

Linear Scaling DFT with in-situ-optimised Local Orbitals using the Projector Augmented Wave Formalism

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ONETEP Masterclass 2023, RAL, August 2023



ONETEP

Outline

1 The Projector Augmented Wave Method

2 PAW in ONETEP

3 Applications

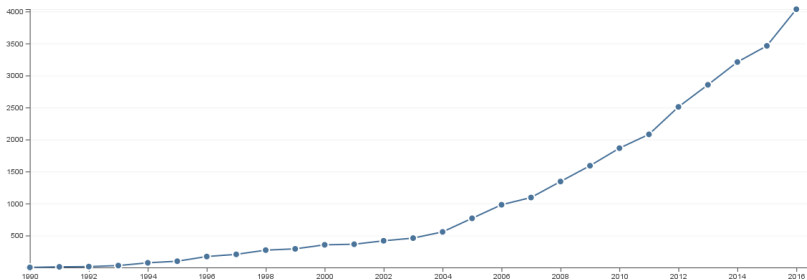
Why PAW?

Projector Augmented Waves:

- Best aspects of PWSP & best aspects of AE calculations
- Well-established formalism, implemented in ABINIT, VASP, PWSCF, etc
- Access to all-electron orbitals, density & potential near nucleus
- Allows softer pseudopotentials than Norm Conserving psp (many similarities to Vanderbilt usps)

P. E. Blöchl, Phys. Rev. B 50, 17953 (1994) (> 32000 citations)

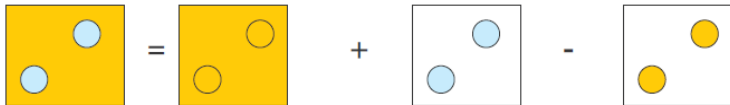
Sum of Times Cited per Year



PAW transformation in Traditional DFT

Relates AE orbitals $|\psi_n\rangle$ to PS orbitals $|\tilde{\psi}_n\rangle$:

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i (|\varphi_i\rangle - |\tilde{\varphi}_i\rangle) \langle \tilde{p}^i | \tilde{\psi}_n \rangle = \tau |\tilde{\psi}_n\rangle$$



AE expectation values in terms of PS orbitals:

$$\langle A \rangle = \sum_n f_n \langle \psi_n | \hat{A} | \psi_n \rangle = \sum_n f_n \langle \tilde{\psi}_n | \tau^\dagger \hat{A} \tau | \tilde{\psi}_n \rangle$$

Wavefunctions in PAW

Within a sphere around each atom:

- $|\varphi_i\rangle$: AE *partial waves* (radial grid)
- $|\tilde{\varphi}_i\rangle$: PS *partial waves* (radial OR cartesian grid)
- $|\tilde{p}^i\rangle$: PAW *projectors* (cartesian grid)
dual to PS partial waves for complete pw basis: $\langle \tilde{p}^i | \tilde{\varphi}_j \rangle = \delta_{ij}$

Kohn-Sham Eq:

$$\begin{aligned}\hat{H}|\psi_n\rangle &= \epsilon_n|\psi_n\rangle \\ \tau^\dagger \hat{H} \tau |\tilde{\psi}_n\rangle &= \epsilon_n \tau^\dagger \tau |\tilde{\psi}_n\rangle\end{aligned}$$

Modified orthogonality condition for PS wfns:

$$\langle \psi_m | \psi_n \rangle = \delta_{mn} \quad \Rightarrow \quad \langle \tilde{\psi}_m | \hat{S} | \tilde{\psi}_n \rangle = \delta_{mn} \quad \text{with} \quad \hat{S} = 1 + |\tilde{p}^i\rangle (\langle \varphi_i | \varphi_j \rangle - \langle \tilde{\varphi}_i | \tilde{\varphi}_j \rangle) \langle \tilde{p}^j |$$

