

Notes on PAW

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1 Motivation

The valence wavefunctions have rapid oscillations near atomic cores (see Figure 1), which is partly due to the requirement that they be orthogonal to all the core states, which are all non-zero in this region. This makes the valence wavefunctions hard to represent on a finite-size basis of any kind (Fourier components, real space grid, plane waves, ...). Note that the core wavefunctions also may have oscillations near atomic cores (the strong Coulomb potential near the nuclei leads to sharply varying wavefunctions altogether) but they vanish fast far from the nuclei (see again Figure 1), so that the chemical properties are largely determined by the valence electrons. This motivates approaches where the core and valence states are treated differently.

One strategy to make us of this observation is to use pseudopotentials, where a smooth potential is constructed to describe the nuclei and core electrons together and the Kohn-Sham equations are solved for the valence electrons only. The relativistic effects being mostly important for the core electron, the pseudopotentials are constructed with relativist considerations, and the non-relativistic valence electrons are treated by the normal, non-relativistic, Kohn-Sham equations. With this method, though, the complete wavefunction is *not* accessible, that is to say that the fine structure of the complete wavefunction close to the nuclei is lost, and this can have an impact on the values of properties. Additionally, there is no systematic way to generate good pseudopotentials, so the method is somewhat ill-defined and not well controlled.

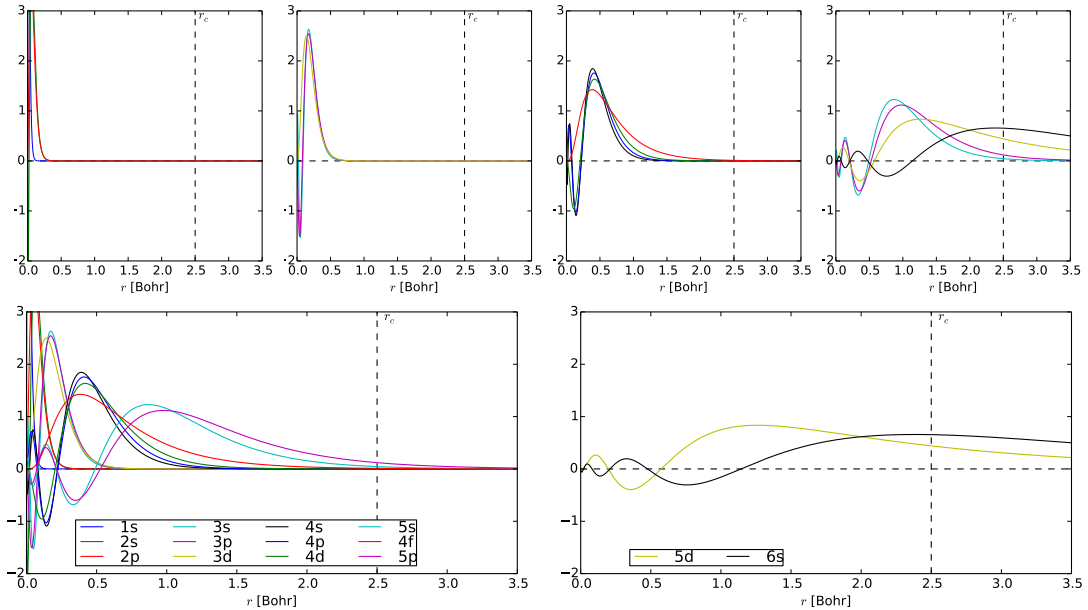


Figure 1: Orbitals of the Platinum atom. The first row shows the $n=1$ and $n=2$ (left), $n=3$ (second), $n=4$ (third), and $n=5$ and $n=6$ (right) orbitals. The second row shows the core orbitals (left) and the valence orbitals (right), with the same color coding. The r_c quantity highlights the typical cut-off of a PAW implementation, which is about half of the Pt-Pt distance in bulk Platinum.

Another strategy is to use the projector augmented wave method (PAW). The core idea of the PAW method is to replace the oscillating all-electron wavefunction with a smooth wavefunction involving smooth pseudo objects plus rigorous corrections, leading to a transformation of the variational problem into a more convenient (computationally speaking) Kohn-Sham problem. The method still provides a way to calculate all-electron properties from the smooth objects. (Note that the “all-electron” naming here refers to wavefunctions of a problem containing all the electrons, but all quantities here are single-particle Kohn-Sham-like objects.) The PAW is more general than the pseudopotential (both ultra-soft and norm-conserving pseudopotentials can be found as approximation in the PAW formalism), and LAPW can be seen as a special case of the PAW method, which is often described as having the formal simplicity of pseudopotentials with the versatility of LAPW.

