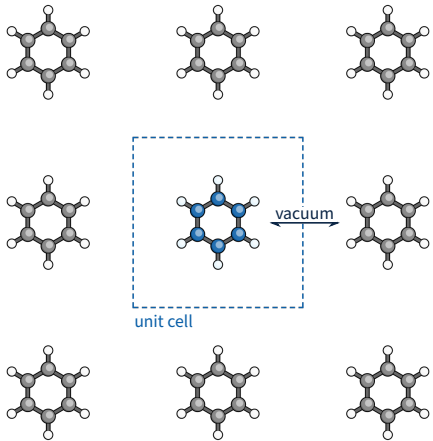
centred on the atoms

$$\frac{1}{\sqrt{\Omega}}\, e^{i\vec{G}\cdot\vec{r}}$$

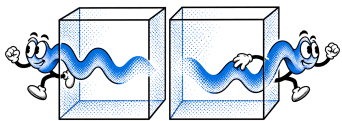


spread over the unit cell

Molecules in a box

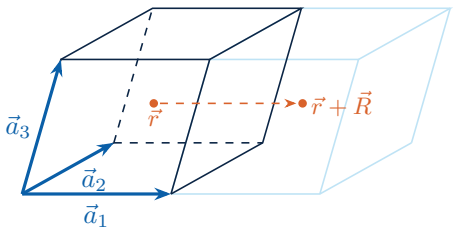


- one molecule per **supercell**
- surrounded by **vacuum**
- repeated in every direction



I went next door. It was still here.

The unit cell



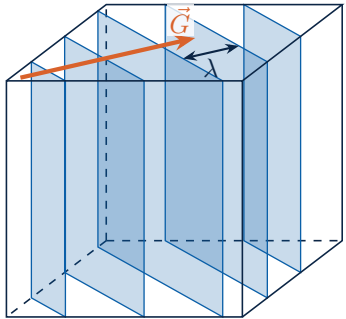
$$\mathbf{M} = \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{a}_3 \end{pmatrix}, \quad \Omega = |\det \mathbf{M}|$$

$$f(\vec{r}+\vec{R}) = f(\vec{r})$$

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

n_1, n_2, n_3 integers

A plane wave



$$\phi(\vec{G},\vec{r}) = \frac{1}{\sqrt{\Omega}} \exp\left(i\vec{G}\cdot\vec{r}\right)$$

constant on planes perpendicular to $\vec{G}$

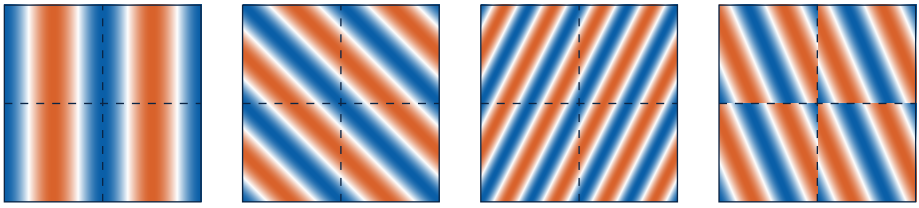
$$\lambda = \frac{2\pi}{|\vec{G}|}$$



A change of basis? I'm on board.

Only waves that fit the cell

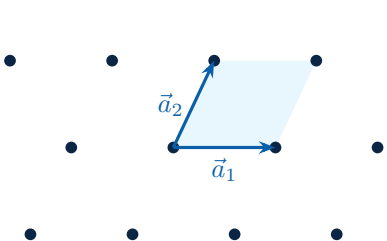
each wave drawn over 2×2 unit cells



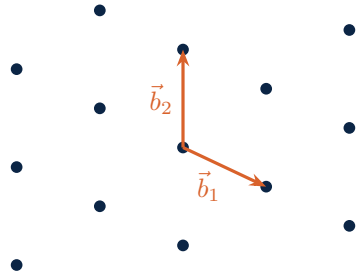
✔ $\vec{G} = (1, 0)$ ✔ $\vec{G} = (1, 1)$ ✔ $\vec{G} = (2, -1)$ ✘ $\vec{G} = (1.4,\ 0.6)$

$e^{i\vec{G}\cdot\vec{R}} = 1$ for every $\vec{R} \quad \Longleftrightarrow \quad \vec{G} = j_1\vec{b}_1 + j_2\vec{b}_2 + j_3\vec{b}_3, \quad j_k \in \mathbb{Z}$

The reciprocal lattice



real lattice



reciprocal lattice (units of 2π)

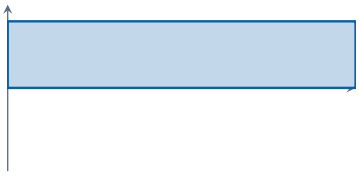
$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\Omega} \qquad \vec{a}_i \cdot \vec{b}_j = 2\pi\, \delta_{ij} \qquad \text{cubic: } \vec{b}_k = \frac{2\pi}{a}\, \vec{e}_k$$

$\vec{b}_2$ and $\vec{b}_3$ by cyclic permutation; equivalently $\mathbf{B} = 2\pi\,(\mathbf{M}^{\intercal})^{-1}$

Plane waves are orthonormal

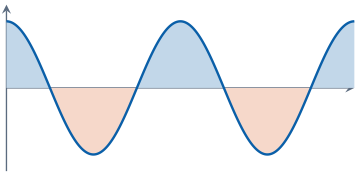
$$\langle \phi(\vec{G}', \vec{r}) | \phi(\vec{G}, \vec{r}) \rangle = \frac{1}{\Omega} \int_{\Omega} e^{i(\vec{G}-\vec{G}')\cdot\vec{r}} \, d\vec{r} = \delta_{\vec{G},\vec{G}'}$$

$\vec{G}' = \vec{G}$



area Ω, so the overlap is 1

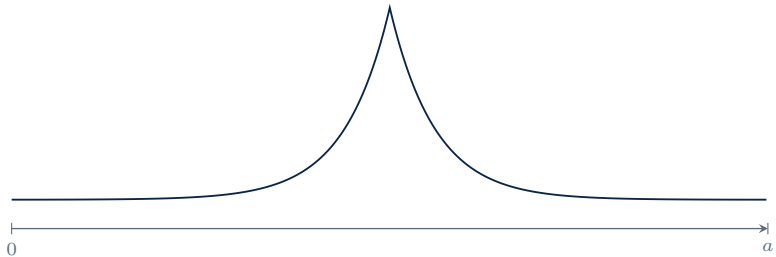
$\vec{G}' \neq \vec{G}$



whole oscillations: areas cancel

Building a function from plane waves

$$u(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{u}(\vec{G})\, e^{i\vec{G}\cdot\vec{r}} \qquad \tilde{u}(\vec{G}) = \langle \phi(\vec{G}, \vec{r}) | u(\vec{r}) \rangle$$



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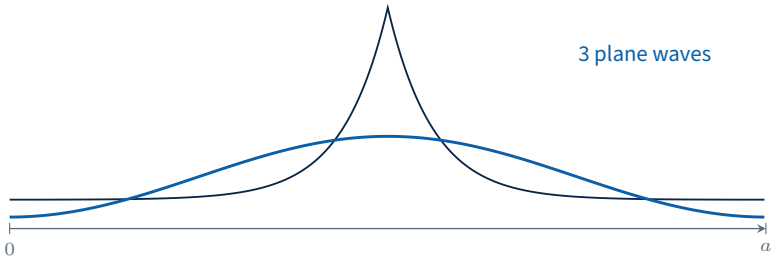

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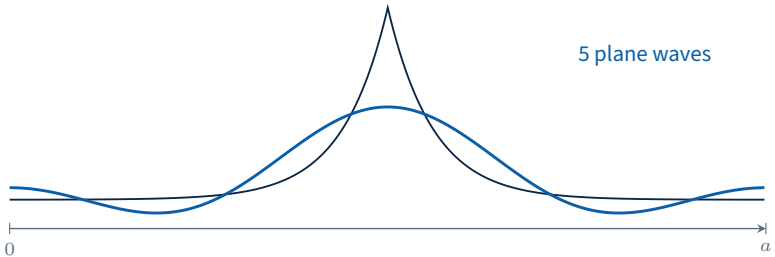

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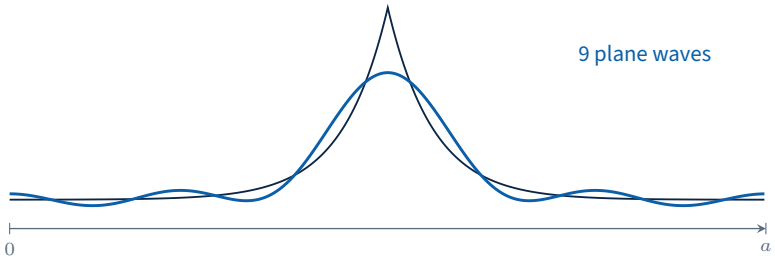

Building a function from plane waves

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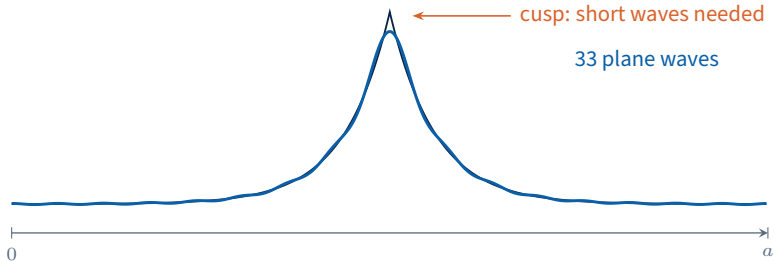
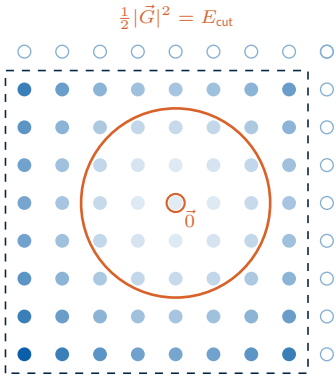


