Accurate Ground State Computations of Atoms and Ions in Extended Kohn-Sham Theory

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Abstract

AtomicKohnSham.jl is a ***Julia code*** that enables to compute the ground-state of atoms and ions within the framework of the ***Extended Kohn-Sham model***. It employs a carefully chosen ***finite element basis***, achieving ***arbitrarily high accuracy*** both in the discretization (basis set) and in the finite-precision arithmetic, to represent the electronic states.

Quantum Mechanics in a Nutshell

The **electronic state of an atom** of N electrons and a nucleus of charge Z (centered at the origine) can be fully described by a function

$$\Psi(x_1, x_2, \cdots, x_N) \text{ where } x_i \in \mathbb{R}^3,$$

and behaves according to a linear operator acting on Ψ, the **Hamiltonian**

$$H = \underbrace{\sum_{i=1}^{N} -\frac{1}{2}\Delta_{x_i}}_{\text{Kinetic energy of electrons}} \underbrace{-\sum_{i=1}^{N} \frac{Z}{|x_i|}}_{\text{Nucleus-electrons}} + \underbrace{\sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}}_{\text{Electrons-electrons}}.$$

What is a ground-state of an atom ?

It is a state Ψ^{GS} associated to the lowest eigenvalue of H :

$$H\Psi^{GS} = E^{GS}\Psi^{GS}$$

where $E^{GS} \in \mathbb{R}$ is the lowest energy the atoms can have.

Why calculate the groundstate of atoms ?

- Fundamental reference: the ground state is the starting point for many quantum simulations.
- Material properties: determines stability, structure, and electronic behaviour of atoms.

How to calculate the groundstate of atoms ?

Minimization problem :

$$E^{GS} = \langle \Psi^{GS} | H\Psi^{GS} \rangle = \min_{\Psi \neq 0} \frac{\langle \Psi | H\Psi \rangle}{||\Psi||^2}.$$

Minimization in $L^2(\mathbb{R}^{3N})$: Curse of dimensionality $\Rightarrow$ Need approximate models.

From Model to Algorithm

We use the ***Extended-Kohn-Sham Model*** [1].

Idea : Approximate the two-body interaction by a one-body potential v_{KS} $\Rightarrow$ Enables to write a set of one-body eigenvalue problems in $L^2(\mathbb{R}^3)$!

The **Euler-Lagrange equations** of the **EKS** model reads :

$$\begin{cases} \text{Find } (\varphi_i) \text{ and } (n_i) \text{ s.t. :} \\ H^{EKS}(\rho)\varphi_i = \epsilon_i \varphi_i, \\ \rho(x) = \sum_i n_i |\varphi_i(x)|^2 \\ \int_{\mathbb{R}^3} \varphi_i \varphi_j = \delta_{ij}, \\ \sum_i n_i = N \text{ and } 0 \le n_i \le 1, \\ \text{Aufbau principle for } (n_i)_i. \end{cases}$$

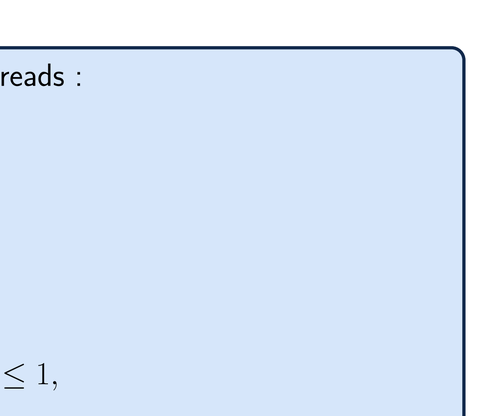
We assume no spherical symmetry breaking $\Rightarrow$ the eigenvalue problem in $L^2(\mathbb{R}^3)$ reduces to a set of eigenvalue problems in $L^2(\mathbb{R}^+)$.

Algorithm: Self-consistent field procedure via the Optimal Damping Algorithm (a fixed-point method with acceleration techniques)

Discretization : Finite Element method

In FEM, to build your discretization basis, you need three components:

- **A Mesh** : for example the exponential mesh is defined by
$$r_k = (1 + R_{max})^{\left(\frac{k}{N_{mesh}-1}\right)^s} - 1$$
with s a parameter.
- **Generators** : A set of polynomials $(\tilde{Q}_j)$ of different degree (from 1 to D) defined on $[-1, 1]$.
- **Shift functions** : Linear maps f_k that matches the cells $[r_k, r_{k+1}]$ to $[-1, 1]$.



Finally, we have

$$\varphi_i(r) = \sum_{j=1}^{N_{basis}} U_{ij} Q_j(r) = \sum_{j=1}^{N_{basis}} U_{ij} \left(\tilde{Q}_{G(j)} \circ f_{S(j)}(r)\right)$$

Features

Currently supported features :

- **Algorithms**: self-consistent field iterations with ODA
- **Discretization**: FEM with customizable grids and polynomial basis
- **Models**: LDA and LSDA exchange–correlation functionals via `Libxc.jl`
- **Visualization**: fast plotting of densities and orbitals via `CairoMakie.jl`
- **Precision**: support for arbitrary precision (tested for `Double64`)
- **Performance**: optimized for low memory allocation and fast runtimes (seconds to minutes)

Libraries : `TensorOperations.jl`, `SparseArrays.jl`, `FastGaussQuadrature.jl`, `Optim.jl`, `LinearAlgebra`, `HypergeometricFunctions.jl`

Integration Challenges

H^{EKS}_{dis} is the sum of several matrices. One of them is

$$M_{ij} = \int_0^{R_{max}} \frac{Q_i(r)Q_j(r)}{r} \mathrm{d}r = \delta_{S(i),S(j)}\, A \int_{-1}^{1} \frac{\tilde{Q}_i(r)\tilde{Q}_j(r)}{Ar + B} \mathrm{d}r$$

where $f^{-1}_{S(i)}(r) = Ar + B$.

