

Notes on atompaw 4.0.0.0

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Changes to *atompaw* introduced in Version 4.0.0.0

Among the changes are

1. A new option to control the shape of the radial pseudo wavefunction; keyword – MODRRKJ
2. A mechanism to “explore” ranges of radii and energy parameters of the the PAW dataset; keyword – EXPLORE

MODRRKJ

Among the most productive schemes for constructing PAW datasets are those based on the ideas of David Vanderbilt[1] designed for ultra-soft pseudopotentials. These are available in *atompaw* with the keyword VANDERBILT and are based on the following equations. In this scheme, the shape of the smooth basis functions are directly controlled, while the projector functions are derived from them. Each radial smooth function is chosen to have the form

$$\tilde{\phi}_{n_i l_i}(r) = \begin{cases} r^{l_i+1} \sum_{m=0}^4 C_m r^{2m} & \text{for } r < r_i \\ \phi_{n_i l_i}(r) & \text{for } r \geq r_i \end{cases} \quad (1)$$

where $\phi_{n_i l_i}(r)$ denotes the corresponding all-electron basis function. The matching radii $r_i \leq r_c$ are used to control the shapes. The 5 coefficients $\{C_m\}$ are chosen so that $\tilde{\phi}_{n_i l_i}(r) = \phi_{n_i l_i}(r)$ at 5 points in the neighborhood of r_i which is roughly equivalent to ensuring that the function at its first 4 derivatives match at r_i .

Another scheme to control the shape of the smooth basis functions was developed by Rappe, Rabe, Kaxiras, and Joannopoulos[2] which using spherical Bessel functions instead of polynomial functions. We have slightly modified the original idea in order to ensure the derived projector functions are also smooth and that we can control the desired number of nodes in the pseudowave function. The details of the scheme (keyword MODRRKJ) are as follows.

$$\tilde{\phi}_{n_i l_i}(r) = \begin{cases} \sum_q C_q^i r j_{l_i}(k_q r) & \text{for } r \leq r_i \\ \phi_{n_i l_i}(r) & \text{for } r > r_i \end{cases} \quad (2)$$

Again the matching radii are chosen $r_i \leq r_c$. The nodes are controlled by the choice of k_q . In practice, we choose 5 values of k_q :

$$k_q = k_0 + (q - 3)\delta k \quad \text{where } q = 1, 2, \dots, 5, \quad (3)$$

and where k_0 is chosen so that $k_0 r$ has the correct number of nodes in the range $0 \leq r \leq r_i$ and so that

$$\left. \frac{d(r j_{l_i}(k_0 r))/dr}{r j_{l_i}(k_0 r)} \right|_{r=r_i} = \left. \frac{d\phi_{n_i l_i}(r)/dr}{\phi_{n_i l_i}(r)} \right|_{r=r_i}. \quad (4)$$

In practice, $\delta k r_i \approx \pi/20$. The coefficients C_q^i are determined by fitting the spherical Bessel function expansion to the all-electron function at 5 radial points r_n points in the vicinity of r_i :

$$\sum_q C_q^i r_n j_{l_i}(k_q r_n) = \phi_{n_i l_i}(r_n). \quad (5)$$

In fact, because of the choice of k_0 , the set of linear equations has rank 4 and the solution is obtained with the help of “singular value decomposition” and using the 4 largest ”singular values”. We find that the resulting MODRRKJ pseudowavefunctions $\tilde{\phi}_{n_i l_i}(r)$ are very similar to those obtained with the VANDERBILT scheme. However, we expect that the MODRRKJ scheme may have slight convergence advantages. This expectation remains to be further investigated.

Along with the construction of the all-electron $|\phi_i\rangle$ and pseudo $|\tilde{\phi}_i\rangle$ basis functions, it is necessary to also construct the projector functions $|p_i\rangle$. Here we use the notation

$$|\phi_i\rangle \equiv \frac{\phi_{n_i l_i}}{r} Y_{m_i l_i}(\hat{\mathbf{r}}). \quad (6)$$

It is assumed that the basis functions $|\phi_i\rangle$ are eigenstates of the all-electron Hamiltonian \mathcal{H} :

$$\mathcal{H}|\phi_i\rangle = \epsilon_i|\phi_i\rangle. \quad (7)$$

The pseudo functions obey the following corresponding equations:

$$\left(\tilde{H} - \epsilon_k\right) |\tilde{\phi}_k\rangle = \sum_j |p_j\rangle \langle \tilde{\phi}_j | \tilde{H} - \epsilon_k | \tilde{\phi}_k\rangle. \quad (8)$$

The projector functions are related to the pseudobasis functions with the following identity:

$$\langle \tilde{\phi}_j | p_k\rangle = \delta_{jk}. \quad (9)$$

Given the pseudo basis functions $|\tilde{\phi}_i\rangle$ using the MODRRKJ scheme or other scheme, there are several choices on how to generate the projector functions $|p_i\rangle$.

Vanderbilt -type projector; keyword VANDERBILTORTHO

This method works well in most cases and is based on the original idea presented by Vanderbilt in the formulation of the ultra-soft pseudopotentials[1].

In this case, we construct the $n \times n$ matrix (where n denotes the number of basis functions for a particular l value):

$$M_{jk} \equiv \langle \tilde{\phi}_j | \tilde{H} - \epsilon_k | \tilde{\phi}_k\rangle. \quad (10)$$

Define the intermediate projector function:

$$|\pi_k\rangle \equiv \left(\tilde{H} - \epsilon_k\right) |\tilde{\phi}_k\rangle. \quad (11)$$

Then the projector function can be formed from the inverse of the M matrix:

$$|p_j\rangle = \sum_k |\pi_k\rangle (M^{-1})_{kj}. \quad (12)$$

Singular value decomposition -type projector; keyword SVDORTHO

In principle, this should be a more robust, in practice the projectors do not have an obviously recognizable shape and this option has not been thoroughly tested.