Total Energies in PAW

AE total energy is:

$$E_T = \sum_n f_n \langle \psi_n | -\frac{1}{2} \nabla^2 | \psi_n \rangle + E_H[n_v + n_{Zc}] + E_{xc}[n_v + n_c] + E_{II}$$

Decomposes as:

$$E = \tilde{E} + E^1 - \tilde{E}^1, \quad (1)$$

where:

- \tilde{A} refers to a quantity evaluated for the PS orbitals
- A^1 refers to a quantity evaluated for the AE partial waves
- \tilde{A}^1 refers to a quantity evaluated for the PS partial waves
- \hat{A} refers to a quantity involving the compensation density

Densities in PAW

We represent the density on a cartesian grid as usual, $\tilde{n}(\mathbf{r})$, plus/minus AE and PS core terms

$$\begin{aligned}n(\mathbf{r}) &= \sum_n f_n |\psi_n(\mathbf{r})|^2 = \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r}) \\ &= \sum_n f_n |\tilde{\psi}_n(\mathbf{r})|^2 + \sum_{ij} \rho^{ij} \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) - \sum_{ij} \rho^{ij} \tilde{\varphi}_i(\mathbf{r}) \tilde{\varphi}_j(\mathbf{r})\end{aligned}$$

ρ^{ij} is a density matrix for the sphere part:

$$\rho^{ij} = \sum_n f_n \langle \tilde{\psi}_n | \tilde{\rho}^i \rangle \langle \tilde{\rho}^j | \tilde{\psi}_n \rangle$$



$\tilde{n}(\mathbf{r})$ can be treated on regular grid, but $n^1(\mathbf{r})$ and $\tilde{n}^1(\mathbf{r})$ must be treated on radial grid around each atom for high accuracy.

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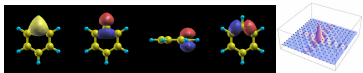
3 Applications

ONETEP

Represent DM with non-orthogonal local orbitals $\phi_\alpha(\mathbf{r})$ and density kernel $K^{\alpha\beta}$

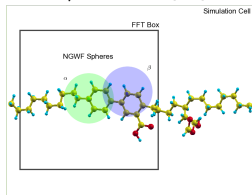
$$\rho(\mathbf{r}, \mathbf{r}') = \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi_\beta(\mathbf{r}')$$

NGWFs on Psinc basis equivalent to plane-waves:



Minimal local orbital basis, systematic wrt real & recip-space cutoffs

FFT Boxes: Local $\phi_\alpha \Rightarrow$ moving FFT box for Kinetic/NL in recip-space



- Local orbitals and *sparse matrices* eg $H_{\alpha\beta} = \langle \phi_\alpha | \hat{H} | \phi_\beta \rangle$ and $S_{\alpha\beta} = \langle \phi_\alpha | \phi_\beta \rangle$
- Enforce normalisation and idempotency of DM while minimising energy E_T to optimise kernel $K^{\alpha\beta}$
- Energy $E_T = \text{Tr}(KH) - E_{\text{dc}}$
- Optimise form of $\phi_\alpha(\mathbf{r})$ via systematic underlying basis

... Problems

No use of eigenstates: how to apply PAW transformation?

How to design a general approach to augmentation

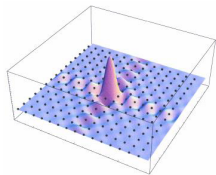
PAW with Density Matrices

Need equivalent PAW transformation on DM:

$$\rho = \tilde{\rho} + \sum_{ij} (|\phi_i\rangle\langle\tilde{\rho}^i|\tilde{\rho}|\tilde{\rho}^j\rangle\langle\phi_j| - |\tilde{\phi}_i\rangle\langle\tilde{\rho}^i|\tilde{\rho}|\tilde{\rho}^j\rangle\langle\tilde{\phi}_j|)$$