As mentioned above, the all-electron wavefunction behaves very differently in different regions of space, namely the region far from all nuclei is smooth while the region near any nucleus features rapid oscillations. The idea of the PAW method is to use this to separate the all-electron wavefunction into a smooth envelope in the region between the nuclei and a partial wave expansion around the nuclei, the two parts being matched at the frontier. The ingredients used to setup the PAW procedure come from easy-to-carry isolated atomic DFT calculations that can be tabulated for each chemical element involved.

As we will demonstrate, in the PAW method, an all-electron single-particle wavefunction for state n is written as:

$$|\Psi^n\rangle = |\tilde{\Psi}^n\rangle + \sum_{iA} \left(|\phi_{iA}\rangle - |\tilde{\phi}_{iA}\rangle \right) \langle \tilde{p}_{iA} | \tilde{\Psi}^n \rangle \quad (1)$$

i.e. is separated into “tilde” objects that are smooth everywhere (obtained for example from alternative, smoothed, Kohn-Sham equations) and a contribution which contains rapid oscillations but exists only in spheres around the nuclei (see the sketch Figure 2). The smooth wavefunction $\tilde{\Psi}^n$ can be represented on coarse finite-size basis while the atom-centered parts (under the sum) can be represented on corresponding atom-centered radial grids of high resolution. (Remember that in the context of an isolated atom the density and potentials can be written using only radial functions, and the entire Kohn-Sham equations can be reduced to a one dimensional radial problem that can easily integrated using standard techniques, the angular dependences being treated analytically.)

The ingredients of the PAW method are as follow:

- The all-electron partial waves ϕ_{iA} which are solutions of the radial Schrödinger equation for the isolated atom. They are used as basis for the all-electron wavefunctions within the spheres.
- The smooth partial waves $\tilde{\phi}_{iA}$ which are smooth continuation inside the spheres of the corresponding all-electron partial waves. They are used as basis for the smooth wavefunctions.
- The smooth projector functions \tilde{p}_{iA} which are so that $\langle \tilde{p}_{iA} | \tilde{\phi}_{jA} \rangle = \delta_{ij}$ and that are involved in the link between the two representations.

2 Notations and Definitions

The PAW method is a very general augmentation scheme with smooth partial waves that are identified with the envelop functions. The objective is to determine a linear mapping \hat{T} between a smooth, computationally efficient, single-particle wavefunction for state n , $\tilde{\Psi}^n$, and an all-electron single-particle wavefunction Ψ^n :

$$|\Psi^n\rangle = \hat{T}|\tilde{\Psi}^n\rangle \quad (2)$$

yielding a tranformed set of Kohn-Sham equations solved instead of the normal Kohn-Sham equations:

$$\hat{T}^\dagger \hat{H} \hat{T} |\tilde{\Psi}^n\rangle = \epsilon \hat{T}^\dagger \hat{T} |\tilde{\Psi}^n\rangle \quad (3)$$

where the wavefunctions solutions of these transformed equations need to be smooth. The all-electron wavefunction is already smooth enough

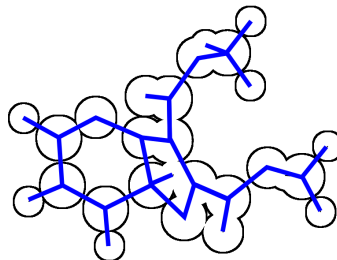


Figure 2: A sketch of the slightly overlapping spheres around atoms of a molecule. The overlap of the spheres that should formally not overlap is considered an approximation in the implementations of PAW.