Kinetic energy and the cut-off



FFT grid (this primer)

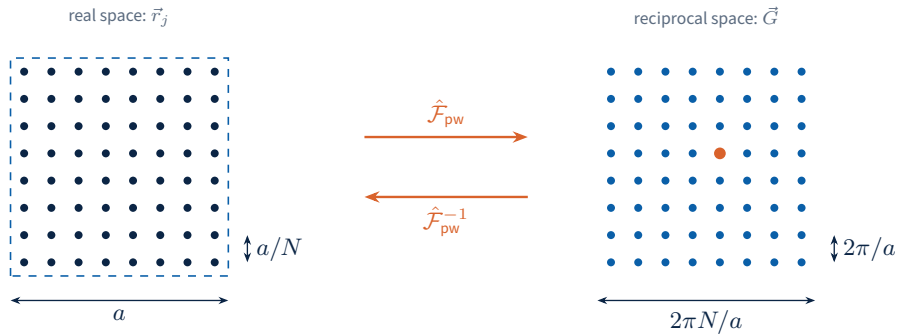
$$E_k = \left\langle \phi(\vec{G},\vec{r}) \left| -\frac{1}{2}\nabla^2 \right| \phi(\vec{G},\vec{r}) \right\rangle = \frac{1}{2}|\vec{G}|^2$$

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



Sorry, your kinetic energy is above the dress code.

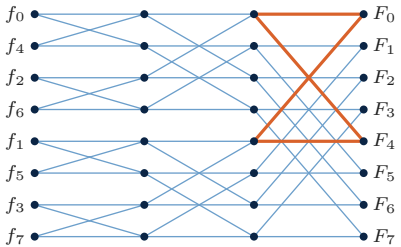
Two grids, one function



$$\vec{G} = \sum_{k=1}^{3} \left(j_k - \frac{N_k}{2} \right) \vec{b}_k, \quad 0 \leq j_k < N_k$$

$N_1 N_2 N_3$ points $\leftrightarrow$ $N_1 N_2 N_3$ plane waves

Why the FFT is fast



$$F_k = F_k^{\text{even}} + \omega_N^k F_k^{\text{odd}}$$
$$F_{k+N/2} = F_k^{\text{even}} - \omega_N^k F_k^{\text{odd}}$$

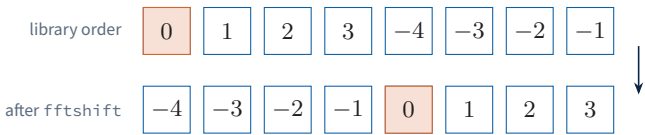
F^{even}, F^{odd}: transforms of length $N/2$; $\omega_N = e^{-2\pi i/N}$
one multiplication, two outputs

	operations	64^3 grid
direct	N^2	7×10^{10}
FFT	$\frac{N}{2}\log_2 N$	2×10^6

What the library computes

$$\underbrace{f(\vec{r}_j) = \frac{1}{N_1 N_2 N_3} \sum_{\vec{G}} \tilde{f}(\vec{G})\, e^{i\vec{G}\cdot\vec{r}_j}}_{\text{library}} \qquad \underbrace{u(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{u}(\vec{G})\, e^{i\vec{G}\cdot\vec{r}}}_{\text{plane-wave basis}}$$

$$\tilde{u}(\vec{G}) = C_t\, \hat{\mathcal{F}}\big[u(\vec{r})\big] = \hat{\mathcal{F}}_{\mathsf{pw}}\big[u(\vec{r})\big], \qquad C_t = \frac{\sqrt{\Omega}}{N_1 N_2 N_3}$$



Kinetic energy is diagonal

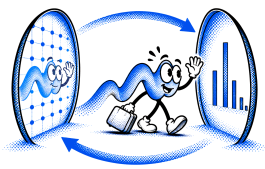
$$-\frac{1}{2}\nabla^2\phi(\vec{G},\vec{r}) = \frac{1}{2}|\vec{G}|^2\,\phi(\vec{G},\vec{r})$$

$$E_{\text{kin}} = \left\langle \psi \left| -\frac{1}{2}\nabla^2 \right| \psi \right\rangle = \frac{1}{2}\sum_{\vec{G}'}\sum_{\vec{G}} \tilde{\psi}^*(\vec{G}')\tilde{\psi}(\vec{G})\,|\vec{G}|^2 \underbrace{\langle\phi(\vec{G}',\vec{r})|\phi(\vec{G},\vec{r})\rangle}_{\delta_{\vec{G},\vec{G}'}}$$

$$= \frac{1}{2}\sum_{\vec{G}} |\tilde{\psi}(\vec{G})|^2\,|\vec{G}|^2$$

Choose the right space

	real space	reciprocal space
electron density	$\rho = 2\sum_i \lvert\psi_i\rvert^2$ ✔	convolution
kinetic energy	derivatives	$\frac{1}{2}\lvert\vec{G}\rvert^2\,\tilde{\psi}(\vec{G})$ ✔
Hartree potential	convolution	$4\pi\,\tilde{\rho}(\vec{G})/\lvert\vec{G}\rvert^2, \vec{G} \neq \vec{0}$ ✔
exchange–correlation (LDA)	$\nu_{\text{xc}}\big(\rho(\vec{r})\big)$ ✔	—



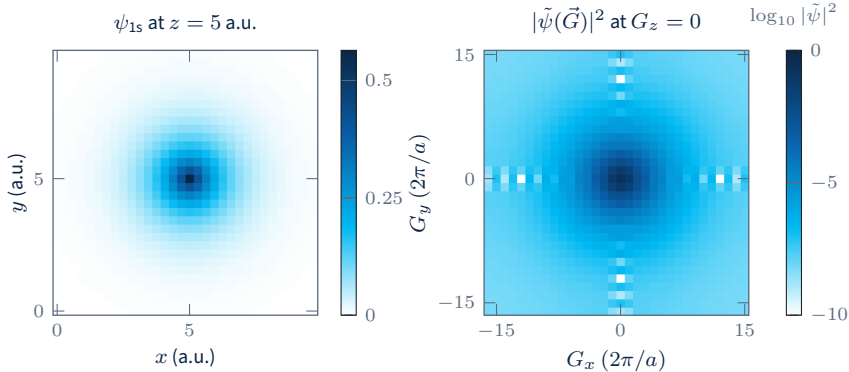
Reciprocal space: lovely place to work, easy trip home.

convolution in one space = product in the other · real $f(\vec{r})$: $\tilde{f}(-\vec{G}) = \tilde{f}(\vec{G})^*$

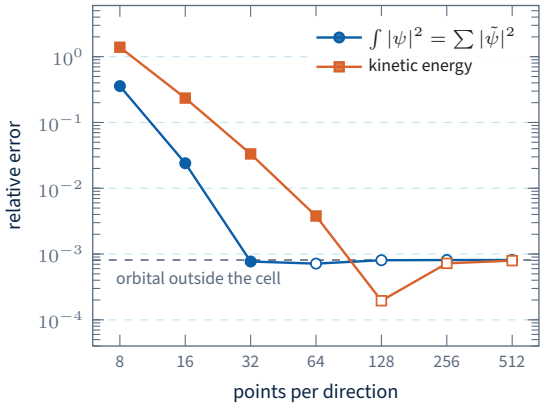
Example: the 1s orbital of hydrogen

$$\psi_{1s}(\vec{r}) = \frac{1}{\sqrt{\pi}}\, e^{-|\vec{r}-\vec{R}|}$$

cell edge 10 a.u., $N = 32$



Convergence



Key idea

The number of sampling points per direction fixes the longest $\vec{G}$-vector, and thereby the cut-off energy. A single parameter controls both the accuracy and the cost.

filled: above the exact value; open: below

3

Potentials

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Three potentials

$$\left(-\tfrac{1}{2}\nabla^2 + \nu_{\text{eff}}(\vec{r})\right)\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r})$$

$$\nu_{\text{eff}}(\vec{r}) = \underbrace{\nu_{\text{ext}}(\vec{r})}_{\text{nuclei}} + \underbrace{\nu_{\text{H}}(\vec{r})}_{\text{classical e–e repulsion}} + \underbrace{\nu_{\text{xc}}(\vec{r})}_{\text{exchange–correlation}}$$

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reciprocal space — reciprocal space — real space

depends on $\vec{R}_j$ — depend on $\rho(\vec{r})$

Poisson’s equation in reciprocal space

$$\nabla^2 V(\vec{r}) = -4\pi\rho(\vec{r})$$

atomic units · ν_{H}: ρ is the electron density · ν_{ext}: the sign flips (attraction)

Poisson's equation in reciprocal space

$$\nabla^2 V(\vec{r}) = -4\pi\rho(\vec{r})$$

$$\rho(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{\rho}(\vec{G})\, e^{i\vec{G}\cdot\vec{r}} \qquad V(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{V}(\vec{G})\, e^{i\vec{G}\cdot\vec{r}} \qquad \nabla^2 e^{i\vec{G}\cdot\vec{r}} = -|\vec{G}|^2 e^{i\vec{G}\cdot\vec{r}}$$