NGWFs constructed out of psinc functions, equivalent to plane-waves: $\phi_\alpha(r) = \sum_i c_{\alpha i} D(r - r_i)$

$$D(r) = \frac{1}{N_1 N_2 N_3} \sum_{K=-J_1}^{J_1} \sum_{L=-J_2}^{J_2} \sum_{M=-J_3}^{J_3} e^{i(KB_1 + LB_2 + MB_3) \cdot r}$$



Ideal for soft part of DM:

$$\tilde{\rho} = |\phi_\alpha\rangle K^{\alpha\beta} \langle\phi_\beta|$$

PAW with Density Matrices

But it is the all-electron density matrix which must be normalised:

$$\int \rho(\mathbf{r}, \mathbf{r}) d\mathbf{r} = N_e$$

and idempotent:

$$\int \rho(\mathbf{r}, \mathbf{r}'') \rho(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' = \rho(\mathbf{r}, \mathbf{r}')$$

ONETEP (& other LS-DFT codes) uses a variety of methods (purification, LNV, penalty-functionals...) to enforce these conditions while minimising energy

For NCPPs, this means, for $S_{\alpha\beta}^{\text{NC}} = \langle \phi_\alpha | \phi_\beta \rangle$

$$\text{Tr}(KS) = N_e$$

$$(KSK)^{\alpha\beta} = K^{\alpha\beta}$$

PAW with Density Matrices

We can use the PAW overlap operator

$$\hat{S} = \hat{1} + |\tilde{\rho}^i\rangle(\langle\phi_i|\phi_j\rangle - \langle\tilde{\phi}_i|\tilde{\phi}_j\rangle)\langle\tilde{\rho}^j|$$

to define an 'augmented' overlap matrix:

$$S_{\alpha\beta} = \langle\phi_\alpha|\phi_\beta\rangle + \langle\phi_\alpha|\tilde{\rho}^i\rangle O_{ij}\langle\tilde{\rho}^j|\phi_\beta\rangle$$

which can be constructed easily with sparse matrix algebra

Retain exact same algorithms for normalisation, LNV etc:

$$N_e = \text{Tr}(KS); \quad K = 3LSL - 2LSLSL \quad \text{etc}$$

so LNV/Penalty algorithms remain the same.

PAW with Density Matrices

PS Hamiltonian retains same general form – obtained via $d/d\tilde{p}$

$$\begin{aligned}\tilde{H}_{\alpha\beta} &= \langle \phi_\alpha | \tilde{H} | \phi_\beta \rangle \\ &= \langle \phi_\alpha | \left(-\frac{1}{2} \nabla^2 + \tilde{V}_{\text{eff}}(r) + \sum_{ij} |\tilde{p}_i\rangle \left(\hat{D}_{ij} + D_{ij}^1 - \tilde{D}_{ij}^1 \right) \langle \tilde{p}_j| \right) | \phi_\beta \rangle \\ &= T_{\alpha\beta} + \tilde{V}_{\alpha\beta}^{\text{eff}} + \langle \phi_\alpha | \tilde{p}_i \rangle \left(\hat{D}_{ij} + D_{ij}^1 - \tilde{D}_{ij}^1 \right) \langle \tilde{p}_j | \phi_\beta \rangle\end{aligned}$$

Nonlocal energies are dependent on local electronic structure:

$$\begin{aligned}\hat{D}_{ij} &= \sum_{LM} \int \tilde{v}_H[\tilde{n} + \hat{n} + \tilde{n}_{Zc}](r) \hat{Q}_{ij}^{LM}(r) dr, \\ D_{ij}^1 &= \langle \varphi_i | -\frac{1}{2} \nabla^2 + v_{\text{eff}}^1 | \varphi_j \rangle \\ \tilde{D}_{ij}^1 &= \langle \tilde{\varphi}_i | -\frac{1}{2} \nabla^2 + \tilde{v}_{\text{eff}}^1 | \tilde{\varphi}_i \rangle + \sum_{LM} \int \tilde{v}_H[\tilde{n}^1 + \hat{n} + \tilde{n}_{Zc}](r) \hat{Q}_{ij}^{LM}(r) dr\end{aligned}$$