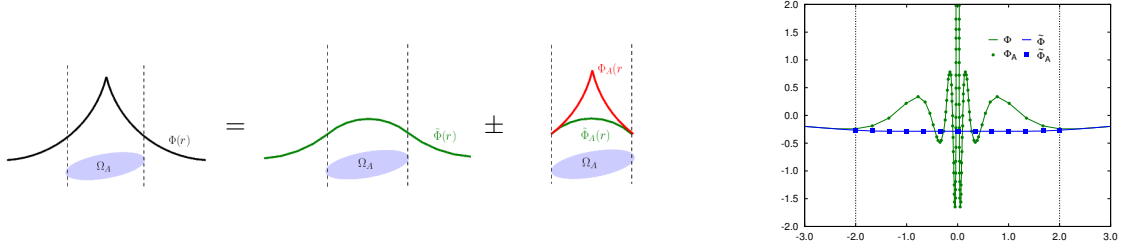


Figure 3: (left) A sketch of the decomposition involved in the PAW implementations. The actual quantity, in black, is replaced but the more computationally convenient smooth quantity in green. The two differ only within spheres $\Omega = \bigcup \Omega_A$ surrounding the atoms, and the atom-centered corrections allows to recover the actual quantity. (right) Example of a PAW implementation for the 6s orbital of the Platinum atom: $\Phi(r) = \tilde{\Phi}(r) + \Phi_A(r) - \tilde{\Phi}_A(r)$, where the atomic quantities (with a subscript A) exist within a sphere highlighted but the vertical black dotted lines.

far from the cores, so the transformation \hat{T} is required to take place only within atom-centered spheres Ω_A (and be the unity operator outside):

$$\hat{T} = \hat{1} + \sum_A \hat{T}_A \quad (4)$$

so that all derivations in the following take place within the spheres (outside of all spheres, all “tilde” quantities and “non-tilde” quantities are equivalent). These spheres are analogous to the muffin-tin spheres of the linear muffin-tin orbital method or to the “core region” in the pseudopotential method.

The smooth wavefunction is expanded on a complete first set of functions, the smooth partial waves:

$$|\tilde{\Psi}^n\rangle = \sum_{iA} c_{iA}^n |\tilde{\phi}_{iA}\rangle \quad (5)$$

where application of Eq. (2) allows to define a second set of one-to-one mapped all-electron partial waves on which the all-electron wavefunction is expanded:

$$|\Psi^n\rangle = \sum_{iA} c_{iA}^n |\phi_{iA}\rangle \quad (6)$$

with

$$|\phi_{iA}\rangle = \hat{T}|\tilde{\phi}_{iA}\rangle = (\hat{1} + \hat{T}_A)|\tilde{\phi}_{iA}\rangle \quad (7)$$

where one needs to remember that, of all \hat{T}_A in \hat{T} , only the one in the sphere of the particular atom involved is non-zero. This fully determines \hat{T} in terms of the all-electron and smooth partial waves, as:

$$\hat{T}_A|\tilde{\phi}_{iA}\rangle = |\phi_{iA}\rangle - |\tilde{\phi}_{iA}\rangle \quad (8)$$

and allows to express the all-electron wavefunction as:

$$|\Psi^n\rangle = |\tilde{\Psi}^n\rangle + \sum_{iA} c_{iA}^n \left(|\phi_{iA}\rangle - |\tilde{\phi}_{iA}\rangle \right) \quad (9)$$

Figure 3 shows a drawing and an example that illustrates this decomposition.

[not well understood] *Because the transformation is linear, the coefficients c_{iA}^n , purposefully left unknown until now, are linear functionals of $\tilde{\Psi}^n$* and are expressed using a third set of functions, called the smooth projector functions:

$$c_{iA}^n = \langle \tilde{p}_{iA} | \tilde{\Psi}^n \rangle \quad (10)$$

with the required property that $\langle \tilde{p}_{iA} | \tilde{\phi}_{jA} \rangle = \delta_{ij}$ inside the spheres, that is to say that the smooth projector functions and the smooth partial waves are mutually orthonormal within the spheres. This is the most general and most computationally efficient scheme to get the right coefficients ensuring the smooth continuity between the different objects.

