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 auxilary wave functions $\tilde{\Psi}(r)$

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

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

PAW Transformation theory

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

$$\Psi_n(r) = \hat{\mathcal{T}}\tilde{\Psi}_n(r) \quad \Longleftrightarrow \quad \tilde{\Psi}_n(r) = \hat{\mathcal{U}}\Psi_n(r)$$

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

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

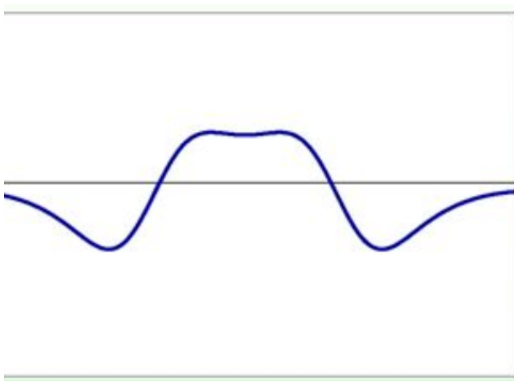
$$E = E[\Psi_n(r)] = E[\hat{\mathcal{T}}\tilde{\Psi}_n(r)]$$

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

$$\frac{\partial E}{\partial \tilde{\Psi}_n^*(r)} = \left(\mathcal{T}^\dagger H \mathcal{T} - \mathcal{T}^\dagger \mathcal{T} \epsilon_n\right)\tilde{\Psi}_n(r) \; = \; 0$$

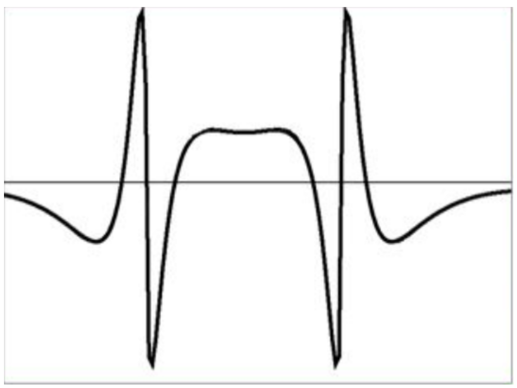
Find a transformation $\hat{\mathcal{T}}$ so,
that the auxiliary wave function are well behaved

$\tilde{\Psi}_n(r)$



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

$\Psi_n(r)$



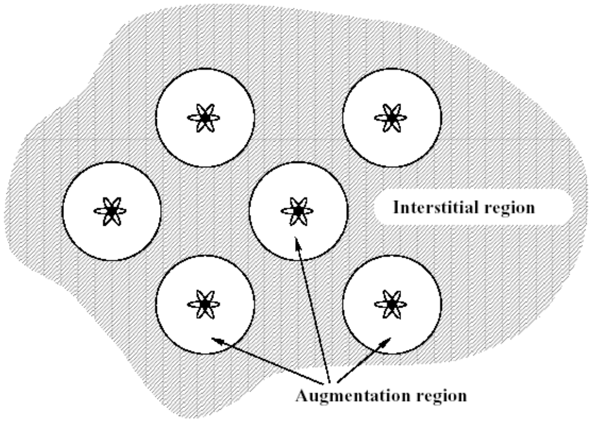
Requirements for a suitable transformation operator