PAW with Density Matrices

Density is 'augmented' with soft charges to get right multipole moments LM :

$$\hat{n}(r) = \sum_{LM} \sum_{ij} \rho^{ij} \hat{Q}_{ij}^{LM}(r)$$

Augmentation density is constructed in small reciprocal space FFTboxes centered on atoms:

$$\hat{n}(r) = \mathcal{F} \left[\sum_{LM} \sum_{ij} \rho^{ij} \hat{Q}_{ij}^{LM}(G) e^{iG \cdot (R_I - R_{\text{box}})} \right]$$

Augmentation box also used for screening of nonlocal energies

⇒ All PAW extensions are confined to spheres around each atom and thus are $O(N)$

PAW optimisation of NGWFs

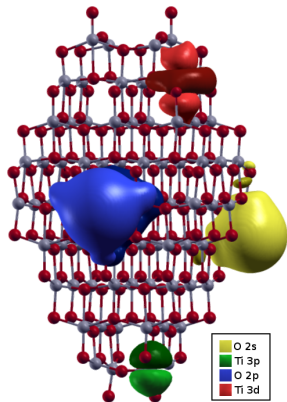
Initialise NGWFs to pseudoatomic orbitals of PAW dataset

Change of overlap matrix with NGWFs is now

$$\frac{\partial S_{\beta\alpha}}{\partial \langle \phi_\gamma |} = \left(|\phi_\alpha\rangle + \sum_{ij} |\tilde{p}_i\rangle O_{ij} \langle \tilde{p}_j | \phi_\beta \rangle \right) \delta_{\beta\gamma}.$$

Leads to extra term in NGWF gradient:

$$\begin{aligned} \frac{\partial E}{\partial \phi_\gamma(\mathbf{r})} &= \frac{\partial}{\partial \phi_\gamma(\mathbf{r})} \left[\frac{K^{\alpha\beta} \tilde{H}_{\beta\alpha} N_e}{K^{\kappa\lambda} S_{\lambda\kappa}} \right] \\ &= K_n^{\alpha\beta} [\tilde{H}\phi_\beta](\mathbf{r}) + \left(\phi_\beta(\mathbf{r}) + \sum_{ij} \tilde{p}_i(\mathbf{r}) O_{ij} \langle \tilde{p}_j | \phi_\beta \rangle \right) \tilde{Q}^{\alpha\beta} \end{aligned}$$



Forces

$$\begin{aligned}
 F_I &= -\frac{\partial E}{\partial R_I} - \left\{ \frac{\partial E}{\partial |\phi_\alpha\rangle} \frac{d|\phi_\alpha\rangle}{dR_I} + \frac{\partial E}{\partial \langle\phi_\alpha|} \frac{d\langle\phi_\alpha|}{dR_I} \right\} \\
 &= -\frac{\partial E}{\partial R_I} - \left\{ K^{\alpha\beta} \langle\phi_\beta|\hat{H} \frac{d|\phi_\alpha\rangle}{dR_I} + \frac{d\langle\phi_\alpha|}{dR_I} \hat{H} |\phi_\beta\rangle K^{\beta\alpha} \right\} \\
 &= -\frac{\partial E}{\partial R_I} + K^{\alpha\delta} H_{\delta\gamma} S^{\gamma\beta} \langle\phi_\beta| \frac{d\hat{S}}{dR_I} |\phi_\alpha\rangle,
 \end{aligned}$$

