Optimization of pseudopotentials for electronic structure calculations

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The electronic structure calculations represent a rigorous tool for predicting and understanding the properties of materials from first principles. In our research devoted to understanding crack propagation in iron we have developed a new software [2] for electronic structure calculations that is based on the pseudopotential approach [5, 7] within the context of the density functional theory [4]. A properly constructed pseudopotential can be used both to reduce numerical difficulties by hiding the core singularity as well as to substantially reduce the number of the electrons (degrees of freedom) required to calculate with by hiding non-valence electrons. However, designing an accurate and efficient pseudopotential is a non-trivial task as there are many, often contradictory, criteria on the pseudopotential optimality, such as smoothness, softness (no strongly oscillating pseudo-wavefunctions), transferability (validity in different neighboring atom configurations, reproduction of scattering properties in a wide range of energies), computational efficiency, etc.

Our approach to generating and optimizing pseudopotentials is based on the algorithm proposed in the dissertation work [6], where so called environment-reflecting all-electron pseudopotentials were introduced. The original fortran77 implementation, while still working very well, started to be a maintenance burden over the years, which motivated us to begin with the development of a new, easily maintainable and extensible implementation using Python as the top-level programming language. In this contribution we describe the new implementation and present preliminary numerical examples.

In our approach [6], a pseudopotential is generated for the given energy E and orbital quantum number l, and is assumed to be a linear combination of basis functions $F_i(r)$, $i = 0, \ldots, 4$

$$V_{E,l}^{\mathrm{PS}}(r) = \sum_{j=0}^{4} a_j F_j(r) \,, \tag{1}$$

where

$$F_0(r) = 1 \,, \quad F_1(r) = e^{-(\rho_1 r)^2} - 1 \,, \quad F_2(r) = (\rho_2 r)^2 e^{-(\rho_2 r)^2} \,,$$
$$F_3(r) = e^{-(\rho_3 r)^2} - 1 \,, \quad F_4(r) = (\rho_4 r)^2 e^{-(\rho_4 r)^2} \,. \tag{2}$$

Pseudopotentials are generated for individual atoms by repeatedly solving the Schrödinger equation numerically in spherical coordinates: for this purpose we can use either our test implementation in Python (mainly for debugging), or a very fast and accurate implementation

of dftatom [1]. We denote the resulting all-electron wavefunctions by $\psi_{E,l}^{\mathrm{AE}}(r)$ and the corresponding energy by E, when solving with the original all-electron potential $V^{\mathrm{AE}}(r)$, and the pseudofunctions by $\psi_{E,l}^{\mathrm{PS}}(r)$ for the calculation with $V_{E,l}^{\mathrm{PS}}(r)$. For a given cut-off radius R_c, the following conditions have to hold

$$V_{E,l}^{\mathrm{PS}}(r) = V^{\mathrm{AE}}(r) , \qquad r \geq R_c , \tag{3}$$

$$\frac{\partial^i}{\partial r^i} V_{E,l}^{\mathrm{PS}}(r) = \frac{\partial^i}{\partial r^i} V^{\mathrm{AE}}(r) , \qquad r = R_c , \quad i = 1, 2 . \tag{4}$$

Using normalization constants such that $\psi_{E,l}^{\mathrm{PS}}(R_c) = \psi_{E,l}^{\mathrm{AE}}(R_c)$, the following conditions are required to hold

$$\frac{\partial}{\partial r} \psi_{E,l}^{\mathrm{PS}}(r) = \frac{\partial}{\partial r} \psi_{E,l}^{\mathrm{AE}}(r) , \qquad r = R_c , \tag{5}$$

$$\int_0^{R_c} \left| \psi_{E,l}^{\mathrm{PS}}(r) \right|^2 r^2 \, \mathrm{d}r = \int_0^{R_c} \left| \psi_{E,l}^{\mathrm{AE}}(r) \right|^2 r^2 \, \mathrm{d}r . \tag{6}$$

The condition (6) corresponds to the charge conservation and makes the resulting pseudopotentials "norm-conserving", which implies transferability, i.e., use at different energies.

The pseudopotential basis functions $F_j(r)$ in (2) have free parameters $\boldsymbol{\rho} \equiv [\rho_1, \rho_2, \rho_3, \rho_4]^T$. Those parameters can be chosen in a way that is optimal w.r.t. some selected criterion Θ — an optimization problem is defined as follows: Find $\hat{\boldsymbol{\rho}}$ such that

$$[\hat{\boldsymbol{a}}, \hat{\boldsymbol{\rho}}] = \mathrm{argmin}_{\boldsymbol{\rho}} \{ \Theta(V_{E,l}^{\mathrm{PS}}(\boldsymbol{a}, \boldsymbol{\rho}, r)) \} , \tag{7}$$

where the linear combination (1) parameters $\hat{\boldsymbol{a}} \equiv [\hat{a}_0, \dots, \hat{a}_4]^T$ follow from (3) – (6). Many optimization criteria are possible, for instance:

- minimizing the "length" of Fourier image of the pseudopotential;
- minimizing the integrated curvature;
- minimizing the depth of the pseudopotential.

