PAW Notes

ffr

Ultrasoft pseudopotential is fully determined by the quantities:

- $V_{\rm loc}^{I}(r)$
- $D_{nm,I}^{(0)}$
- $Q_{nm,I}(\mathbf{r})$
- $\beta_n^I(\mathbf{r})$

Nonlocal operator:

$$V_{\rm NL} = \sum_{nm,I} D_{nm}^{(0)} |\beta_n^I\rangle\langle\beta_m^I|$$

n, m: beta func indices

$\beta_n^I(\mathbf{r}) = \beta_n(\mathbf{r} - \mathbf{R}_I)$

Electron density:

$$n(\mathbf{r}) = \sum_i \left[|\psi_i(\mathbf{r})|^2 + \sum_{nm,I} Q_{nm}^I(\mathbf{r}) \langle\psi_i|\beta_n\rangle\langle\beta_m|\psi_i\rangle \right]$$

Orthonormality conditions:

$$\langle \psi_i | S | \psi_j \rangle = \delta_{ij}$$

overlap operator:

$$S = 1 + \sum_{nm,I} q_{nm} \, |\beta_n^I\rangle\langle\beta_m^I|$$

$$q_{nm} = \int Q_{nm}(\mathbf{r}) \, \mathrm{d}\mathbf{r}$$

KS equation:

$$H\left|\psi_i\right\rangle = \epsilon_i S\left|\psi_i\right\rangle$$

Hamiltonian operator:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V_{\mathrm{eff}} + \sum_{nm,I} D^I_{nm}\left|\beta^I_n\right\rangle\left\langle\beta^I_m\right|$$

Screened coefficients:

$$D^I_{nm} = D^{(0)}_{nm} + \int V_{\mathrm{eff}}(\mathbf{r})\, Q^I_{nm}(\mathbf{r})\,\mathrm{d}\mathbf{r}$$

$$E = \sum_n f_n \left\langle \psi_n \middle| -\frac{1}{2}\nabla^2 \middle| \psi_n \right\rangle + E_{\mathrm{H}}\left[n + n_Z\right] + E_{\mathrm{xc}}\left[n\right]$$

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle \tilde{p}_i | \tilde{\psi}_n \rangle$$

Index i: atomic site $\mathbf{R}$, angular momentum $L = (l, m)$, and additional index k for reference energy ϵ_{kl}.

AE partial waves ϕ_i are obtained for a reference atom

PS partial waves $\tilde{\phi}_i$ are equivalent to the AE partial waves outside a core radius r_c^l and match continuously onto $\tilde{\phi}_i$ inside the core radius.

Projector functions $\tilde{p}_i$ are dual to the partial waves:

$$\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij}$$

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r})$$

$$\tilde{n}(\mathbf{r}) = \sum_n f_n \langle \tilde{\psi}_n | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\psi}_n \rangle$$

Onsite electron densities n^1 and $\tilde{n}^1$ are treated on a radial support grid, that extends up to r_{rad} around each ion.

$$n^1(\mathbf{r}) = \sum_{i,j} \rho_{ij} \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle$$

$$\tilde{n}^1(\mathbf{r}) = \sum_{i,j} \rho_{ij} \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle$$

ρ_{ij} are the occupancies of each augmentation channel (i, j):

$$\rho_{ij} = \sum_n f_n \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_i | \tilde{\psi}_n \rangle$$

Assuming frozen core approximation.

Introduce four quantities that will be used for the description of the core charge density:

n_c: charge density of frozen core all-electron wave functions in the reference atom.

$\tilde{n}_c$: partial electronic core density $\tilde{n}_c$ is equivalent to the frozen core AE charge density outside a certain radius r_{pc}, which lies inside the argumentation radius. Used in order to calculate nonlinear core corrections

n_{Zc}: point charge density of the nuclei n_Z plus the frozen core AE charge density n_c:

$$n_{Zc} = n_Z + n_c$$

$\tilde{n}_{Zc}$: pseudized core density, equivalent to n_{Zc} outside the core radius and shall have the same moment as n_{Zc} inside the core region:

$$\int_{\Omega_r} n_{Zc}(\mathbf{r})\,\mathrm{d}\mathbf{r} = \int_{\Omega_r} \tilde{n}_{Zc}(\mathbf{r})\,\mathrm{d}\mathbf{r}$$