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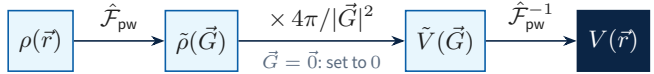
$$|\vec{G}|^2\, \tilde{V}(\vec{G}) = 4\pi\tilde{\rho}(\vec{G}) \qquad \Longrightarrow \qquad \tilde{V}(\vec{G}) = \frac{4\pi}{|\vec{G}|^2}\, \tilde{\rho}(\vec{G})$$

a differential equation becomes a multiplication, one $\vec{G}$ at a time

atomic units · ν_{H}: ρ is the electron density · ν_{ext}: the sign flips (attraction)

Electrostatics in three steps



$$V(\vec{r}) = \hat{\mathcal{F}}_{\text{pw}}^{-1}\left[\frac{4\pi}{|\vec{G}|^2}\,\hat{\mathcal{F}}_{\text{pw}}\left[\rho(\vec{r})\right]\right]_{\vec{G}\neq\vec{0}}$$

one forward and one inverse transform: their normalisation drops out

The troublesome $\vec{G} = \vec{0}$ term

$$\frac{4\pi}{|\vec{G}|^2} \xrightarrow{\vec{G}\to\vec{0}} \infty \qquad \tilde{\rho}(\vec{0}) = \frac{1}{\sqrt{\Omega}} \int_\Omega \rho(\vec{r})\, d\vec{r}$$

total charge in the cell

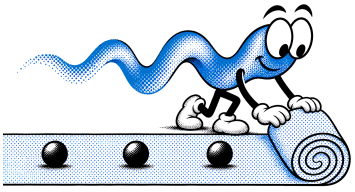
The troublesome $\vec{G} = \vec{0}$ term

$$\frac{4\pi}{|\vec{G}|^2} \xrightarrow{\vec{G}\to\vec{0}} \infty \qquad \tilde{\rho}(\vec{0}) = \frac{1}{\sqrt{\Omega}} \int_\Omega \rho(\vec{r})\, d\vec{r}$$

total charge in the cell

Setting $\tilde{V}(\vec{0}) = 0$:

- adds a **uniform background** that makes every cell neutral
- fixes the average of V over the cell to 0



Wall-to-wall neutrality, fitted free of charge.

Nuclei are point charges

$$\rho_{\text{nuclei}}(\vec{r}) = \sum_j Z_j \, \delta(\vec{r} - \vec{R}_j)$$

a delta function cannot be sampled on a grid … but its coefficients are easy

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$$\langle \phi(\vec{G}, \vec{r}) | Z_j \, \delta(\vec{r} - \vec{R}_j) \rangle = \frac{Z_j}{\sqrt{\Omega}} \, e^{-i\vec{G}\cdot\vec{R}_j}$$

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$$\nu_{\text{ext}}(\vec{r}) = -\frac{4\pi}{\sqrt{\Omega}} \, \hat{\mathcal{F}}_{\text{pw}}^{-1} \left[\frac{1}{|\vec{G}|^2} \sum_j Z_j \underbrace{e^{-i\vec{G}\cdot\vec{R}_j}}_{\text{structure factor}} \right]_{\vec{G} \neq \vec{0}}$$

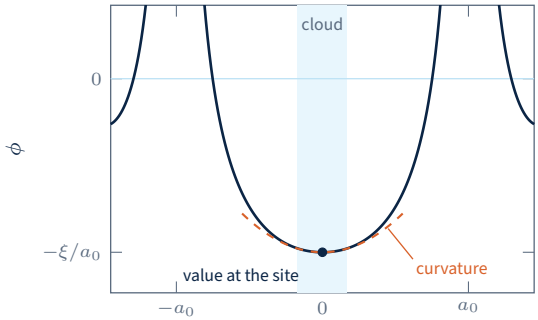
A periodic array of protons



$$E_{\text{pot}}(a_0) \approx \underbrace{E_{\text{pot}}^{\text{iso}}}_{\text{isolated atom: } -1\ \text{Ht}} + \underbrace{\frac{\xi}{a_0}}_{\text{Madelung, } \xi = 2.837} - \underbrace{\frac{2\pi \langle r^2 \rangle}{3a_0^3}}_{\text{spread of the electron}}$$

a_0: edge of the cubic cell · $\langle r^2 \rangle = 3$ a.u.^{2} for the 1s orbital · rock salt: $\xi = 1.748$ in the Born–Landé equation

Where the corrections come from



position along a line through the protons

ϕ: all charges except the central proton

value at the site $\rightarrow +\dfrac{\xi}{a_0}$

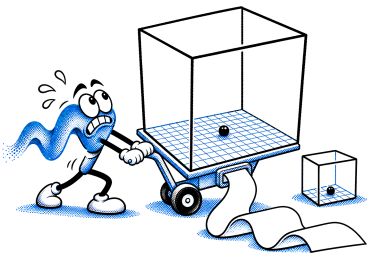
curvature $\rightarrow -\dfrac{2\pi \langle r^2 \rangle}{3a_0^3}$

the background fills the cloud, so ϕ rises as r^2

A bigger box helps only slowly

a_0 (a.u.)	ξ/a_0 (Ht)	plane waves
10	0.28	$\times 1$
20	0.14	$\times 8$
40	0.07	$\times 64$

A single electrostatic term never equals its value for the isolated molecule.



Double the elbow room, eight times the bill.

The Hartree potential

$$\nu_{\mathrm{H}}(\vec{r}) = \hat{\mathcal{F}}_{\mathrm{pw}}^{-1}\left[\frac{4\pi}{|\vec{G}|^2}\,\hat{\mathcal{F}}_{\mathrm{pw}}\left[\rho(\vec{r})\right]\right]_{\vec{G}\neq\vec{0}} \qquad g(\vec{r}) = \left(\frac{2}{\pi}\right)^{3/4} e^{-|\vec{r}|^2}$$

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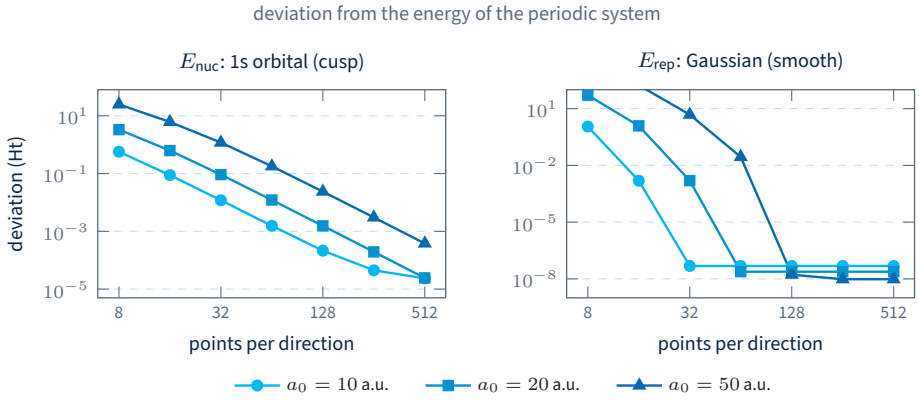
$$E_{\mathsf{rep}}(a_0) \approx \underbrace{E_{\mathsf{rep}}^{\mathsf{iso}}}_{2/\sqrt{\pi}} - \underbrace{\frac{\xi}{a_0}}_{\text{same charges: sign flips}} + \underbrace{\frac{4\pi\,\langle r^2\rangle}{3a_0^3}}_{\text{source spread out too: twice}}$$

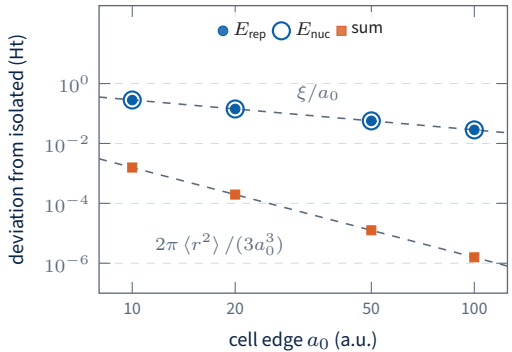
periodic array of electron clouds in a uniform *positive* background · $\langle r^2\rangle = 3/4$ a.u.^{2}

Testing the implementation



what matters is the spacing a_0/N: fine enough to resolve the cusp

Attraction and repulsion cancel



$$\pm\frac{\xi}{a_0} \text{ cancel in } E_{\text{nuc}} + E_{\text{rep}}$$

Key idea

Each electrostatic term carries a large finite-size error, but for a neutral system the errors cancel.

what remains cancels too, once the n–n repulsion is added (Section 4)

Local density approximation

$$E_{\text{xc}}^{\text{LDA}}[\rho] = \int \rho(\vec{r})\, \underbrace{\epsilon_{\text{xc}}\big(\rho(\vec{r})\big)}_{\text{homogeneous electron gas}}\, d\vec{r}$$

exchange: exact

$$E_x = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(\vec{r})\, d\vec{r}$$

correlation: fitted

$$\epsilon_c(r_s), \qquad r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}$$

fits (VWN) to quantum Monte Carlo data

D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980) S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. **58**, 1200 (1980)

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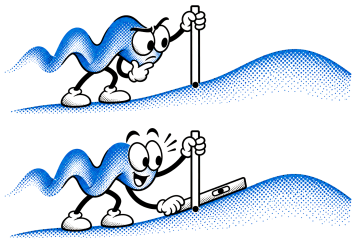
fits (VWN) to quantum Monte Carlo data

$$\nu_{\text{xc}}(\vec{r}) = \epsilon_{\text{xc}} - \frac{r_s}{3}\frac{d\epsilon_{\text{xc}}}{dr_s}$$ point by point, in real space

D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980) S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. **58**, 1200 (1980)

Generalised gradient approximation

$$E_{\text{xc}}^{\text{GGA}}[\rho] = \int \rho\, \epsilon_{\text{xc}}\big(\rho, |\nabla\rho|\big)\, d\vec{r}$$



LDA asks how high you are. GGA also asks how steep.