With all three ingredients, the all-electron wavefunction is expressed as:

$$|\Psi^n\rangle = |\tilde{\Psi}^n\rangle + \sum_{iA} \left(|\phi_{iA}\rangle - |\tilde{\phi}_{iA}\rangle \right) \langle \tilde{p}_{iA} | \tilde{\Psi}^n \rangle \quad (11)$$

and the transformation is defined as:

$$\hat{T} = \hat{1} + \sum_{iA} \left(|\phi_{iA}\rangle - |\tilde{\phi}_{iA}\rangle \right) \langle \tilde{p}_{iA}| \quad (12)$$

The all-electron wavefunction can be written in real space as:

$$\Psi^n(\mathbf{r}) = \tilde{\Psi}^n(\mathbf{r}) + \sum_A \psi_A(\mathbf{r}) - \tilde{\psi}_A(\mathbf{r}) \quad (13)$$

where the first term is the contribution obtained with smooth quantities from Eq. (3) and the second term is a summation of atom-centered corrections involving quantities like $\psi_A(\mathbf{r}) = \sum_i c_{iA}^n \phi_{iA}(\mathbf{r})$. All ingredients needed to make \hat{T} are system-dependent (atom-specific) and can be computed and tabulated in advance.

3 In practice

There is little requirements for the construction of all three basic ingredients of a PAW procedure: a) the all-electron and smooth partial waves need to be atom-specific complete basis sets inside the spheres and b) the smooth projector functions need to satisfy $\langle \tilde{p}_{iA} | \tilde{\phi}_{jA} \rangle = \delta_{ij}$ inside the spheres. Hence there is considerable freedom in their choice and numerous considerations of speed and reliable convergence can be taken into account to constrain the choices. All the data are atom-specific and atom-centered and can be generated using an atomic DFT code.

The all-electron partial wave ϕ_{iA} are chosen to ensure a fast convergence of the Kohn-Sham all-electron wavefunction Ψ^n , and are hence often the eigenstates of the radial Schrödinger equation for isolated atoms:

$$(\hat{t} + \hat{v}_{\text{atomic}}) |\phi_{iA}\rangle = \epsilon_{iA} |\phi_{iA}\rangle \quad (14)$$

The number of partial waves taken into account is increased until the scattering properties of the valence band region are well described (often one partial wave per site and angular momentum is sufficient).

The smooth partial waves $\tilde{\phi}_{iA}$ are either really any smooth continuations of the all-electron partial waves within the spheres (polynomials, Bessel functions, Gaussians, ...), or solutions of the same Schrödinger equations with a smooth atomic potential:

$$(\hat{t} + \hat{v}_{\text{smooth}}) |\tilde{\phi}_{iA}\rangle = \tilde{\epsilon}_{iA} |\tilde{\phi}_{iA}\rangle \quad (15)$$

To allow for good convergence, the smooth projector functions are often calculated as:

$$|\tilde{p}_{iA}\rangle = (\hat{t} + \hat{v}_{\text{smooth_also}} - \tilde{\epsilon}_{iA}) |\tilde{\phi}_{iA}\rangle \quad (16)$$

with further imposition of the orhogonality condition.

The PAW method is typically implemented in the context of the frozen core approximaton, where it is supposed that the core states are localized within the spheres around the nuclei and are not changed by the environment (the presence of the rest of the atoms in a molecule). Hence the Kohn-Sham core states are identical to the atomic states and can be calculated and tabulated once and held fixed. Only the valence states are explicitly calculated in the expressions derived above (the i index only runs over valence states).

4 Expectation values and Hamiltonian

Together with a procedure to transform between Ψ^n and $\tilde{\Psi}^n$, one needs both a way to access *all-electron* quantities and a way to obtain a smoothed-out variational problem. In the PAW literature, the transformed Hamiltonian is most often obtained by deriving the total energy, which requires the knowledge of the aforementioned all-electron expectation values, shown here.

An expectation value $O = \sum_n f_n \langle \Psi^n | \hat{O} | \Psi^n \rangle$ can be written using:

$$\langle \Psi^n | \hat{O} | \Psi^n \rangle = \langle \tilde{\Psi}^n | \hat{T}^\dagger \hat{O} \hat{T} | \tilde{\Psi}^n \rangle = \langle \tilde{\Psi}^n | \hat{\tilde{O}} | \tilde{\Psi}^n \rangle \quad (17)$$

where

$$\hat{\tilde{O}} = \hat{O} + \sum_{ijA} |\tilde{p}_{iA}\rangle \left(\langle \phi_{iA} | \hat{O} | \phi_{jA} \rangle - \langle \tilde{\phi}_{iA} | \hat{O} | \tilde{\phi}_{jA} \rangle \right) \langle \tilde{p}_{jA}| \quad (18)$$

This expression of the expectation value is invariant under addition of a term of a particular form, which is useful for operators that can't be easily evaluated in a plane-wave expansion. For example, such a term can smooth the problematic singularity of the Coulomb potential at the nucleus without affecting the expectation value.

