NCPP for Si(LDA)

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1 Algorithms and implementing details

$$R_l^{PP}(r) = \begin{cases} R_l^{AE}(r), r \geq r_{cl} \\ r^l \exp{[p(r)]}, r \leq r_{cl} \end{cases}$$

Kerker pseudopotential:

$$p(r) = c_0 + c_2 r^2 + c_3 r^3 + c_4 r^4$$

Troullier-Martins pseudopotential:

$$p(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12}$$

For both PPs, we define $P(r) = rR_l^{AE}(r)$ and V_{AE} being the all-electron atomic screened potential. In Kerker PP, the parameters are solved from the following equations:

$$\int_0^{r_{cl}} r^{2(l+1)} \exp{[2p(r)]} \mathrm{d}r = \int_0^{r_{cl}} |R_l^{AE}(r)|^2 r^2 \mathrm{d}r,$$

$$p(r_{cl}) = \ln\left[\frac{P(r_{cl})}{r_{cl}^{l+1}}\right],$$

$$p'(r_{cl}) = \frac{P'(r_{cl})}{P(r_{cl})} - \frac{l+1}{r_{cl}},$$

$$p''(r_{cl}) = \frac{P''(r_{cl})P(r_{cl}) - [P'(r_{cl})]^2}{P^2(r_{cl})} + \frac{l+1}{r_{cl}^2}.$$

Note that the fourth equation contains the second derivative of $P(r_{cl})$, which is numerical unstable. By utilizing radical Kohn-Sham equation, we can express the additional equations for Troullier-Martins pesudopotential as follows:

$$p''(r_{cl}) = 2V_{AE}(r_{cl}) - 2\epsilon_l - \frac{2(l+1)}{r_{cl}} p'(r_{cl}) - [p'(r_{cl})]^2,$$

$$p'''(r_{cl}) = 2V'_{AE} + \frac{2(l+1)}{r_{cl}^2}p'(r_{cl}) - \frac{2(l+1)}{r_{cl}}p''(r_{cl}) - 2p'(r_{cl})p''(r_{cl}),$$

$$p''''(r_{cl}) = 2V''_{AE}(r_{cl}) - \frac{4(l+1)}{r_{cl}^3}p'(r_{cl}) + \frac{4(l+1)}{r_{cl}^2}p''(r_{cl}) - \frac{2(l+1)}{r_{cl}}p'''(r_{cl}) - 2\left[p''(r_{cl})\right]^2 - 2p'(r_{cl})p'''(r_{cl}),$$

$$c_2^2 + c_4(2l+5) = 0.$$

Except the norm conserving equation and the last equation, all the equations are linear and can be trivially solved with Gauss-Jordan elimination. By substituting the the relationship of the parameters into the remaining non-linear equations, they can be solved with false method and bisection methods respectively.

A remaining problem is to acquire the derivatives of $P(r_{cl})$, because the output of all electron function is discrete. Typically, numerical differentiation can be used to estimate the derivatives from a discrete function, for instance

$$f'_{(x_0)} \approx \frac{1}{12h}\left[f(x_0-2h) - 8f(x_0-h) + 8f(x_0+h) - f(x_0+2h)\right] + \frac{h^4}{39}f^{(5)}(\xi)$$

where $\xi \in [x_0-2h, x_0+2h]$. The second derivative can be derived from the first. However, with the logarithmic grid, the intervals of the data points are unequal which means the traditional method is just a approximation.

2 Results

The coefficients are given as follows:

$$p(r) = c_0 + c_2r^2 + c_3r^3 + c_4r^4$$

$$3p : c_0 = -1.7741\ c_2 = 1.1831\ c_3 = -0.7857\ c_4 = 0.1344$$

$$3s : c_0 = -2.4342\ c_2 = 3.4798\ c_3 = -2.3994\ c_4 = 0.4617$$

$$2p : c_0 = 1.6586\ c_2 = 0.4391\ c_3 = -15.488\ c_4 = 17.431$$

$$2s : c_0 = -1.4273\ c_2 = 43.501\ c_3 = -117.317\ c_4 = 88.408$$

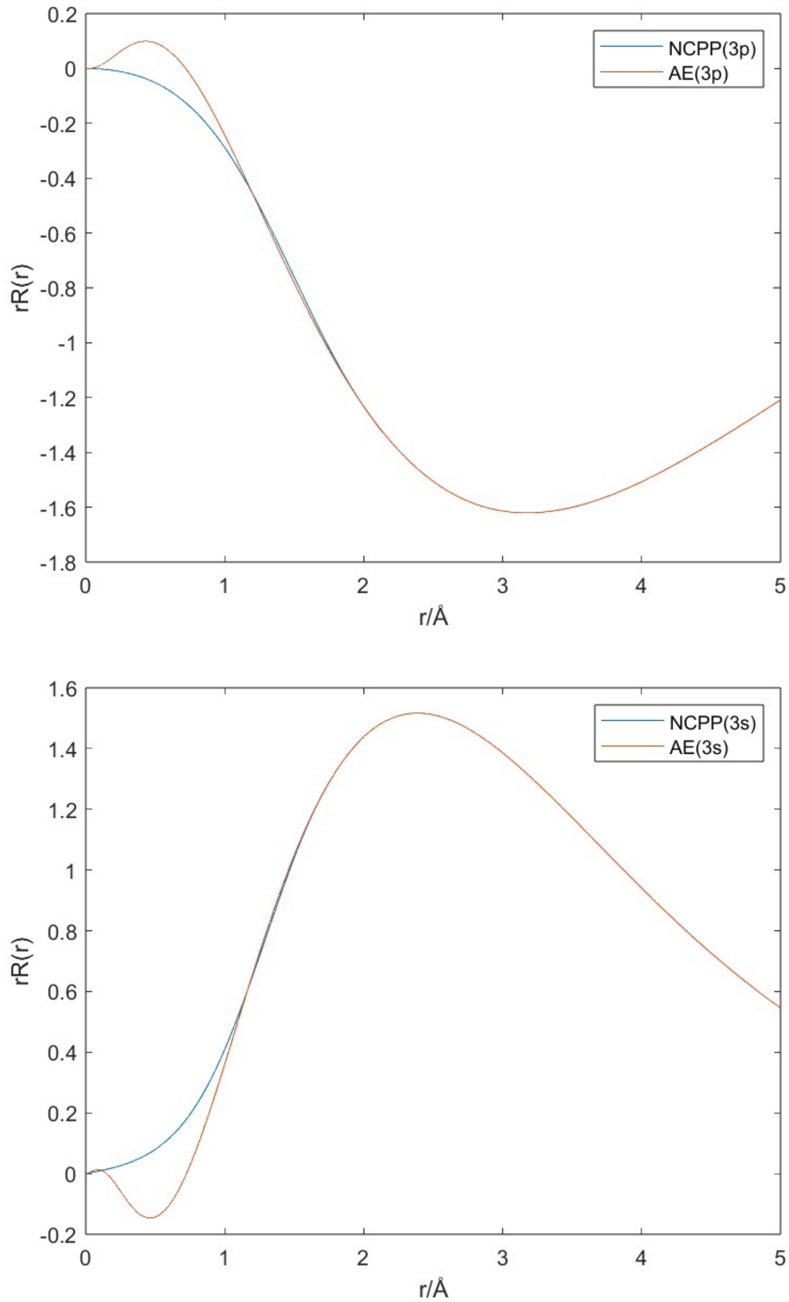

Figure 1: NCPP and AE of 3p and 3s orbital of Si

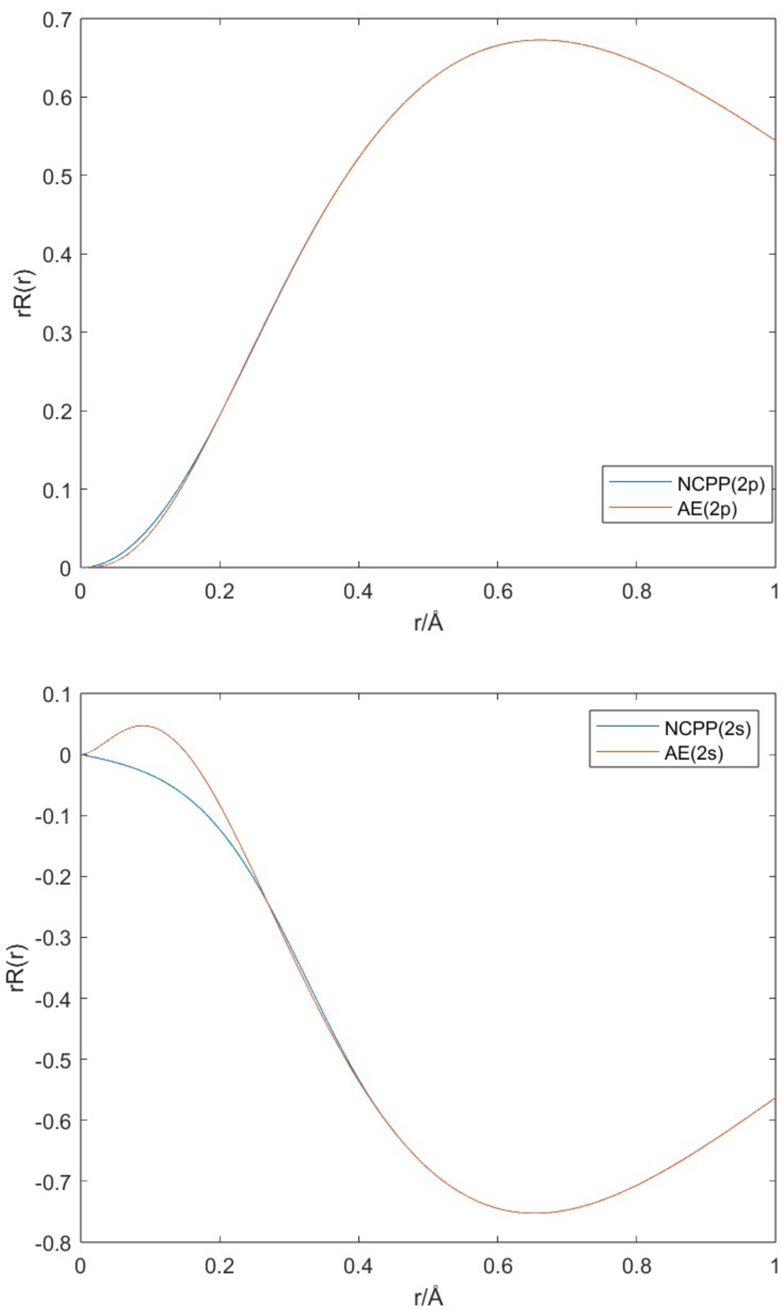

Figure 2: NCPP and AE of 2p and 2s orbital of Si