J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996)

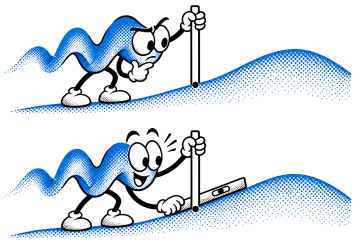
Generalised gradient approximation

$$E_{\text{xc}}^{\text{GGA}}[\rho] = \int \rho\, \epsilon_{\text{xc}}\big(\rho, |\nabla\rho|\big)\, d\vec{r}$$

PBE exchange

$$E_x^{\text{PBE}} = \int \rho\, \epsilon_x(\rho)\, F_x(s)\, d\vec{r} \qquad s = \frac{|\nabla\rho|}{2k_F\rho}$$

$s = 0$: $F_x = 1$ (LDA) · $F_x \leq 1.804$



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Gradients from FFTs

$$\nabla e^{i\vec{G}\cdot\vec{r}} = i\vec{G}\, e^{i\vec{G}\cdot\vec{r}} \qquad \Longrightarrow \qquad \nabla\rho(\vec{r}) = \hat{\mathcal{F}}_{\text{pw}}^{-1}\left[i\vec{G}\,\tilde{\rho}(\vec{G})\right]$$

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$$\nu_{\mathsf{xc}}(\vec{r}) = \frac{\partial f}{\partial \rho} - \underbrace{\nabla\cdot\left(\frac{\partial f}{\partial \nabla\rho}\right)}_{\hat{\mathcal{F}}_{\mathsf{pw}}^{-1}\left[i\vec{G}\cdot\hat{\mathcal{F}}_{\mathsf{pw}}[\,\cdot\,]\right]}, \qquad f = \rho\,\epsilon_{\mathsf{xc}}(\rho, |\nabla\rho|)$$

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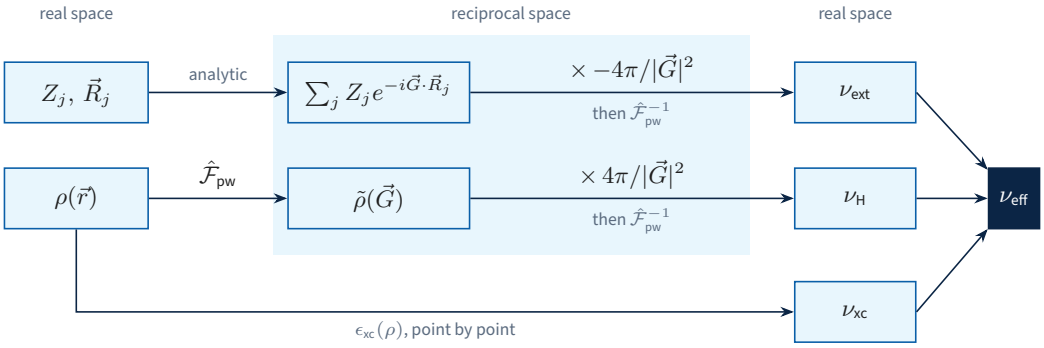
a few extra FFTs per iteration

in the vacuum $\rho \to 0$ and s diverges: gradient terms only above a density threshold

Building ν_{eff}



4

Ewald summation



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The nuclei repel each other

$$E_{\text{nuc-nuc}} = \frac{1}{2} \underbrace{\sum_{\vec{n}}}_{\text{all images}} \sum_{i,j}{}' \frac{q_i q_j}{\left|\vec{R}_{ij} + \vec{n}\right|}$$

$\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$ $\cdot$ $'$: omit $i = j$ for $\vec{n} = \vec{0}$

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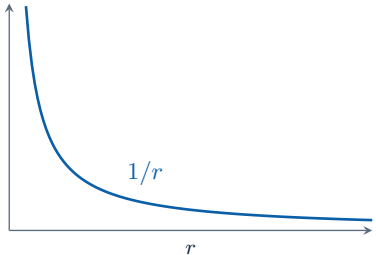
$\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$ $\quad\cdot\quad$ $'$: omit $i = j$ for $\vec{n} = \vec{0}$

images at distance r: $\propto r^2$ each contributes $\propto 1/r$

converges, if at all, extremely slowly

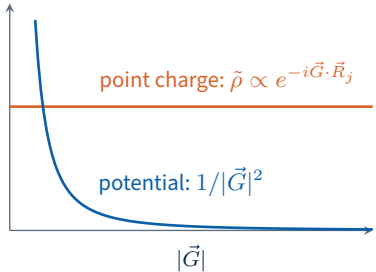
Slow in both spaces

real space



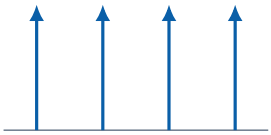
long tail

reciprocal space



no decay: the charge is infinitely sharp

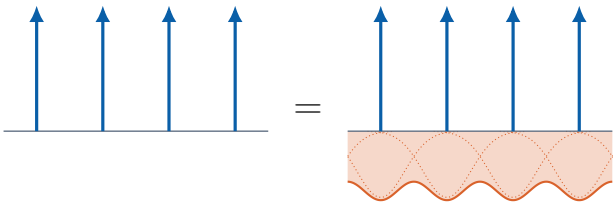
Ewald's trick



point charges

P. P. Ewald, Ann. Phys. **369**, 253 (1921)

Ewald's trick



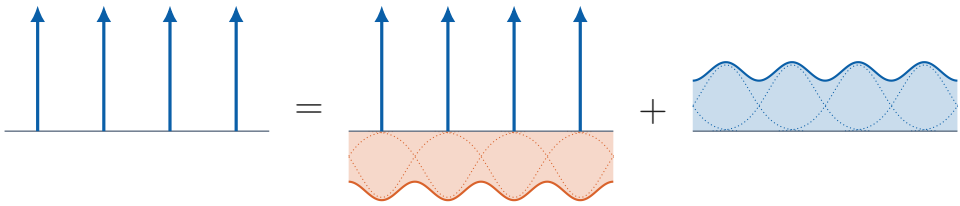
point charges

screened

short range: real space

P. P. Ewald, Ann. Phys. **369**, 253 (1921)

Ewald's trick



P. P. Ewald, Ann. Phys. **369**, 253 (1921)

Four terms

$$E_{\text{Ewald}} = \underbrace{E_{\text{sr}}}_{\text{real space}} + \underbrace{E_{\text{lr}}}_{\text{reciprocal space}} - \underbrace{E_{\text{s}}}_{\text{self}} - \underbrace{E_{\text{en}}}_{\text{neutrality}}$$

E_{sr}	screened charges, nearby images
E_{lr}	all compensating Gaussians, own included
E_{s}	each nucleus with its own Gaussian
E_{en}	the nuclei alone are not neutral



A little screening makes the long-distance relationship manageable.

Long range: Gaussians in reciprocal space

$$\rho_c(\vec{r}) = \sum_{\vec{n}} \sum_j q_j \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha|\vec{r}-\vec{R}_j-\vec{n}|^2}$$

Long range: Gaussians in reciprocal space

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$$E_{\text{lr}} = \frac{2\pi}{\Omega} \sum_{\vec{G}\neq\vec{0}} \sum_{i,j} \frac{q_i q_j}{|\vec{G}|^2} \cos\left(\vec{G}\cdot\vec{R}_{ij}\right) e^{-|\vec{G}|^2/4\alpha}$$

α: width of the Gaussians · $\vec{G}$ and $-\vec{G}$ pair up, the imaginary parts cancel

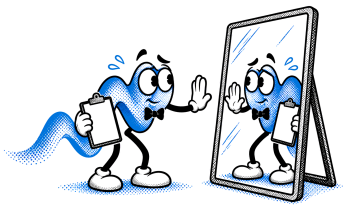
Self-interaction

$$\nu_{\mathsf{s}}(r) = \frac{q_i}{r}\,\mathrm{erf}\left(\sqrt{\alpha}\,r\right)$$

$$\nu_{\mathsf{s}}(0) = 2q_i\sqrt{\frac{\alpha}{\pi}}$$

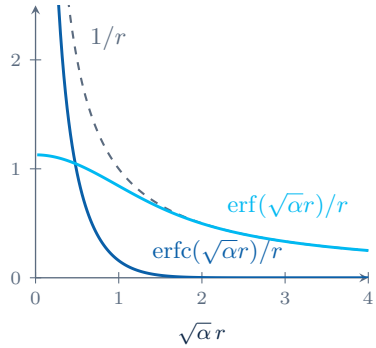
$$E_{\mathsf{s}} = \frac{1}{2}\sum_i q_i\,\nu_{\mathsf{s}}(0) = \sqrt{\frac{\alpha}{\pi}}\sum_i q_i^2$$

included in E_{lr} on purpose: one periodic potential for all nuclei



Please remove yourself from your own guest list.

