

# Notes for revised form of *atompaw* code.

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For some of the materials (such as SiC), we noticed that our scheme of constructing the PAW functions give incorrect lattice constants. One possible reason for this systematic error is our previous choice of for  $\tilde{v}_{\text{loc}}(r)$  which is very good for avoiding ghost states[1, 2] but which does a very poor job of describing high angular momentum components in the augmentation sphere. Therefore we, have now introduced an option of constructing  $\tilde{v}_{\text{loc}}(r)$  using a norm-conserving pseudopotential[3] approach. The idea is that in this way, the local potential can be constructed to force the good representation of partial wave components with the chosen angular momentum  $L_v$ . The partial wave components with smaller angular momentum will be represented with the non-local terms in the usual PAW construction. This is by no means a new idea and was inspired by David Vanderbilt's webpage on soft-pseudopotential generation <http://www.physics.rutgers.edu/~dhv/uspp/>.

The main equations describing the method are as follows.  $L_v$  represents the angular momentum chosen for constructing the norm-conserving (screened) pseudopotential. The pseudowavefunction is chosen to have the form:

$$\tilde{\phi}(r) = \begin{cases} r^{L_v+1} f(r) & \text{for } r \leq r_c \\ \phi(r) & \text{for } r > r_c. \end{cases} \quad (1)$$

Here  $\phi(r)$  represents a chosen continuum wavefunction of the all-electron Hamiltonian at energy  $E$ . The function  $f(r)$  is chosen to be one of the following types:

$$f(r) = e^{p(r)} \quad \text{keyword : EXPF.} \quad (2)$$

$$f(r) = p(r) \quad \text{keyword : POLY.} \quad (3)$$

In both cases,  $p(r)$  represents a polynomial of the form

$$p(r) = C_0 + C_1 r^{m_1} + C_2 r^{m_2} + C_3 r^{m_3} + C_4 r^{m_4}, \quad (4)$$

where the  $\{C_i\}$ 's represent coefficients to be determined to satisfy 5 matching conditions and the  $\{m_i\}$ 's represents polynomial powers chosen by the user. The exponential form was that presented in the original paper of Kerker[3], while the polynomial form allows additional flexibility.

For the EXPF form, the screened norm-conserving pseudopotential can be determined from

$$V^{PS}(r) = E + \frac{\hbar^2}{2m} \left( \frac{d^2 p}{dr^2} + \frac{dp}{dr} \left( \frac{dp}{dr} + \frac{2(L_v + 1)}{r} \right) \right). \quad (5)$$

For the POLY form, the screened norm-conserving pseudopotential can be determined from

$$V^{PS}(r) = E + \frac{\hbar^2}{2m} \frac{1}{p(r)} \left( \frac{d^2 p}{dr^2} + \frac{2(L_v + 1)}{r} \frac{dp}{dr} \right). \quad (6)$$

In both cases the 5 matching conditions which determine the coefficients  $\{C_i\}$  require that  $\tilde{\phi}(r)$  and its first 3 derivatives are continuous at  $r_c$  in addition to the norm-conserving condition:

$$\int_0^{r_c} dr |\tilde{\phi}(r)|^2 = \int_0^{r_c} dr |\phi(r)|^2. \quad (7)$$

Once the screen pseudopotential is constructed, the PAW functions can be constructed in the usual way. For example, we must solve for the smooth functions according to the equations

$$\left(\tilde{H}(\mathbf{r}) - \varepsilon_i\right) |\tilde{\phi}_i^0(\mathbf{r})\rangle = C_i k(r) |\tilde{\phi}_i^0(\mathbf{r})\rangle, \quad (8)$$

where  $k(r)$  is the chosen shape function. Note: the shape function  $k(r)$  which is also used to determine the shapes of the compensation charge density  $\hat{n}(r)$  is taken to have the squared sinc function shape:

$$k(r) = \begin{cases} \left(\frac{\sin(\pi r/r_c)}{\pi r/r_c}\right)^2 & \text{for } r \leq r_c \\ 0 & \text{for } r > r_c \end{cases}, \quad (9)$$

since we have found this shape to have much better convergence properties than other forms such as the Gaussian form.

The Hamiltonian is

$$\tilde{H}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V^{PS}(r). \quad (10)$$

Once the smooth basis functions  $\{|\tilde{\phi}_i^0(\mathbf{r})\rangle\}$  are determined and the smooth density  $\tilde{n}(r)$  and compensation charge density  $\hat{n}(r)$  are constructed, the local potential term can be determined according to

$$\tilde{v}_{\text{loc}}(r) = V^{PS}(r) - e^2 \int d^3r' \frac{\tilde{n}(r') + \hat{n}(r')}{|\mathbf{r} - \mathbf{r}'|} - \mu_{\text{xc}}[\tilde{n}(r)]. \quad (11)$$

The output of this new *atompaw* code is very similar to that of the old code with some additional diagnostic files. However, the [atom].atomicdata file that is read by the *pwpaw* program now lists the radial form of  $v_{\text{loc}}(r)$  using the keyword “VLOCFUN”. This required a very minor change in the *pwpaw* code (which can also read the old form of [atom].atomicdata).

## References

- [1] Xavier Gonze, Peter Käckell, and Matthias Scheffler. Ghost states for separable, norm-conserving, *ab initio* pseudopotentials. *Phys. Rev. B*, 41:12264–12267, 1990.
- [2] Xavier Gonze, Roland Stumpf, and Matthias Scheffler. Analysis of separable potentials. *Phys. Rev. B*, 44:8503–8513, 1991.
- [3] G. P. Kerker. Non-singular atomic pseudopotentials for solid state applications. *J. Phys. C: Solid St. Phys.*, 13:L189–L194, 1980.