$$\begin{aligned}
 F_I^{\text{loc}} &= -\int (\tilde{n}(r) + \hat{n}(r)) \frac{\partial v_H[\tilde{n}_{zc}](r)}{\partial R_I} dr, \\
 F_I^{\text{nlcc}} &= -\int v_{xc}[\tilde{n} + \tilde{n}_c] \frac{\partial \tilde{n}_c(r)}{\partial R_I} dr \\
 \hat{F}_I &= -\int \tilde{v}_H[\tilde{n} + \hat{n} + \tilde{n}_{zc}](r) \frac{\partial \hat{n}(r)}{\partial R_I} dr \\
 F_I^{\text{nl}} &= \sum_{v \in I} \left[-D_{v\mu} \langle \tilde{p}^\mu | \phi_\alpha \rangle K^{\alpha\beta} \langle \phi_\beta | \frac{\partial \tilde{p}^v}{\partial R_I} \rangle \right. \\
 &\quad \left. - \langle \frac{\partial \tilde{p}^v}{\partial R_I} | \phi_\alpha \rangle K^{\alpha\beta} \langle \phi_\beta | \tilde{p}^\mu \rangle D_{\mu v} \right. \\
 &\quad \left. + O_{v\mu} \langle \tilde{p}^\mu | \phi_\alpha \rangle K^{\alpha\gamma} H_{\gamma\delta} S^{\delta\beta} \langle \phi_\beta | \frac{\partial \tilde{p}^v}{\partial R_I} \rangle \right. \\
 &\quad \left. + \langle \frac{\partial \tilde{p}^v}{\partial R_I} | \phi_\alpha \rangle K^{\alpha\gamma} H_{\gamma\delta} S^{\delta\beta} \langle \phi_\beta | \tilde{p}^\mu \rangle O_{\mu v} \right].
 \end{aligned} \tag{2}$$

PAW Datasets

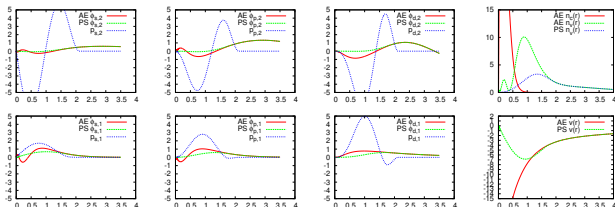
How do you activate PAW?

PAW : True

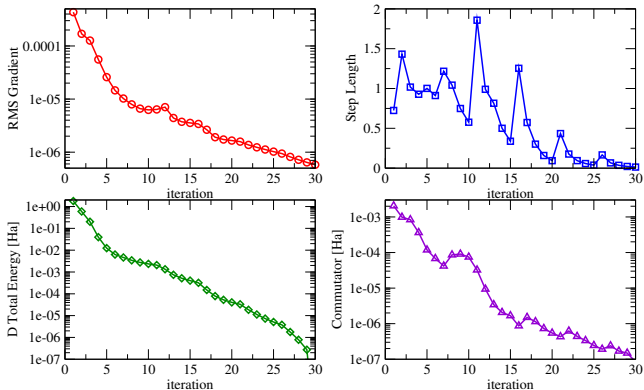
But then you need PAW Datasets rather than NCPPs.

Precalculated $|\varphi_i\rangle$, $|\tilde{\varphi}_i\rangle$, $|\tilde{p}^i\rangle$, $n_c(r)$, $\tilde{n}_c(r)$, D_{ij}^0 , $v_H[\tilde{n}_{Zc}](r)$

- AtomPAW or Vanderbilt uspp codes can create them, in same format as ABINIT
- Existing “JTH” library available in suitable format (links on ONETEP FAQ)
https://github.com/onetep-devel/Utils-devel/tree/main/JTH_v1.0_PAW_datasets
- Some elements misbehave! eg Selenium. In such cases the GBRV library is a reasonable option:
<http://www.physics.rutgers.edu/gbrv/>
- Important that projectors are smooth (be careful if developing your own!)