Short range: screened charges



$1/r$ = screened + Gaussian

$$\nu_{\text{sr}} = \sum_{\vec{n}} \sum_{j} \frac{q_j}{r_{j\vec{n}}} \operatorname{erfc}\left(\sqrt{\alpha}\, r_{j\vec{n}}\right)$$

$$E_{\text{sr}} = \frac{1}{2} \sum_{\vec{n}} \sum_{i,j}{}' \frac{q_i q_j}{|\vec{R}_{ij} + \vec{n}|} \operatorname{erfc}\left(\sqrt{\alpha}\, |\vec{R}_{ij} + \vec{n}|\right)$$

only a few neighbouring cells needed

The nuclei alone are not neutral

$$\tilde{\rho}(\vec{0}) = \frac{1}{\sqrt{\Omega}} \sum_j q_j \neq 0 \qquad \Longrightarrow \qquad \text{background } \rho_{\text{bg}} = -\frac{1}{\Omega} \sum_j q_j$$

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$$\frac{4\pi}{|\vec{G}|^2} e^{-|\vec{G}|^2/4\alpha} = \underbrace{\frac{4\pi}{|\vec{G}|^2}}_{\substack{\text{removed by} \\ \text{the background}}} - \underbrace{\frac{\pi}{\alpha}}_{\substack{\text{artefact} \\ \text{of the split}}} + \mathcal{O}\big(|\vec{G}|^2\big)$$

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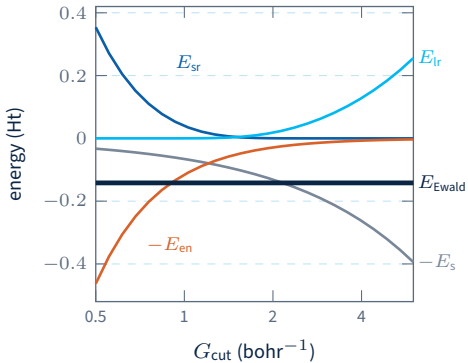
$$E_{\text{en}} = \frac{\pi}{2\alpha\Omega} \Big(\sum_i q_i \Big)^2 \qquad \text{restored by hand}$$

α only divides the work



one unit charge, cubic cell of 10 a.u.

Key idea

Each term depends on the splitting parameter α; their sum does not.

$$E_{\text{Ewald}} = -\frac{\xi}{2a_0}$$

the Madelung energy of Section 3

Choosing the parameters

$$\alpha = -\frac{1}{4}\frac{G_{\text{cut}}^2}{\ln \gamma}$$

$$e^{-|\vec{G}|^2/4\alpha} = \gamma \text{ at } |\vec{G}| = G_{\text{cut}}$$

$$\gamma = 10^{-8} \qquad G_{\text{cut}} = 2\,\text{bohr}^{-1}$$

G_{cut} (bohr^{-1})	cells, $n^{\max}$	plane waves, $m^{\max}$
0.1	28	2
2	**3**	**5**
10	2	17

cubic cell of 10 a.u.

A. Kustepeli and A. Q. Martin, IEEE Microw. Guided Wave Lett. **10**, 168 (2000)

Three backgrounds

E_{H}	electrons in a uniform **positive** background
E_{nuc}	electrons with the nuclei and a uniform **negative** background
E_{Ewald}	nuclei in a uniform **negative** background

Three backgrounds

E_{H}	electrons in a uniform **positive** background
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each term shifted by $-\xi q^2/(2L)$ to leading order

$$-\frac{\xi}{2L}\Big(\underbrace{Q_{\mathsf{e}}^2}_{E_{\mathsf{H}}}+\underbrace{2Q_{\mathsf{e}}Q_{\mathsf{n}}}_{E_{\mathsf{nuc}}}+\underbrace{Q_{\mathsf{n}}^2}_{E_{\mathsf{Ewald}}}\Big)=-\frac{\xi}{2L}\big(Q_{\mathsf{e}}+Q_{\mathsf{n}}\big)^2=0$$

Only the sum is meaningful

normalised Gaussian density on a proton; energies in Ht

L (a.u.)	E_{H}	E_{nuc}	E_{Ewald}	sum
10	0.4239	-1.3136	-0.1419	-1.0316
20	0.4935	-1.4541	-0.0709	-1.0316
40	0.5287	-1.5249	-0.0355	-1.0316
∞	0.5642	-1.5958	0.0000	-1.0316

each term converges only as $1/L$; the sum is right at every L

Two consequences

1. Compare only the **total energy** with a calculation on an isolated molecule.
   what remains: interactions between dipoles (and higher multipoles) of the images, decaying much faster with L

2. The average electrostatic potential in the cell is **zero**.
   orbital energies are measured from this average, not from the vacuum level: their differences are meaningful, their absolute values are not

Key idea

Discarding $\vec{G} = \vec{0}$ neutralises every cell. Individual electrostatic terms are shifted by amounts that decay only as $1/L$; for a neutral system the shifts cancel exactly in the total energy.

5

Self-consistent field procedure



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A matrix eigenvalue problem

$$\mathbf{HC} = \mathbf{SCE} \xrightarrow{\mathbf{S}=\mathbf{1}} \mathbf{HC} = \mathbf{CE}$$

plane waves are orthonormal: no overlap matrix

$C_{ij} = \tilde{\psi}_j(\vec{G}_i)$ column j: the coefficients of orbital j

A matrix eigenvalue problem

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plane waves are orthonormal: no overlap matrix

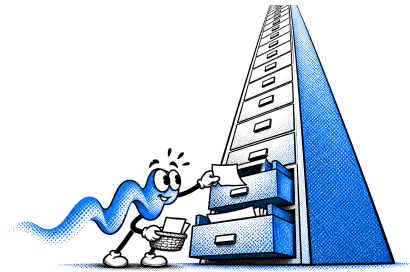
$C_{ij} = \tilde{\psi}_j(\vec{G}_i)$ column j: the coefficients of orbital j

full diagonalisation: $\mathcal{O}\left(N_{\text{pw}}^3\right)$ H_2O in a cell of 10 a.u., $N = 32$: $N_{\text{pw}} = 32\,768$

Only the lowest states are needed



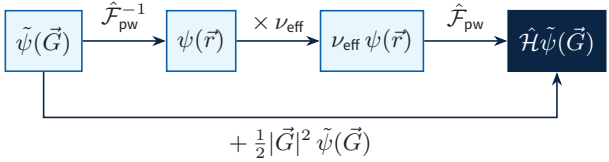
H_2O, schematic



I only asked for the lowest states, not the whole building.

Applying $\hat{\mathcal{H}}$ without storing it

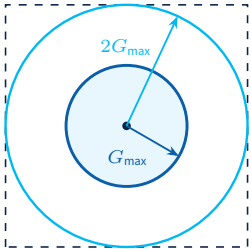
$$\hat{\mathcal{H}}\tilde{\psi}(\vec{G}) = \underbrace{\tfrac{1}{2}|\vec{G}|^2 \circ \tilde{\psi}(\vec{G})}_{\text{kinetic: diagonal}} + \underbrace{\hat{\mathcal{F}}_{\text{pw}}\left[\hat{\mathcal{F}}_{\text{pw}}^{-1}\left[\tilde{\psi}(\vec{G})\right] \circ \nu_{\text{eff}}(\vec{r})\right]}_{\text{potential: point by point in real space}}$$



convolution $\mathcal{O}\left(N_{\text{pw}}^2\right)$ $\longrightarrow$ two FFTs $\mathcal{O}\left(N_{\text{pw}} \log N_{\text{pw}}\right)$

$\circ$: element-wise product · $\mathbf{H}$ itself is dense: $32\,768^2$ complex numbers $\approx$ 17 GB

Two cut-offs



FFT grid: cube of edge $4G_{\max}$

$$e^{i\vec{G}\cdot\vec{r}}\, e^{i\vec{G}'\cdot\vec{r}} = e^{i(\vec{G}+\vec{G}')\cdot\vec{r}}$$

$|\psi|^2$ and $\nu_{\text{eff}}\psi$ reach $2G_{\max}$

orbitals	$\frac{1}{2}\lvert\vec{G}\rvert^2 \leq E_{\text{cut}}$
density, grid	$E^{\rho}_{\text{cut}} \geq 4E_{\text{cut}}$

grid too coarse: short waves fold back onto long ones (**aliasing**)

$N_{\text{grid}} \approx 15\, N_{\text{pw}}$ · the primer's examples use all grid points as the basis

Inside the Arnoldi method

$$\mathcal{K}_m = \operatorname{span}\left\{\vec{c},\, \mathbf{H}\vec{c},\, \mathbf{H}^2\vec{c},\, \ldots,\, \mathbf{H}^{m-1}\vec{c}\right\}$$

only matrix–vector products · $m \ll N_{\text{pw}}$

W. E. Arnoldi, Quart. Appl. Math. **9**, 17 (1951)

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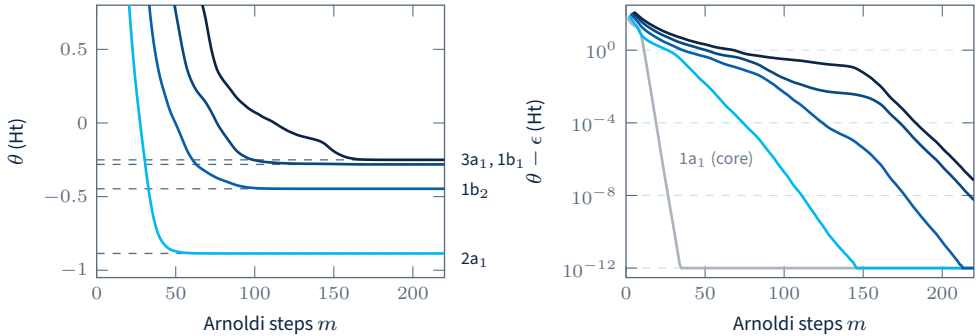
Key idea

The linear variational method, but $\mathbf{H}$ chooses the basis: each Ritz value is an upper bound.