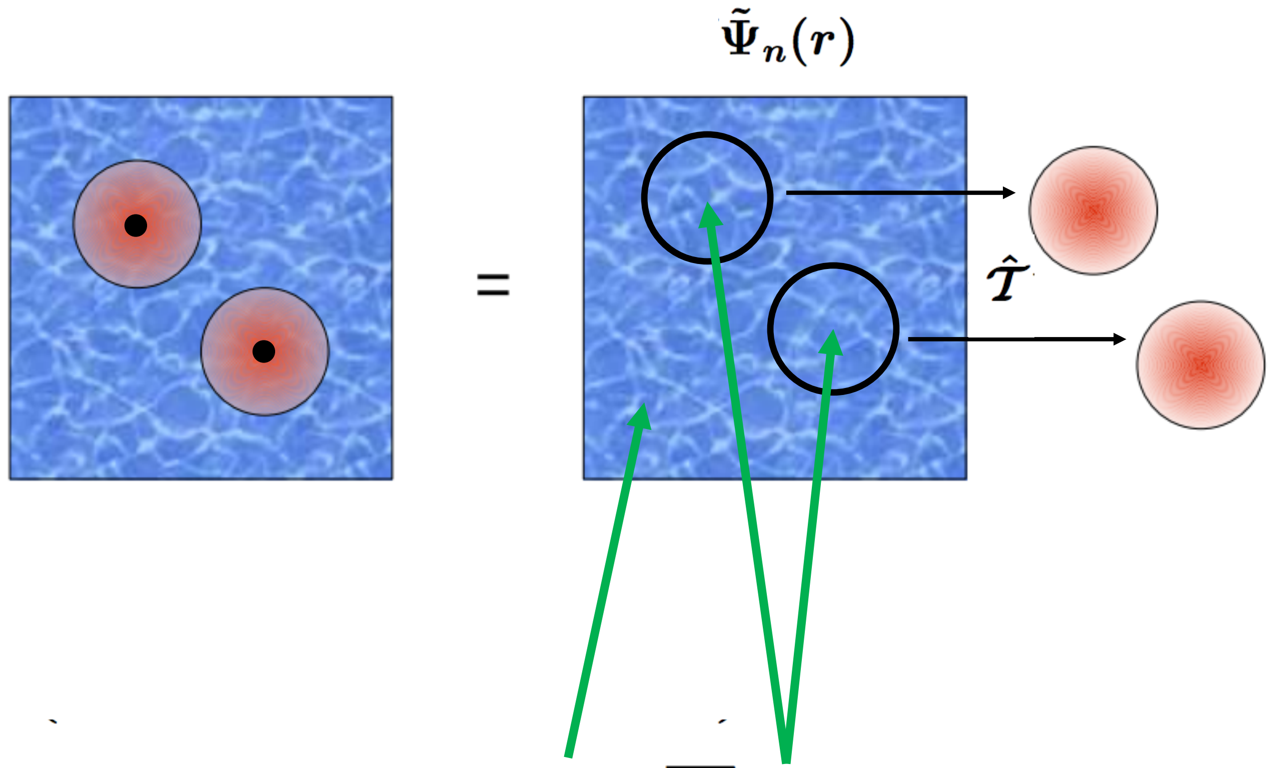
- the relevant wave functions shall be transformed onto numerically convenient auxiliary wave functions

$$\tilde{\Psi}_n(\vec{r}) = \sum_{\vec{G}} \mathrm{e}^{i\vec{G}\vec{r}} \tilde{\Psi}_n(\vec{G})$$

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

$$\mathcal{T} = 1 + \sum_R \mathcal{S}_R$$





$$\mathcal{T} = 1 + \sum_{R} \mathcal{S}_{R}$$

PAW Transformation operator II

Find a closed expression for the transformation operator

$$\mathcal{T} = 1 + \sum_R \mathcal{S}_R$$

Derivation:

$$\overbrace{|\phi_i\rangle}^{true} = \underbrace{\overbrace{|\tilde\phi_i\rangle}^{aux.} + \mathcal{S}_{R_i} \overbrace{|\tilde\phi_i\rangle}^{aux.}}_{\mathcal{T}|\tilde\phi_i\rangle}$$

$$\Rightarrow \mathcal{S}|\tilde\phi_i\rangle = |\phi_i\rangle - |\tilde\phi_i\rangle = \sum_j \Big(|\phi_j\rangle - |\tilde\phi_j\rangle\Big) \underbrace{\langle\tilde p_j|\tilde\phi_i\rangle}_{\delta_{i,j}}$$

$$\Rightarrow \mathcal{T} = 1 + \underbrace{\sum_j \Big(|\phi_j\rangle - |\tilde\phi_j\rangle\Big) \langle\tilde p_j|}_{\mathcal{S}_R}$$

Projector functions $\langle\tilde{p}_i|$

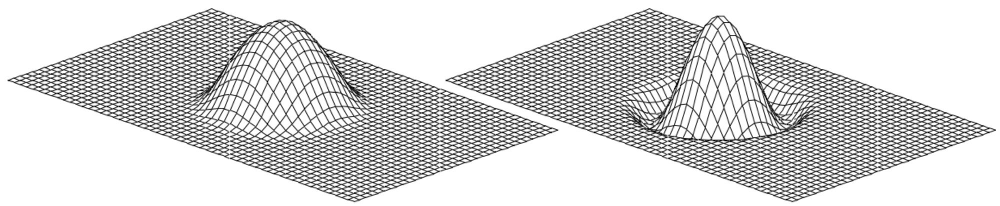
- **must be localized within its own augmentation region**
- **obey bi-orthogonality condition**

