

Mixed-basis (semi-empirical) pseudopotential method

Tyler C. Sterling^{1,2,*} and Dmitry Reznik^{1,2}

¹*Department of Physics, University of Colorado at Boulder, Boulder, Colorado 80309, USA*

²*Center for Experiments on Quantum Materials,
University of Colorado at Boulder, Boulder, Colorado 80309, USA*

(Dated: August 25, 2021)

This is a **work-in-progress** document where I am keeping notes for a project I am working on. I am writing a density functional theory (DFT) package that will use a combination of atom-centered Gaussian functions and plane-waves (PW) as the basis-set. The atom-cores will be replaced with a *semi-empirical* pseudopotential. Semi-empirical, in this context, means that I will treat the pseudopotentials as fitting parameters. I plan to fit bands calculated from my code to all-electron (or other high quality) DFT calculations. This is really no more 'empirical' than the typical ab-initio pseudopotential method which involves fitting the pseudopotential for the isolated atom to all-electron calculations. The ab-initio pseudopotential is more ab-initio in the sense that it does not depend on the atom's environment and can be 'plugged-in' to any crystal. (Well, not really: there has been considerable effort in making them as *transferable* as possible). In my case, the *semi-empirical* pseudopotentials will be fit so that the smallest basis set possible can be used in a particular configuration and still reproduce the ab-initio band structure. Think of it like a tight-binding method, but instead of throwing away all the bonus multi-center integrals, I keep everything and work in reciprocal space. There are 2 primary reasons behind this project: (1) I want to learn more about writing a DFT code and there is no better way than writing a DFT code. (2) If this works well and is efficient, the pseudopotentials and even the SCF potential can be plugged into larger supercell models that include electron-phonon coupling explicitly. I hope this works ...

CONTENTS

I. Introduction	2
References	2

* ty.sterling@colorado.edu

I. INTRODUCTION

This is a **work-in-progress** document where I am keeping notes for a project I am working on. I am writing a density functional theory (DFT) package that will use a combination of atom-centered Gaussian functions and plane-waves (PW) as the basis-set. This is the so called *mixed-basis pseudopotential method* [1].

The atom-cores will be replaced with a *semi-empirical* pseudopotential. Semi-empirical, in this context, means that I will treat the pseudopotentials as fitting parameters. I plan to fit bands calculated from my code to all-electron (or other high quality) DFT calculations. This is really no more 'empirical' than the typical ab-initio pseudopotential method which involves fitting the pseudopotential for the isolated atom to all-electron calculations. The ab-initio pseudopotential is more ab-initio in the sense that it does not depend on the atom's environment and can be 'plugged-in' to any crystal. (Well, not really: there has been considerable effort in making them as *transferable* as possible). In my case, the *semi-empirical* pseudopotentials will be fit so that the smallest basis set possible can be used in a particular configuration and still reproduce the ab-initio band structure. Think of it like a tight-binding method, but instead of throwing away all the bonus multi-center integrals, I keep everything and work in reciprocal space.

The pseudopotentials will be non-local (i.e. angular momentum $l \neq 0$). Non-local pseudopotentials usually look like:

$$\hat{V}_{\tau}^{pp} = V_{\tau,0}(|\mathbf{r}|) + \sum_{l=1}^{l_c} V_{\tau,l}(|\mathbf{r}|) \hat{P}_l \quad (1)$$

Here, l denotes the orbital angular momentum quantum number, τ denotes the atom in the unitcell, and \hat{P}_l is a projector onto angular momentum character l . The radial functions $V_{\tau,l}(|\mathbf{r}|)$ are spherically symmetric. I will probably pick them to be Gaussians too since the matrix elements will be simple. Maybe this will be a bad idea, I don't know yet.

[1] S. G. Louie, K.-M. Ho, and M. L. Cohen, Self-consistent mixed-basis approach to the electronic structure of solids, Physical Review B **19**, 1774 (1979).