W. E. Arnoldi, Quart. Appl. Math. **9**, 17 (1951)

Ritz values sink from above



H_2O, 32 768 plane waves, random start vector, no restarts · dashed: exact levels

The total energy

$$E_{\text{total}} = \underbrace{2 \sum_{i}^{N_{\text{elec}}/2} \left\langle \psi_i \left| -\tfrac{1}{2}\nabla^2 \right| \psi_i \right\rangle}_{\text{kinetic}} + \underbrace{\int_{\Omega} \rho(\vec{r}) \left[\nu_{\text{ext}} + \tfrac{1}{2}\nu_{\text{H}} + \epsilon_{\text{xc}} \right] d\vec{r}}_{\text{electrons in their potentials}} + \underbrace{E_{\text{Ewald}}}_{\text{nuclei, once}}$$

$$\rho(\vec{r}) = 2 \sum_{i}^{N_{\text{elec}}/2} |\psi_i(\vec{r})|^2$$

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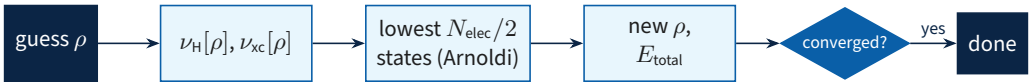
ϵ_i counts every e–e repulsion twice · contains ν_{xc}, not ϵ_{xc} · has no E_{Ewald}

on the grid: kinetic term in reciprocal space, the rest as $\Delta V \sum_k$ over grid points, $\Delta V = \Omega / N_{\text{grid}}$

The self-consistent field cycle

$$\mathbf{H}[\rho]\,\mathbf{C} = \mathbf{C}\mathbf{E} \qquad \rho = 2\sum_j \left|\hat{\mathcal{F}}_{\text{pw}}^{-1}\left[\tilde{\psi}_j(\vec{G})\right]\right|^2$$



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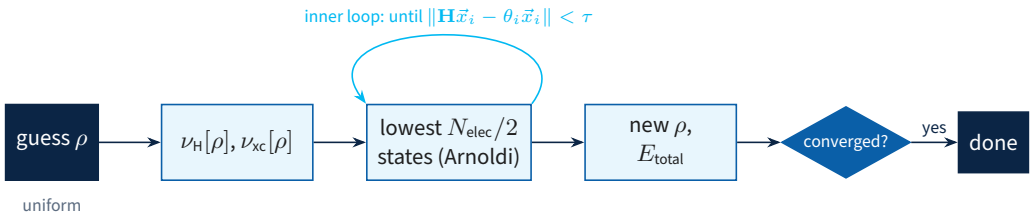

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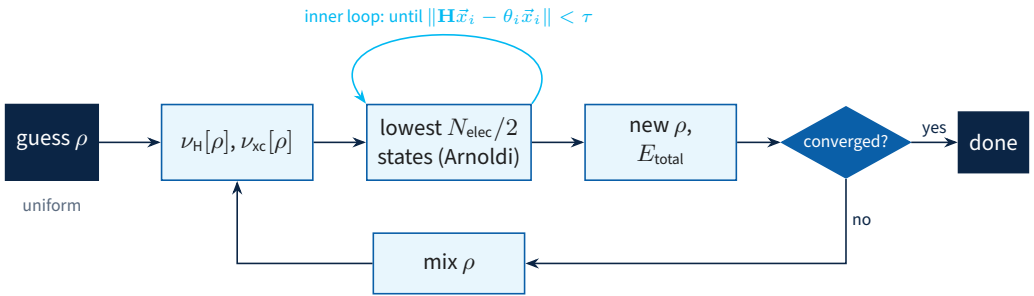

When are we done?

outer loop

$$|\Delta E_{\text{total}}| < \delta_E \quad \textbf{and} \quad \|\Delta\rho\|_{\text{rms}} < \delta_\rho$$

E is stationary in ρ: its error is of second order, so E can look converged while ρ still changes

inner loop

$$\|\mathbf{H}\vec{x}_i - \theta_i\vec{x}_i\| < \tau$$

- start from the previous states
- tighten τ as ρ converges

Density mixing

$$\rho \leftarrow \beta\rho_{\text{new}} + (1-\beta)\rho_{\text{old}}, \qquad 0 < \beta \leq 1$$



Add the new density gently. Nobody likes an SCF soufflé that oscillates.

Density mixing

$$\rho \leftarrow \beta\rho_{\text{new}} + (1-\beta)\rho_{\text{old}}, \qquad 0 < \beta \leq 1$$

why not simply $\beta = 1$?

$$\delta\tilde{\nu}_{\text{H}}(\vec{G}) = \frac{4\pi}{|\vec{G}|^2}\,\delta\tilde{\rho}(\vec{G})$$

long-wavelength errors are amplified: the charge **sloshes** back and forth; worse in large cells and metals



Add the new density gently. Nobody likes an SCF soufflé that oscillates.

Beyond linear mixing

find ρ with $R[\rho] = \rho_{\text{new}} - \rho_{\text{old}} = 0$

Pulay (DIIS)	combine recent densities to minimise the residual
Broyden	quasi-Newton: learn the inverse Jacobian of $R[\rho]$
Kerker	precondition with $\dfrac{\lvert\vec{G}\rvert^2}{\lvert\vec{G}\rvert^2 + q_0^2}$: damps small $\lvert\vec{G}\rvert$

robust default: Pulay over a handful of recent densities, linear mixing in the first step

P. Pulay, Chem. Phys. Lett. **73**, 393 (1980) D. D. Johnson, Phys. Rev. B **38**, 12807 (1988) G. P. Kerker, Phys. Rev. B **23**, 3082 (1981)

Real orbitals at the Γ-point

$$\hat{\mathcal{H}} \text{ real:} \quad \hat{\mathcal{H}}\psi_i = \epsilon_i \psi_i \implies \hat{\mathcal{H}}\psi_i^* = \epsilon_i \psi_i^*$$

Real orbitals at the Γ-point

$\hat{\mathcal{H}}$ real: $\hat{\mathcal{H}}\psi_i = \epsilon_i \psi_i \implies \hat{\mathcal{H}}\psi_i^* = \epsilon_i \psi_i^*$

non-degenerate: $\psi_i^* = e^{2i\theta}\psi_i \implies e^{i\theta}\psi_i$ is real

the eigensolver returns an arbitrary phase: plot $|\psi|^2$, or rotate first

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the eigensolver returns an arbitrary phase: plot $|\psi|^2$, or rotate first

Γ-point

$$\psi(\vec{r} + \vec{R}) = \psi(\vec{r})$$

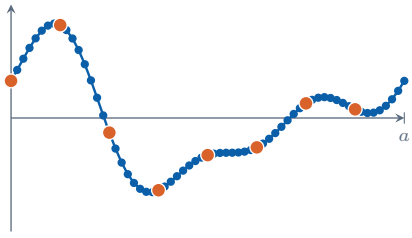
real orbitals, as in quantum chemistry; $\tilde{\psi}(-\vec{G}) = \tilde{\psi}(\vec{G})^*$ halves the work

general $\vec{k}$

$$\psi_{\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi_{\vec{k}}(\vec{r})$$

$\psi^*_{\vec{k}}$ belongs to $-\vec{k}$: complex orbitals

Finer pictures for free



• 8 points • 64 points from the same coefficients

1. pad $\tilde{\psi}(\vec{G})$ with zeros
   e.g. $32^3 \rightarrow 128^3$
2. inverse FFT on the finer grid
3. adjust C_t
   $4\times$ finer: C_t smaller by $4^3 = 64$

exact: the same expansion, evaluated on more points

6

Example calculations

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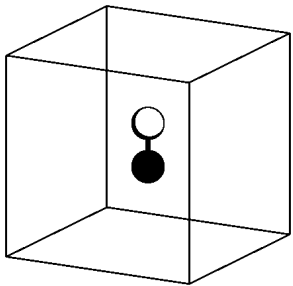
Two molecules, no pseudopotential

	H_2	CO
nuclear charges	1	$6, 8$
core electrons	none	**two 1s pairs**
bond length (PBE)	0.7500 Å	1.1352 Å
E_{ref} (Ht)	-1.16673	-113.2424

everything from Sections 2–5: bare Coulomb nuclei, Γ-point, PBE, iterative eigensolver, density mixing

E_{ref}: all-electron Gaussian basis-set limit, to within about 1 mHt

Two knobs



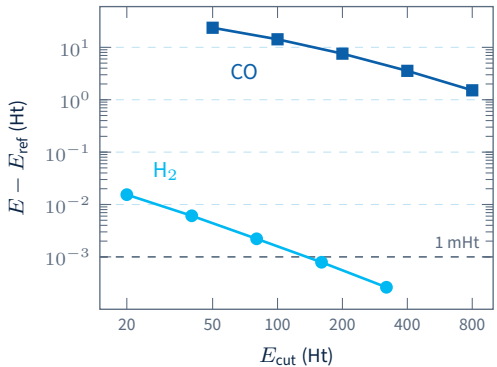
CO at the centre of a cubic cell

$\frac{1}{2}|\vec{G}|^2 \leq E_{\text{cut}}$ shortest wavelength: how much detail

L cell edge: how much vacuum between images

monitor E_{total} and the orbital energies

Convergence with the cut-off



H_2

below 1 mHt from 160 Ht

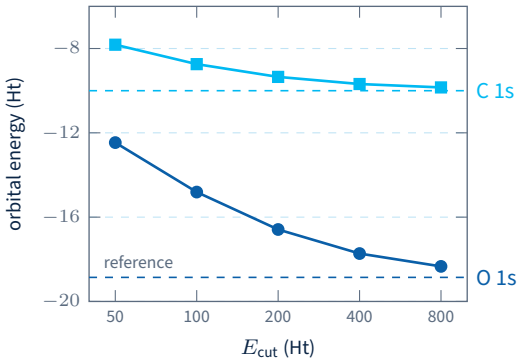
CO

50 Ht: $+24$ Ht

800 Ht, 1.08×10^6 plane waves: still $+1.5$ Ht

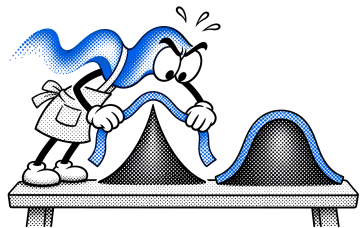
1 mHt would need $E_{\text{cut}} \sim 10^5$ Ht

The core is the culprit



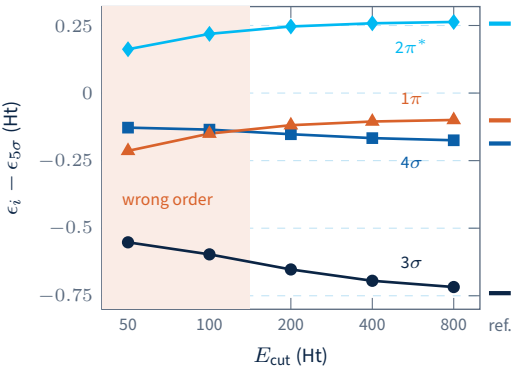
$$\psi_{1s} \propto e^{-Zr}$$

a sharp cusp at every nucleus
needs large $|\vec{G}|$



Gaussians fit off the rack. Cusps take a lot more fabric.