$$\langle\tilde{p}_i|\tilde{\phi}_j\rangle = \delta_{i,j}$$

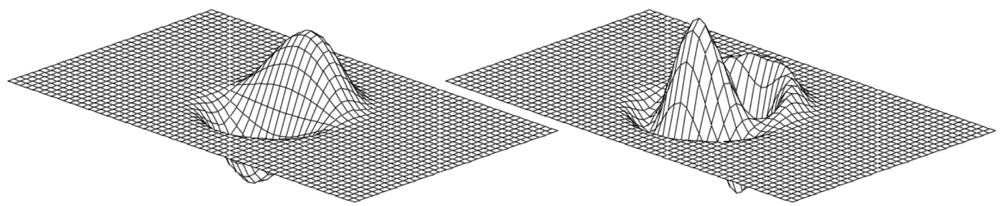
- **projector functions $\langle\tilde{p}|$ are not yet uniquely determined: closure relation will be explained later**

PAW Projector functions $\langle \tilde{p}_i |$

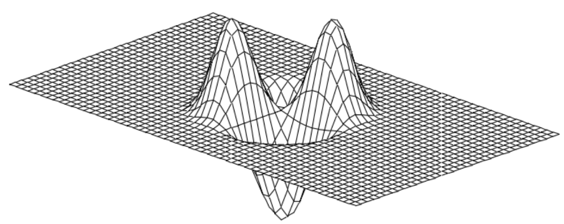
s-type projector functions



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

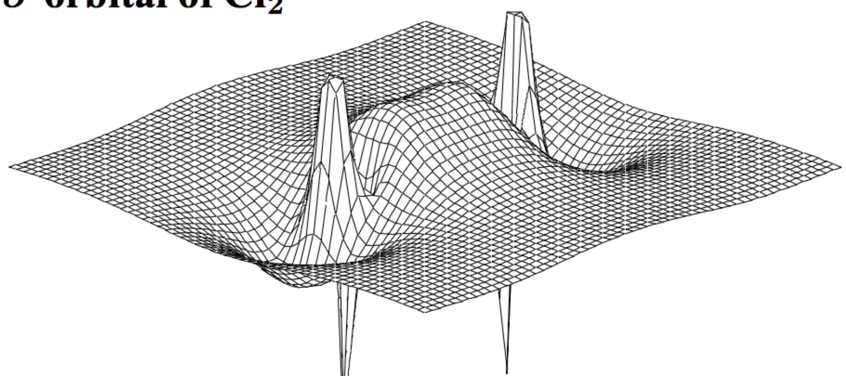
$$\mathcal{T} = 1 + \sum_j \left(|\phi_j\rangle - |\tilde{\phi}_j\rangle \right) \langle \tilde{p}_j |,$$

the all-electron wave function obtaines the form:

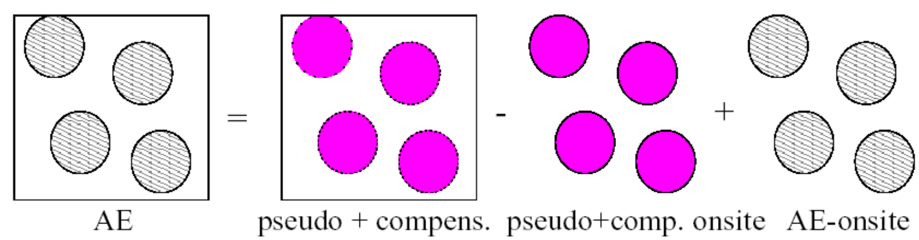
$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_j \left(|\phi_j\rangle - |\tilde{\phi}_j\rangle \right) \langle \tilde{p}_j | \tilde{\Psi}_n\rangle$$