In practice, the expectation value can be obtained via the same kind of separation we saw for the wavefunction, Eq. (9):

$$\begin{aligned}\langle \Psi^n | \hat{O} | \Psi^n \rangle &= \langle \tilde{\Psi}^n | \hat{O} | \tilde{\Psi}^n \rangle = \langle \tilde{\Psi}^n | \hat{O} | \tilde{\Psi}^n \rangle + \sum_{ijA} \langle \tilde{\Psi}^n | \tilde{p}_{iA} \rangle \left(\langle \phi_{iA} | \hat{O} | \phi_{jA} \rangle - \langle \tilde{\phi}_{iA} | \hat{O} | \tilde{\phi}_{jA} \rangle \right) \langle \tilde{p}_{jA} | \tilde{\Psi}^n \rangle \\ &= \langle \tilde{\Psi}^n | \hat{O} | \tilde{\Psi}^n \rangle + \sum_{ijA} c_{iA}^n c_{jA}^n \left(\langle \phi_{iA} | \hat{O} | \phi_{jA} \rangle - \langle \tilde{\phi}_{iA} | \hat{O} | \tilde{\phi}_{jA} \rangle \right)\end{aligned}\quad (19)$$

Following this, all relevant quantities can be separated again in the same way the wavefunction was, like:

$$\begin{aligned}n(\mathbf{r}) &= \tilde{n}(\mathbf{r}) + \sum_A n_A(\mathbf{r}) - \tilde{n}_A(\mathbf{r}) \\ E_{\text{kin}} &= \tilde{E}_{\text{kin}} + \sum_A E_{\text{kin}A} - \tilde{E}_{\text{kin}A} \\ E_{\text{H}} &= \tilde{E}_{\text{H}} + \sum_A E_{\text{H}A} - \tilde{E}_{\text{H}A} \\ E_{\text{xc}} &= \tilde{E}_{\text{xc}} + \sum_A E_{\text{xc}A} - \tilde{E}_{\text{xc}A}\end{aligned}\quad (20)$$

where to obtain some of those expression, like the Hartree energy, in separable form, “Compensation Charges” are introduced ; this will not be treated here. As a result, the transformed Hamiltonian leads to the transformed equations mentioned in Eq. (3). It is expressed simply:

$$\hat{H} = \hat{t} + \hat{v}_{\text{Hxc}}[\tilde{n}] + \sum_{ijA} |\tilde{p}_{iA}\rangle \Delta \hat{H}_{ijA} \langle \tilde{p}_{jA}| \quad (21)$$

where the atom-centered correction term contains quantities involved in the derivation of Eqs. (20), this is also not explicitly shown here.

5 Useful softwares

In the course of gathering material for these notes, I came upon two simple to use softwares related to the PAW: `atompaw` ([link](#)) and `gpaw` ([link](#)) .

The first is a software to easily generate custom PAW datasets to carry PAW calculations (specifying for example a particular xc functional, scalar-relativistic approach, size of obtained basis, etc...). These can be tested and exported to many PAW softwares. I have not used it but it looks simple.

The second is a DFT calculation package based on the PAW method where the wavefunctions are expanded on real space grids, on plane waves, or on atomic orbitals. It's a Python+C package that relies on the `ase` and `numpy` packages for the Python part and on the `fftw` and `libxc` packages for the C part. It's fairly easy to install and to play around with. They base their implementation in part on the `ase` package, which is according to their wiki: “The Atomic Simulation Environment (ASE) is a set of tools and Python modules for setting up, manipulating, running, visualizing and analyzing atomistic simulations.” One can install all that with `apt-get` or `pip`, but that did not work for my machine. It was still easy: I installed `ase` from the `gitlab` repository, `libxc` by downloading a tar from the website, and finally `gpaw` from the `gitlab` repository.