Even the valence order is wrong

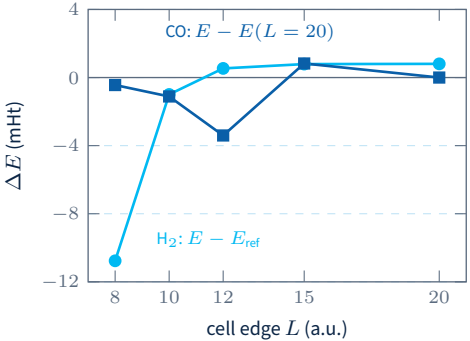


1π below 4σ up to 100 Ht

at 800 Ht, 3σ and 4σ still off by 23 and 12 mHt

valence orbitals have cusps too, and their 2s parts oscillate near the nuclei to stay orthogonal to the 1s orbitals

The cell size: total energy



H_2

8 a.u.: 11 mHt too low

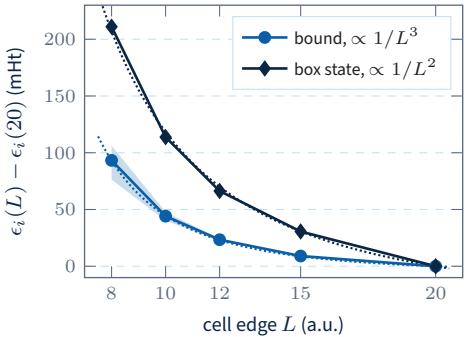
orbital tails of neighbouring cells overlap and add in phase

CO

a few mHt of noise

irrelevant next to its cut-off error of several Ht

The cell size: orbital energies

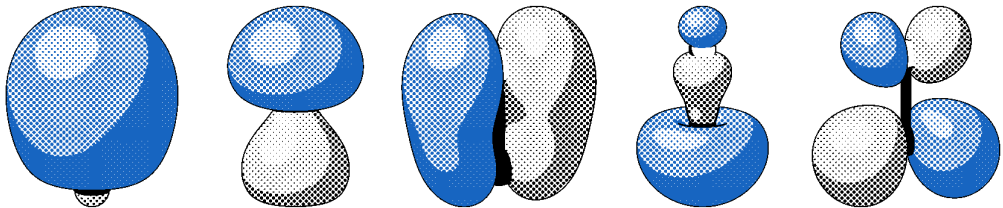


HOMO: -0.289 Ht ($L = 10$)
-0.329 Ht ($L = 20$)
-0.332 Ht (ref.)

all bound levels shift together:
gaps converge fast

zero of energy: the cell average of the potential, not the vacuum level (Section 4)

The orbitals of CO



3σ 4σ 1π 5σ (HOMO) $2\pi^*$ (LUMO)

the familiar molecular-orbital diagram, from plane waves

all-electron, 800 Ht · oxygen at the top · isosurfaces at ± 0.1 a.u. · one member of each degenerate pair

What the examples teach

E_{cut} set by the sharpest features: cusps and core oscillations

H_2: affordable CO: out of reach

L shifts absolute orbital energies; total energy only in small cells

Key idea

Almost all plane waves, and almost all the effort, go into the 1s electrons and the wiggles they impose near the nuclei: a region that matters little for chemistry.

Can we leave the core out?

7

Pseudopotentials



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Why the core is expensive

$$\psi_{1s} \propto e^{-Zr} \quad \Longrightarrow \quad |\vec{G}| \propto Z \quad \Longrightarrow \quad E_{\text{cut}} \propto Z^2$$

oxygen ($Z = 8$): about $64\times$ the cut-off of hydrogen

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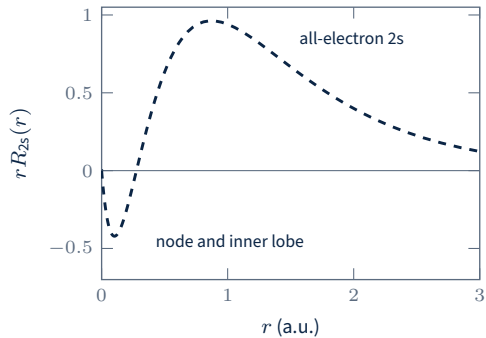
O 1s, cut-off for 10^{-3} of the orbital	612 Ht
plane waves in a cell of 10 a.u.	$> 700\,000$
volume of the core region in that cell	$\approx 0.1\,\%$

almost all effort goes into the part that matters least

Dropping the 1s electrons is not enough



the 2s orbital must be **orthogonal** to 1s
it changes sign close to the nucleus

near the nucleus it feels the same $-Z/r$
and has the same cusp

2s: 10^{-3} of the orbital above 177 Ht

The pseudo-atom

replace the nucleus and its core by an **ion** of charge Z_{ion}, in which the valence electrons have

1. the all-electron **orbital energies**
2. the all-electron **orbitals outside** the core region
3. **smooth** orbitals inside: no nodes, no cusp

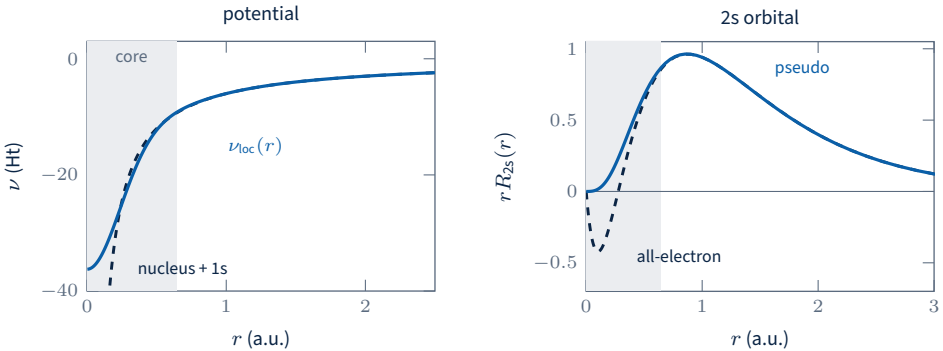
$$\nu_{\text{ps}}(r) \xrightarrow{r \to \infty} -\frac{Z_{\text{ion}}}{r}$$

oxygen: $Z_{\text{ion}} = 6$



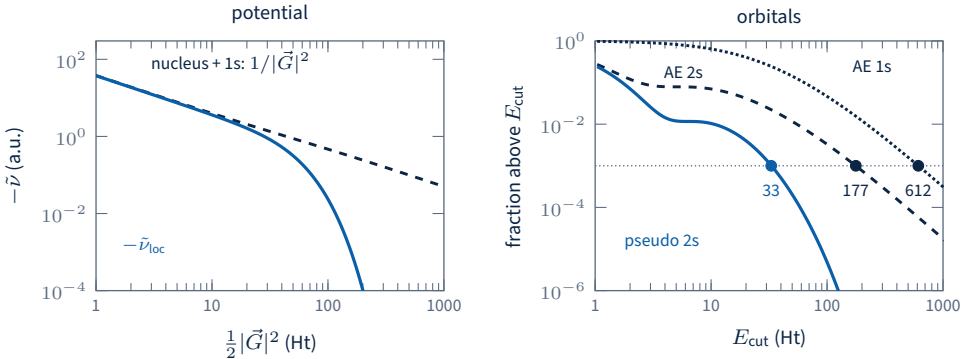
Just a quick press at the core. Outside, nobody will notice.

