Report 1: Methods to Compute Pseudopotential

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1 Introduction to pseudopotential

A pseudopotential (effective potential) is used as an approximation for the simplified description of complex systems. For example, replacing the complex core elections and nucleus inside an atomic with a simplified potential V_{pseudo} so that Schrödinger equation contains a modified effective potential term instead of the Coulombic potential term for core electrons normally found in the Schrödinger equation. In this way the core states are eliminated and the valence elections are described by pseudo-wavefunctions ψ_{pseudo} with significantly fewer nodes. And because the core electrons are usually more local, so require more higher energy plane waves in the basis set, which means higher cutoff energy $E_{cut} = \frac{\hbar^2 G_{cut}^2}{2m}$. With pseudopotential we can ignore these so valence elections + pseudopotential are much more efficient than considering all electrions.

First-principles pseudopotentials are derived from an atomic reference state, requiring that the pseudo and all electron valence eigenstates have the same energies and amplitude (and thus density) outside a chosen core cut-off radius r_c. And thus there are two approximation:

1. It's a picture of one election,

2. The small-core approximation assumes that there is no significant overlap between core and valence wavefunction.

2 Pseudopotentials

Norm-conserving and ultrasoft are the two most common forms of pseudopotential used in modern plane-wave electronic structure codes. They allow a basis-set with a significantly lower cut-off (the frequency of the highest Fourier mode) to be used to describe the electron wavefunctions and so allow proper numerical convergence with reasonable computing resources.

2.1 Norm-conserving pseudopotential

Norm-conserving pseudopotential was first proposed by Hamann, Schlüter, and Chiang (HSC) in 1979. The original HSC norm-conserving pseudopotential takes the following form:

$$\hat{V}_{ps}(r) = \sum_l \sum_m |Y_{lm}\rangle V_{lm}(r) \langle Y_{lm}| \tag{1}$$

where $|Y_{lm}\rangle$ projects a one-particle wavefunction, such as one Kohn-Sham orbital, to the angular momentum labeled by $\{l, m\}$. $V_{lm}(r)$ is the pseudopotential that acts on the projected component. Different angular momentum states then feel different potentials, thus the HSC norm-conserving pseudopotential is non-local, in contrast to local pseudopotential which acts on all one-particle wave-functions in the same way. Norm-conserving pseudopotentials are constructed to enforce two conditions:

1. Inside the cut-off radius r_c, the norm of each pseudo-wavefunction be identical to its corresponding all-electron wavefunction:

$$\int_0^{r_c} dr^3 \phi_{\mathbf{R},i}(\vec{r}) \phi_{\mathbf{R},j}(\vec{r}) = \int_0^{r_c} dr^3 \tilde{\phi}_{\mathbf{R},i}(\vec{r}) \tilde{\phi}_{\mathbf{R},j}(\vec{r}) \tag{2}$$

where $\phi_{\mathbf{R},i}$ and $\tilde{\phi}_{\mathbf{R},i}$ are the all-electron and pseudo reference states for the pseudopotential on atom $\mathbf{R}$.

2. All-election and pseudo wavefunctions are identical outside cutoff radius r_c.