PAW Augmentation

Example: p-σ orbital of Cl_2



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



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

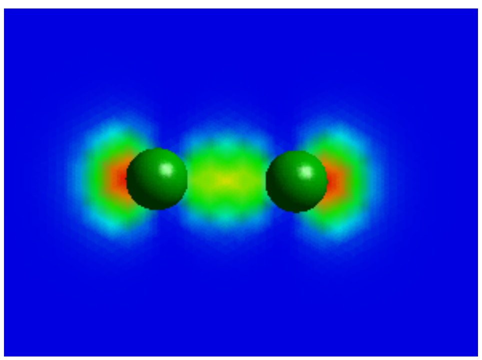
$$\begin{aligned}
\tilde{H} &= \mathcal{T}^{\dagger} H \mathcal{T} = -\frac{1}{2}\nabla^2 + \tilde{v} + \sum_{i,j} |\tilde{p}_i\rangle h_{i,j} \langle \tilde{p}_j| \\
\tilde{O} &= \mathcal{T}^{\dagger}\mathcal{T} = 1 + \sum_{i,j} |\tilde{p}_i\rangle o_{i,j} \langle \tilde{p}_j|
\end{aligned}$$

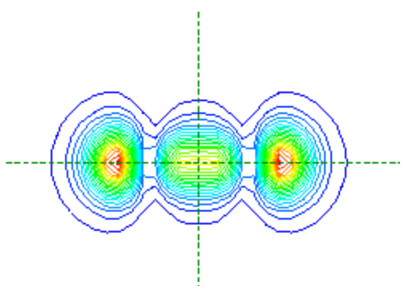
have the form of a separable pseudopotential

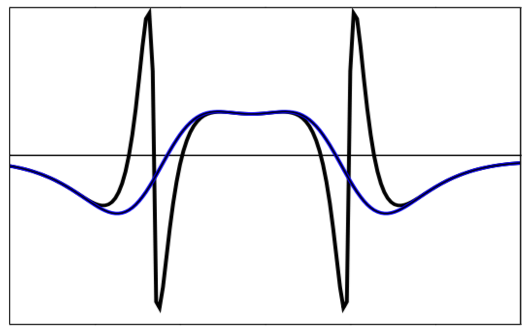
$h_{i,j}$ **and** $o_{i,j}$ **have closed expressions**

$$\begin{aligned}
h_{i,j} &= \langle \phi_i| -\frac{1}{2}\nabla^2 + v|\phi_j\rangle - \langle \tilde{\phi}_i| -\frac{1}{2}\nabla^2 + \tilde{v}|\tilde{\phi}_j\rangle \\
o_{i,j} &= \langle \phi_i|\phi_j\rangle - \langle \tilde{\phi}_i|\tilde{\phi}_j\rangle
\end{aligned}$$

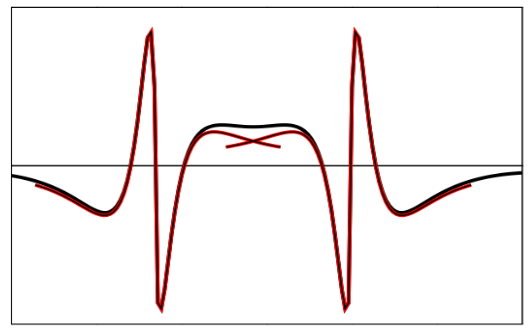
- solve the self-consistent Schrodinger equation
  to get the PS wave function to minimize the total energy functional



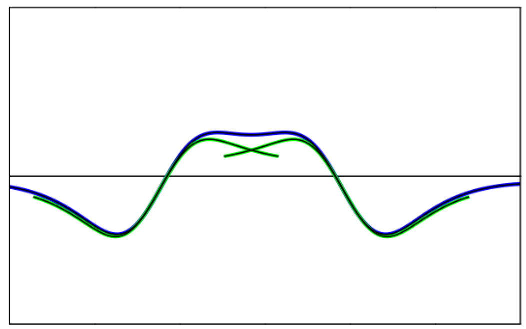




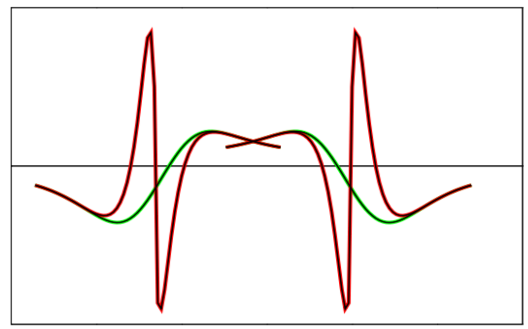
$|\Psi\rangle, |\tilde{\Psi}\rangle$



$|\Psi\rangle, |\Psi^1\rangle$



$|\tilde{\Psi}\rangle, |\tilde{\Psi}^1\rangle$



$|\Psi^1\rangle, |\tilde{\Psi}^1\rangle$

Thanks