Smooth inside, exact outside



oxygen, PBE · core region $r < 0.64$ a.u. · outside: orbitals agree to better than 0.1 %

The payoff in reciprocal space



cut-off of the pseudo-atom ≈ 40 Ht instead of 612 Ht: some $12\,000$ instead of $700\,000$ plane waves

the 2p orbital, with no node to lose, sets the 40 Ht

Construct once, use everywhere

transferability
fitted to the isolated atom, used in any molecule or solid

norm conservation
same charge inside the core region as the all-electron orbital
keeps the pseudo-atom right when its levels shift in a bond

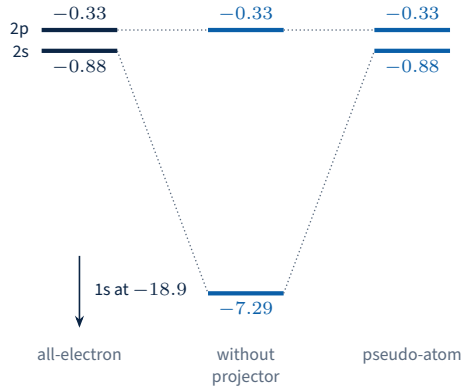
what is lost
everything that needs the density at the nucleus
core-level spectra, hyperfine couplings

D. R. Hamann, M. Schlüter and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979)

Chemistry connection

Chemists already treat the core as inert: frozen-core correlation, and effective core potentials in basis sets for Pd or Au. In a plane-wave basis, pseudopotentials also make the valence orbitals **smooth**.

s and p electrons need different potentials



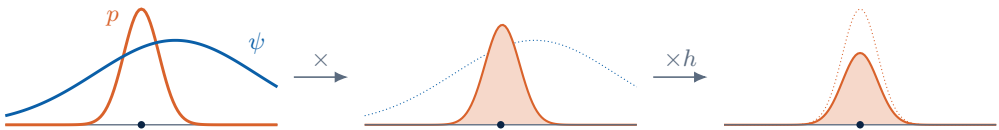
the potential that is right for 2p binds an s electron far too strongly

real atom: 2s must avoid the 1s core (Pauli repulsion); 2p is orthogonal to 1s by shape alone

the repulsion must act on **s electrons only**

Projectors

$$\hat{\mathcal{V}}_{\mathrm{nl}} = |p\rangle\ h\ \langle p| \qquad \left(\hat{\mathcal{V}}_{\mathrm{nl}}\psi\right)(\vec{r}) = p(\vec{r})\, h \int p(\vec{r}\,')\, \psi(\vec{r}\,')\, d\vec{r}\,'$$



non-local: the result at $\vec{r}$ depends on ψ at all $\vec{r}\,'$ near the atom

Only s electrons are stopped

$$\langle\psi|\hat{\mathcal{V}}_{\mathrm{nl}}|\psi\rangle = h \,\big|\, \langle p|\psi\rangle \,\big|^2$$

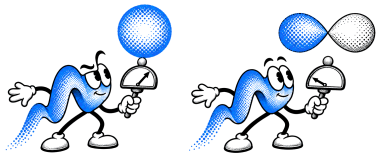
s projector: $\langle p|\psi\rangle = 0$ for p symmetry around the atom

oxygen: $h = 18.3$ Ht, width $r_\mathrm{s} = 0.22$ a.u.

contracted s orbital	$+14.6$ Ht
2s pseudo-orbital	$+0.65$ Ht

the projector **keeps s electrons out of the core**, as orthogonality to 1s does

separable form: L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982)



Anything spherical to declare? Plus and minus cancel, so this one is free to go.

Goedecker–Teter–Hutter pseudopotentials

$$\nu_{\mathrm{loc}}(r) = \underbrace{-\frac{Z_{\mathrm{ion}}}{r}\,\mathrm{erf}\left(\frac{r}{\sqrt{2}\,r_{\mathrm{loc}}}\right)}_{\text{Gaussian ion charge (cf. Ewald)}} + \underbrace{e^{-r^2/2r_{\mathrm{loc}}^2}\sum_{k=1}^{4} C_k \left(\frac{r}{r_{\mathrm{loc}}}\right)^{2k-2}}_{\text{shapes the core region}}$$

$$\hat{\mathcal{V}}_{\mathrm{nl}} = \sum_l \sum_m \sum_{i,j} |p^l_{i,m}\rangle\; h^l_{ij}\; \langle p^l_{j,m}| \qquad p^l_{i,m}(\vec{r}) \propto r^{\,l+2(i-1)}\, e^{-r^2/2r_l^2}\, Y_{lm}(\hat{\vec{r}})$$

analytic in real and reciprocal space · fitted to all-electron atoms, for one functional

S. Goedecker, M. Teter and J. Hutter, Phys. Rev. B **54**, 1703 (1996) C. Hartwigsen, S. Goedecker and J. Hutter, Phys. Rev. B **58**, 3641 (1998)

Oxygen in five numbers

```
O GTH-PBE-q6
         2   4
         s   p
0.24455430   2   -16.66721480   2.48731132
       r_loc   #            C_1          C_2
         2
0.22095592   1    18.33745811
       r_s   #            h_11^s
0.21133247   0
       r_p   #   no p projector
```

$r_{\mathrm{loc}}, C_1, C_2$: local part · $r_{\mathrm{s}}, h_{11}^{\mathrm{s}}$: s projector · r_{p}: listed only because the format asks for it

M. Krack, Theor. Chem. Acc. **114**, 145 (2005)

What changes in the code

$$\nu_{\text{ext}}(\vec{r}) = \frac{1}{\sqrt{\Omega}} \hat{\mathcal{F}}_{\text{pw}}^{-1}\Big[\sum_j \underbrace{\tilde{\nu}_{\text{loc},j}(\vec{G})}_{\substack{\text{instead of} \\ -4\pi Z_j/|\vec{G}|^2}} e^{-i\vec{G}\cdot\vec{R}_j} \Big]$$

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$$\hat{\mathcal{H}}\tilde{\psi} = \tfrac{1}{2}|\vec{G}|^2 \circ \tilde{\psi} + \hat{\mathcal{F}}_{\text{pw}}\Big[\hat{\mathcal{F}}_{\text{pw}}^{-1}\big[\tilde{\psi}\big] \circ \nu_{\text{eff}}\Big] + \mathbf{P}\mathbf{h}\mathbf{P}^\dagger\tilde{\psi}$$

columns of $\mathbf{P}$: projector coefficients $\tilde{p}(\vec{G})$, one per projector and atom

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columns of $\mathbf{P}$: projector coefficients $\tilde{p}(\vec{G})$, one per projector and atom

Key idea

Separable projectors cost one dot product of length N_{pw} each: no $N_{\text{pw}} \times N_{\text{pw}}$ matrix is ever needed.

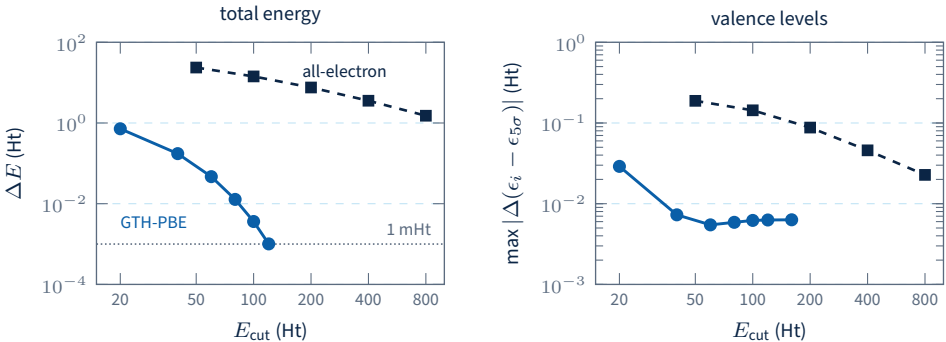
What changes in the numbers

	all-electron	GTH-PBE
electrons in CO	14	10
Ewald energy	nuclei, Z	ions, Z_{ion}
total energy	-113.24 Ht	-21.69 Ht
lowest orbital	1σ (O 1s)	3σ
extra energy term	—	$E_{\text{nl}} = 2\sum_i \langle\psi_i\|\hat{\mathcal{V}}_{\text{nl}}\|\psi_i\rangle$

compare only **energy differences** with all-electron results or experiment

the Hamiltonian stays real: orbitals can still be made real at the Γ-point

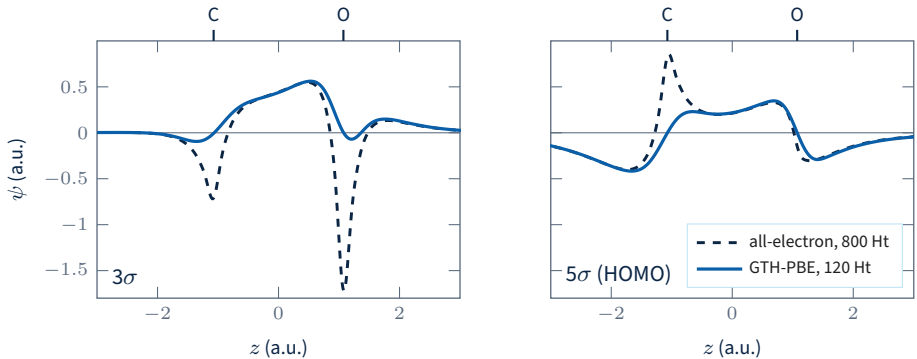
Carbon monoxide revisited



GTH: 1 mHt at 120 Ht with $62\,669$ plane waves · all-electron: 1.5 Ht off with 1.08×10^6

GTH total energy relative to its value at 160 Ht; cell of 10 a.u.

Smooth through the nuclei



cusps and core wiggles are gone; between the atoms the orbitals coincide

A small price

valence levels vs all-electron reference ($L = 15$, 20 a.u.)	3.2–3.3 mHt
bond length, GTH-PBE	1.1356–1.1357 Å
bond length, all-electron PBE	1.1352 Å
bond length, experiment	1.1283 Å

pseudopotential error: **0.5 mÅ** functional error: 7 mÅ

once the core is gone, the cell size becomes a leading source of error

Limitations and beyond

semicore electrons

Na with $Z_{\text{ion}} = 1$ or 9 (2s, 2p included)

$r_{\text{loc}} = 0.71$ vs 0.18 a.u.: more accurate, much higher cut-off

hard elements

compact, nodeless 2p and 3d orbitals have little to smooth away

further developments

ultrasoft pseudopotentials: give up norm conservation

PAW: also recovers the all-electron orbitals near the nucleus

standard in production codes, beyond this primer

Key idea

A pseudopotential replaces nucleus and core by an ion with the right valence levels and orbitals outside a small core region, and smooth orbitals inside.

D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990) P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994)