How to compute this integral ?

Naïve solution : Coefficient by coefficient, one can write

$$I_l := \int_{-1}^{1} \frac{r^l}{Ar + B} \mathrm{d}r = \frac{1}{A^{l+1}} \underbrace{\int_{B-A}^{B+A} \frac{(r - B)^l}{r} \mathrm{d}r}_{\sim A^l} = \frac{1}{A^{l+1}} \sum_{p=0}^{l} \binom{l}{p} (-B)^{l-p} \underbrace{\int_{B-A}^{B+A} r^{p-1} \mathrm{d}r}_{\sim A}$$

Problem when $A = \Delta r/2 \to 0$!

One solution : Use of Hypergeometric functions to compute very precisely the integral :

$$I_l = \frac{1}{B(l+1)} \left[{}_2F_1(1, l+1; l+2; A/B) - (-1)^{l+1} {}_2F_1(1, l+1; l+2; -A/B) \right]$$

Maximal Ionization of atoms

Ionization conjecture :

- Statement: "A neutral atom can bind at most one or two electrons"
- No theoretical proof of the existence of negatives ions for some models [2].

H z=1 0.70																	He z=2 0.38
Li z=3 0.67	Be z=4 0.37											B z=5 0.55	C z=6 0.67	N z=7 0.63	O z=8 0.78	F z=9 0.87	Ne z=10 0.35
Na z=11 0.68	Mg z=12 0.35											Al z=13 0.57	Si z=14 0.70	P z=15 0.70	S z=16 0.82	Cl z=17 0.98	Ar z=18 0.37
K z=19 0.70	Ca z=20 0.42	Sc z=21 0.46	Ti z=22 0.46	V z=23 0.72	Cr z=24 0.59	Mn z=25 0.55	Fe z=26 0.74	Co z=27 0.82	Ni z=28 0.61	Cu z=29 0.80	Zn z=30 0.31	Ga z=31 0.52	Ge z=32 0.70	As z=33 0.67	Se z=34 0.80	Br z=35 1.00	Kr z=36 0.37
Rb z=37 0.70	Sr z=38 0.48	Y z=39 0.46	Zr z=40 0.65	Nb z=41 0.55	Mo z=42 0.82	Tc z=43 0.80	Ru z=44 0.72	Rh z=45 0.61	Pd z=46 0.63	Ag z=47 0.78	Cd z=48 0.35	In z=49 0.57	Sn z=50 0.76	Sb z=51 0.72	Te z=52 0.85	I z=53 1.00	Xe z=54 0.38
Cs z=55 0.70	Ba z=56 0.52		Hf z=72 0.53	Ta z=73 0.57	W z=74 0.67	Re z=75 0.83	Os z=76 0.74	Ir z=77 0.59	Pt z=78 0.63	Au z=79 0.82	Hg z=80 0.37	Tl z=81 0.57	Pb z=82 0.67	Bi z=83 0.74	Po z=84 0.80	At z=85 1.00	Rn z=86 0.38
Fr z=87 0.72	Ra z=88 0.55		Rf z=104 0.67	Db z=105 0.72	Sg z=106 0.76	Bh z=107 0.59	Hs z=108 0.50	Mt z=109 0.65	Ds z=110 0.61	Rg z=111 0.80	Cn z=112 0.38	Nh z=113 0.59	Fl z=114 0.74	Mc z=115 0.87	Lv z=116 0.97	Ts z=117 1.00	Og z=118 0.38

Symbol z
Maximal Ionization

La z=57 0.61	Ce z=58 0.53	Pr z=59 0.46	Nd z=60 0.40	Pm z=61 0.61	Sm z=62 0.44	Eu z=63 0.46	Gd z=64 0.50	Tb z=65 0.35	Dy z=66 0.35	Ho z=67 0.33	Er z=68 1.06	Tm z=69 0.10	Yb z=70 0.44	Lu z=71 0.48
Ac z=89 0.59	Th z=90 0.57	Pa z=91 0.61	U z=92 0.61	Np z=93 0.74	Pu z=94 0.74	Am z=95 0.70	Cm z=96 0.65	Bk z=97 1.19	Cf z=98 1.02	Es z=99 0.59	Fm z=100 0.23	Md z=101 0.70	No z=102 0.40	Lr z=103 0.57

Computations done for the PW exchange correlation using Integrated Legendre polynomials, $D = 10$, $s = 1.3$, and $N_{mesh} = 20$.

Further work

In the future, we plan to:

- Implement a quadratic convergence algorithm to accelerate computations,
- Investigate GPU support for improved performance.

References

[1] Reiner M. Dreizler and Eberhard K. U. Gross. *The Kohn-Sham Scheme*. 1990.

[2] Phan Thành Nam. The ionization problem in quantum mechanics, 2022.

[3] Eric Cancès and Nahia Mourad. A numerical study of the extended kohn–sham ground states of atoms. June 2018.