Projector-Augmented Wave Method

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A presentation prepared for: CSCI699, Spring 2018
PAW Transformation theory

Transform physical wave functions $\Psi(r)$ onto auxiliary wave functions $\tilde{\Psi}(r)$

$$\tilde{\Psi}(r) = \hat{U} \Psi(r)$$

Goal: Smooth auxiliary wave functions $\tilde{\Psi}(r)$ that can be represented in a plane wave expansion
PAW Transformation theory

- start with **auxiliary wave functions** $\tilde{\Psi}_n(r)$
- define **transformation operator** $\hat{T} = \hat{U}^{-1}$

$$\Psi_n(r) = \hat{T} \tilde{\Psi}_n(r) \iff \tilde{\Psi}_n(r) = \hat{U} \Psi_n(r)$$

that maps the auxiliary wave functions $\tilde{\Psi}_n(r)$ onto true wave functions $\Psi_n(r)$

- express **total energy** by auxiliary wave functions

$$E = E[\Psi_n(r)] = E[\hat{T} \tilde{\Psi}_n(r)]$$

- **Schrödinger-like equation** for auxiliary functions

$$\frac{\partial E}{\partial \tilde{\Psi}_n^*(r)} = \left( \mathcal{T}^\dagger H \mathcal{T} - \mathcal{T}^\dagger \mathcal{T} \epsilon_n \right) \tilde{\Psi}_n(r) = 0$$
Find a transformation $\hat{T}$ so, that the auxiliary wave function are well behaved

$$\tilde{\Psi}_n(r) \rightarrow \Psi_n(r) = \hat{T}\tilde{\Psi}_n(r)$$
Requirements for a suitable transformation operator

- the relevant wave functions shall be transformed onto numerically convenient auxiliary wave functions

\[ \tilde{\Psi}_n(\vec{r}) = \sum_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} \tilde{\Psi}_n(\vec{G}) \]

- linear (algebraic operations)
- local (no interaction between sites)

\[ \mathcal{T} = 1 + \sum_{R} S_R \]
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PAW Transformation operator II

Find a closed expression for the transformation operator

\[ \mathcal{T} = 1 + \sum_{R} S_R \]

Derivation:

\[ \left| \phi_i \right\rangle = \left| \phi_i \right\rangle + S_{R_i} \left| \tilde{\phi}_i \right\rangle _{T\left| \tilde{\phi}_i \right\rangle} \]

\[ \Rightarrow S_{\tilde{\phi}_i} = \left| \phi_i \right\rangle - \left| \tilde{\phi}_i \right\rangle = \sum_{j} \left( \left| \phi_j \right\rangle - \left| \tilde{\phi}_j \right\rangle \right) \langle \tilde{p}_j | \tilde{\phi}_i \rangle_{\delta_{i,j}} \]

\[ \Rightarrow \mathcal{T} = 1 + \sum_{j} \left( \left| \phi_j \right\rangle - \left| \tilde{\phi}_j \right\rangle \right) \langle \tilde{p}_j | \right. \]

\[ \left. \underbrace{S_{R_i}}_{\mathcal{T}} \right| \tilde{\phi}_i \rangle \]
Projector functions $\langle \tilde{p}_i |$ 

- must be localized within its own augmentation region 
- obey bi-orthogonality condition 
  
  $\langle \tilde{p}_i \mid \tilde{\phi}_j \rangle = \delta_{i,j}$ 

- projector functions $\langle \tilde{p} |$ are not yet uniquely determined: closure relation will be explained later
PAW Projector functions $\langle \tilde{p}_i \rangle$

s-type projector functions

p-type projector functions

d-type projector function

Projector functions probe the character of the wave function
Reconstruction of the true wave function

Using the transformation operator

$$\mathcal{T} = 1 + \sum_j \left( |\phi_j\rangle - |\tilde{\phi}_j\rangle \right) \langle \tilde{\rho}_j |,$$

the all-electron wave function obtains the form:

$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_j \left( |\phi_j\rangle - |\tilde{\phi}_j\rangle \right) \langle \tilde{\rho}_j |\tilde{\Psi}_n\rangle$$
PAW Augmentation

Example: $p\sigma$ orbital of $\text{Cl}_2$

$$|\Psi\rangle = |\tilde{\Psi}\rangle + |\Psi^1\rangle - |\tilde{\Psi}^1\rangle = |\tilde{\Psi}\rangle + \sum_i \left( |\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle \tilde{\rho}_i | \tilde{\Psi} \rangle$$

Applies to all quantities
The auxiliary Hamiltonian

effective Schrödinger-like equation for auxiliary wave functions

\[
\left( \tilde{H} - \epsilon_n \tilde{O} \right) |\tilde{\Psi}_n\rangle = 0
\]

where

\[
\tilde{H} = T^\dagger HT = -\frac{1}{2} \nabla^2 + \tilde{v} + \sum_{i,j} |\tilde{p}_i\rangle h_{i,j} \langle \tilde{p}_j|
\]

\[
\tilde{O} = T^\dagger T = 1 + \sum_{i,j} |\tilde{p}_i\rangle o_{i,j} \langle \tilde{p}_j|
\]

have the form of a separable pseudopotential

\( h_{i,j} \) and \( o_{i,j} \) have closed expressions

\[
h_{i,j} = \langle \phi_i | - \frac{1}{2} \nabla^2 + v | \phi_j \rangle - \langle \tilde{\phi}_i | - \frac{1}{2} \nabla^2 + \tilde{v} | \tilde{\phi}_j \rangle
\]

\[
o_{i,j} = \langle \phi_i | \phi_j \rangle - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle
\]
• solve the self-consistent Schrödinger equation to get the PS wave function to minimize the total energy functional
Thanks