As an example we show results of pseudopotential optimization for the nitrogen atom and minimize the initial pseudopotential curvature

$$\Theta_0(V_{E,l}^{\mathrm{PS}}(\boldsymbol{a}, \boldsymbol{\rho}, r)) \equiv |\frac{\partial^2}{\partial r^2}(V_{E,l}^{\mathrm{PS}})(\boldsymbol{a}, \boldsymbol{\rho}, 0))| . \tag{8}$$

This atom has 7 electrons in three sub-shells 1s: 2, 2s: 2, 2p: 3, with energies $E_{1s2} \approx -14.01$, $E_{2s2} \approx -0.676$, $E_{2p3} \approx -0.266$ (in atomic units). The pseudopotentials were generated for the valence states 2s ($l = 0$), 2p ($l = 1$) as well as for the first unoccupied state 3d ($l = 2$) with $E_{3d0} \approx 0.018$. The initial parameters were $\boldsymbol{\rho} = [0.5, 0.7, 1.4, 1.3]^T$. For the optimization, the L-BFGS-B solver from SciPy [3] was used: it allowed specifying additional box constraints: $0.001 < \{\rho_1, \rho_2\} < 1.1$, $1.11 < \{\rho_3, \rho_4\} < 2$ to prevent linearly dependent basis functions. The results are summarized in Fig. 1. Adhering (3) – (6), the pseudofunctions are equal to the all-electron wavefunctions outside the cut-off radius $R_c = 1.5$ (Fig. 1a). The optimized pseudopotentials (orange curves in Fig. 1b-d) are equal to all-electron potentials (green curves) outside R_c and are shallower and smoother than the ones obtained for the initial setting of parameters (blue curves), and thus more numerically suitable for electronic structure calculations.
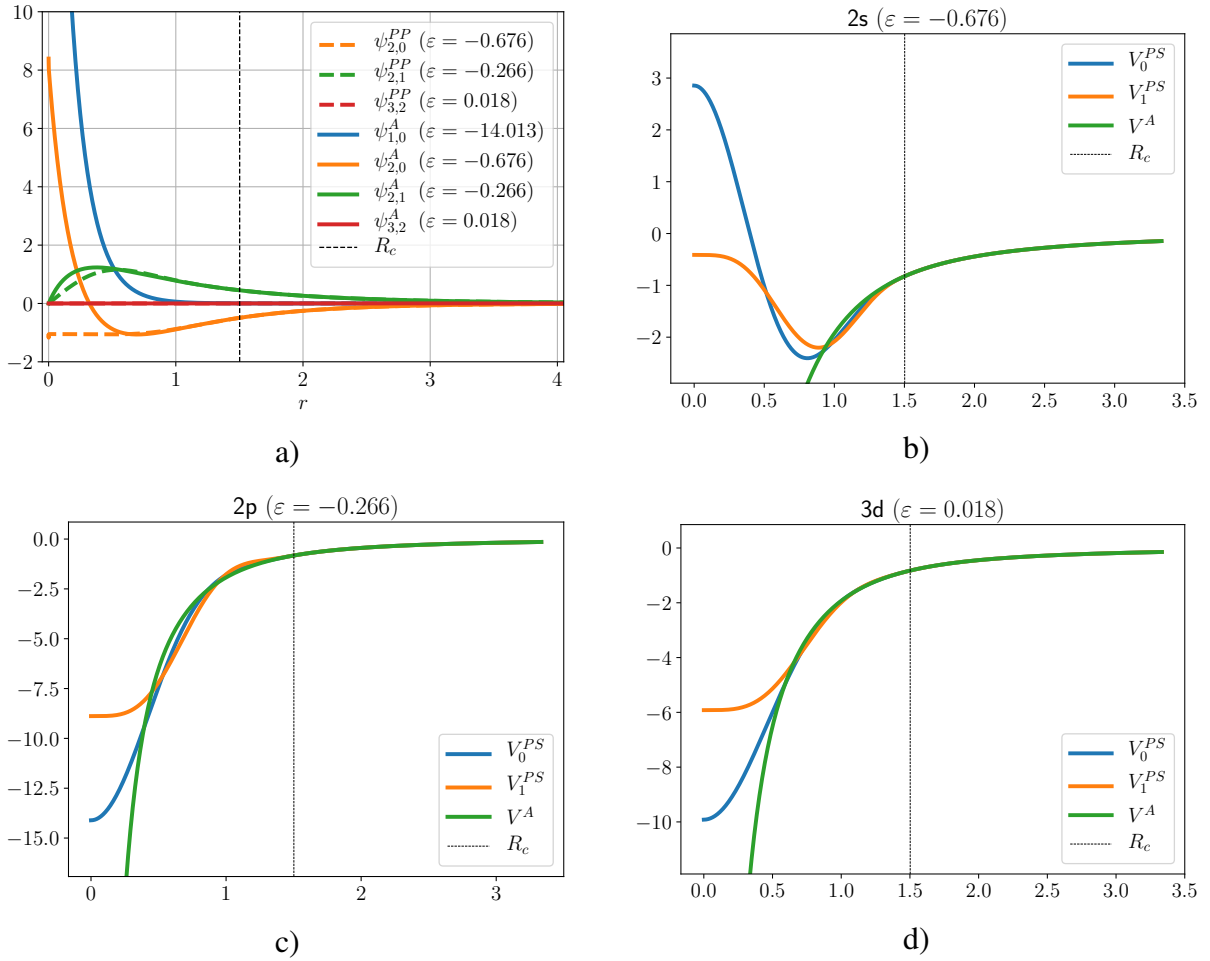
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Fig. 1. The pseudopotential optimization results: a) comparison of the all-electron wavefunctions (solid) and the corresponding pseudofunctions (dashed); b) the initial (blue) and optimized (orange) pseudopotentials compared with the all-electron potential (green) for the state 2s, c) for the state 2p and d) for the state 3d. The cut-off radius $R_c = 1.5$ is denoted by the vertical line.

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