In this case we use the M matrix defined above, but first take its SVD construction:

$$M_{jk} = \sum_{\alpha} u_j^{\alpha} \sigma^{\alpha} v_k^{\alpha*}. \quad (13)$$

Here u_j^{α} and v_k^{α} denote components of orthogonal vectors and σ^{α} denotes a ‘‘singular value’’. We can define the composite projectors and basis functions

$$|p^{\alpha}\rangle \equiv \sum_j |p_j\rangle u_j^{\alpha} \quad (14)$$

and

$$|\tilde{\phi}^{\alpha}\rangle \equiv \sum_j |\tilde{\phi}_j\rangle u_j^{\alpha}. \quad (15)$$

The consistent formula for the composite projector function is:

$$|p^{\alpha}\rangle \equiv \frac{1}{\sigma^{\alpha}} \sum_j |\pi_j\rangle v_j^{\alpha}. \quad (16)$$

Gram-Schmidt orthogonalization -type projector; keyword GRAMSCHMIDTORTHO

In this case we build up the basis and projector functions by sequential orthonormalizations. Here we denote the original constructed functions with a superscript 0 . For the first set ($k = 1$) we have

$$|\tilde{\phi}_1\rangle = |\tilde{\phi}_1^0\rangle \quad |p_1\rangle = \frac{|\pi_1\rangle}{\langle \tilde{\phi}_1 | \pi_1 \rangle}. \quad (17)$$

For the second set ($k = 2$) we have

$$|\tilde{\phi}_2\rangle = \left(|\tilde{\phi}_2^0\rangle - |\tilde{\phi}_1\rangle \langle \tilde{\phi}_2^0 | p_1 \rangle \right). \quad (18)$$

$$|p_2\rangle = \mathcal{N} \left(|\pi_2\rangle - |p_1\rangle \langle \tilde{\phi}_1 | \pi_2 \rangle \right). \quad (19)$$

Here the normalization factor \mathcal{N} are set by the normalization condition.

$$\langle \tilde{\phi}_2 | p_2 \rangle = 1 = \mathcal{N} \left(\langle \tilde{\phi}_2^0 | \pi_2 \rangle - \langle \tilde{\phi}_2^0 | p_1 \rangle \langle \tilde{\phi}_1 | \pi_2 \rangle \right). \quad (20)$$

If additional basis/projector functions are needed, the process is continued.

EXPLORE

A large number of collaborators including Alan Tackett and Greg Walker from Vanderbilt University, Alan Wright from Sandia National Laboratory, Qi Li from Wake Forest University, have helped us realize that the choosing of pseudopotential parameters (augmentation radii r_c , matching radii r_i , continuum basis energies ϵ_i) is a multi-dimensional optimization problem that can be helped with notions computer-aided design. Toward that idea, we have implemented an ‘‘EXPLORE’’ option in running atompaw to scan through many choices of parameters. In order to

```

Al 13
LDA-PW loggrid 2001
3 3 0 0 0
3 1 1
0 0 0
c
c
v
c
v
All-electron solver

2
2.2 2.0 2.2 2.2
y
6.4
n
y
7.1
n
y
0.5
y
7
n
MODRRKJ VANDERBILTORTHO Besselshape
3 0 MTRULLIER
2.2
2.2
2.2
2.2
2.2
2.2
Pseudo function parameters

ABINITOUT
default
XMLOUT
default
PWSCFOUT
UPFDX 0.0125d0 UPFXMIN -7.d0 UPFZMESH 13.d0
END
Output dataset

```

Figure 1: Typical input file for *atompaw*.

explain how this works we first consider the form of the *atompaw* input file. For normal usage, the file can be described in 3 parts as shown in Fig. 1; a section for the all-electron atom, a section for constructing the pseudopotentials, and a section for generating outputs for the various solid codes.

The section setting the pseudopotential parameters generally has many choices. In the “EXPLORE” mode the input file would have the form shown in Fig. 2. There are several possible criteria for choosing the best parameters set. The easiest to study is the comparison of the logderivative of the all-electron and pseudo wavefunctions. In particular we record the logderivative “error” defined according to

$$\epsilon_l \equiv \left| \tan^{-1} \left(\frac{d\phi_{n_l l_l}}{dr} \right) - \tan^{-1} \left(\frac{d\tilde{\phi}_{n_l l_l}}{dr} \right) \right|_{r_c}. \quad (21)$$

Choosing the parameter set with the smallest values of ϵ_l can result in good PAW datasets; unfor-

```

Al 13
LDA-PW loggrid 2001
3 3 0 0 0
3 1 1
0 0 0
All-electron solver
c
c
v
c
v

```

Initial pseudo function parameters

```

EXPLORE
1000 5

```

Pseudo function parameters #1

Pseudo function parameters #2

Pseudo function parameters #3

Pseudo function parameters #4

Pseudo function parameters #5

Pseudo function parameters #1000

```

END

```

Figure 2: Input file for *atompaw* for the “EXPLORE” mode.

tunately, this criterion alone does not *necessarily* screen against possible ghost states.

References

- [1] David Vanderbilt. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Physical Review B*, 41(11):7892, 1990.
- [2] Andrew M. Rappe, Karin M. Rabe, Efthimios Kaxiras, and J. D. Joannopoulos. Optimized pseudopotentials. *Physical Review B*, 41(2):1227, 1990.