An example of a run of the dissociation energy of the nitrogen molecule, doing a PBE calculation with PAWs:

```
from ase import Atoms
from gpaw import GPAW

# some parameters
a = 8.0
h = 0.18
d = 1.1

# define the Atom object
N = Atoms('N', positions=[[0,0,0]],
          cell=(a,a,a), pbc=True)
N.center()
```

```

# define and run the Calc object
calc = GPAW(nbands=4, xc='PBE', h=h)
N.set_calculator(calc)
e1 = N.get_potential_energy()

# define the Atom object
N2 = Atoms('N2', positions=[[0,0,0],[0,0,d]],
           cell=(a,a,a), pbc=True)
N2.center()

# define and run the Calc object
calc = GPAW(nbands=5, xc='PBE', h=h)
N2.set_calculator(calc)
e2 = N2.get_potential_energy()

print 2*e1-e2, 'eV'

```

and another of geometry optimization of dihydrogen:

```

from ase import Atoms
from gpaw import GPAW, PW
from ase.calculators.emt import EMT
from ase.optimize import BFGS
from ase.visualize import view

# some parameters
d = 0.74

# define the Atom object
H2 = Atoms('H2', positions=[[0,0,0],[0,0,d]])
H2.center()

# define the Calc object
H2.calc = EMT()
H2.get_potential_energy()

# opt
opt = BFGS(H2)
opt.run(fmax=0.05)
H2.get_forces()
H2.calc = GPAW(mode=PW(300))
H2.center(vacuum=2)
H2.cell
H2.get_forces()
view(H2)

```

6 Useful literature

I found a lot of good material on the “Literature” section of the **gpaw** wiki ([link](#)), which is in general quite good. In particular, I read parts of three master thesis that were concise and clear enough and that I recommend:

- “Projector Augmented Wave Calculations With Localized Atomic Orbitals”
by Marco Vanin (mainly Chapter 3) [[pdf](#)] [[link](#)]
- “Localized Atomic Orbital Basis Sets in the Projector Augmented Wave Method”
by Ask Hjorth Larsen (mainly Chapter 3) [[pdf](#)] [[link](#)]
- “Exact Exchange in Density Functional Calculations”
by Carsten Rostgaard (mainly Chapter 7) [[pdf](#)] [[link](#)]

I also used three talks I found interesting:

- “Projector augmented-wave method”
by Steffen Backes [[pdf](#)] [[link](#)]
- “Electronic structure calculations with the GPAW code” [[pdf](#)] [[link](#)]
- “The Projector Augmented Wave method”
by Mortensen [[pdf](#)] [[link](#)]

A tutorial explaining the implementation of PAW in the `atompaw` code is very thorough:

- “Notes for revised form of atompaw code.”
by N. A. W. Holzwarth [[pdf](#)] [[link](#)]

I also read parts of the following papers that were interesting (the following original paper is very clear):

- “Projected Augmented-wave Method”
by P.E. Blochl [[pdf](#)] [[bib](#)] [[doi](#)]
- “The Projector Augmented-wave Method”
by C. Rostgaard [[pdf](#)] [[doi](#)]
- “Pseudopotentials Plane Waves–Projector Augmented Waves: A Primer”
by X. Gonze, F. Finocchi [[pdf](#)] [[bib](#)] [[doi](#)]
- “Variational projector augmented-wave method”
by X. Blanc, É. Cancès, M.-S. Dupuy [[pdf](#)] [[bib](#)] [[doi](#)]

These make links with other methods, like pseudopotentials:

- “Electronic Structure Methods: Augmented Waves, Pseudopotentials and the Projector Augmented Wave Method”
by P.E. Blöchl, J. Kästner, C.J. Först [[pdf](#)] [[bib](#)] [[doi](#)]
- “From ultrasoft pseudopotentials to the projector augmented-wave method”
by G. Kresse, D. Joubert [[pdf](#)] [[bib](#)] [[doi](#)]
- “Comparison of the projector augmented-wave, pseudopotential, and linearized augmented-plane-wave formalisms for density-functional calculations of solids”
by N. A. W. Holzwarth, G. E. Matthews, R. B. Dunning, A. R. Tackett, Y. Zeng [[pdf](#)] [[bib](#)] [[doi](#)]

This paper applies the PAW to Gaussian-type discretization, it’s very detailed and easy to follow:

- “Projector Augmented Wave Method Incorporated into Gauss-Type Atomic Orbital Based Density Functional Theory”
by X.-G. Xiong, T. Yanai [[pdf](#)] [[bib](#)] [[doi](#)]