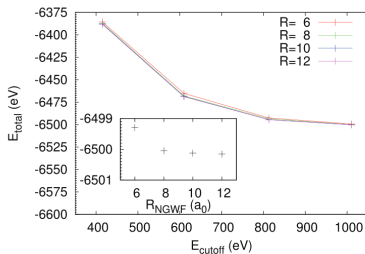
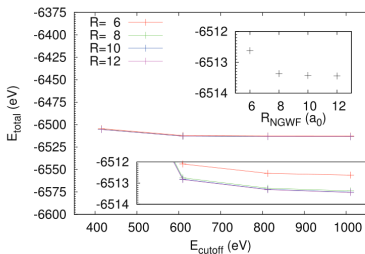


Convergence - Silicon 64-atom cell



- Converges well by all standard measures (step length goes to zero)

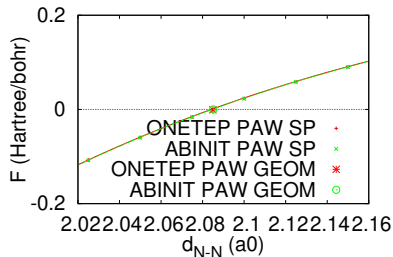
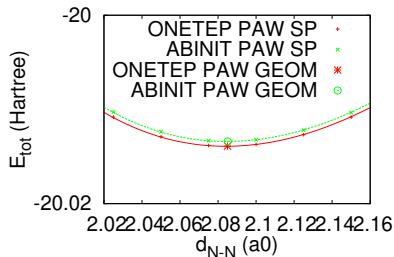
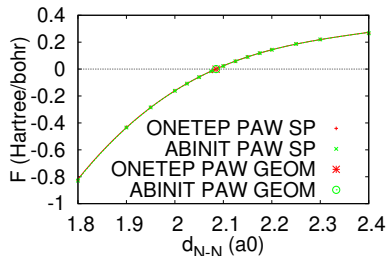
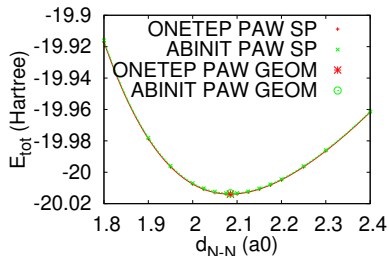
Convergence - NGWFs



- Convergence for a model of PTCTDA - major improvement over NCPPs

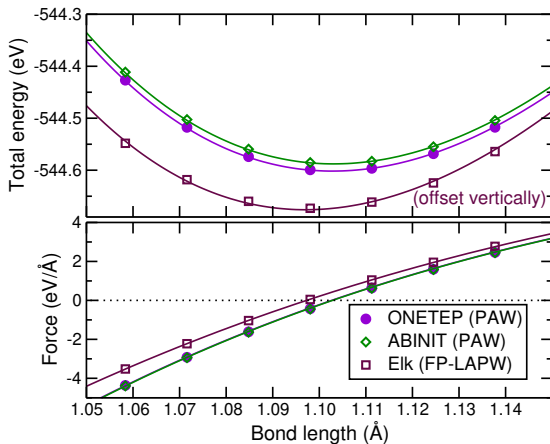
Agreement with ABINIT

Nitrogen molecule: N_2



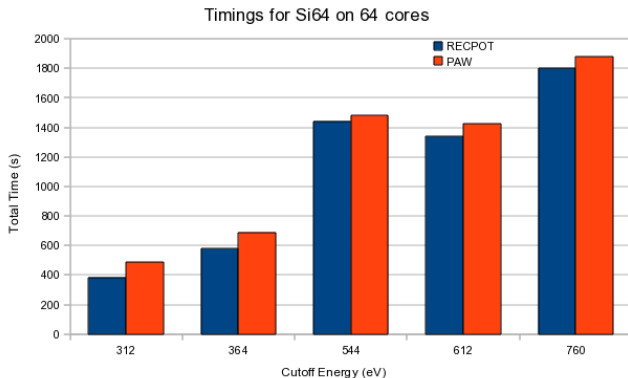
Agreement with All-Electron Calculations

Comparison with Elk FP-LAPW code:

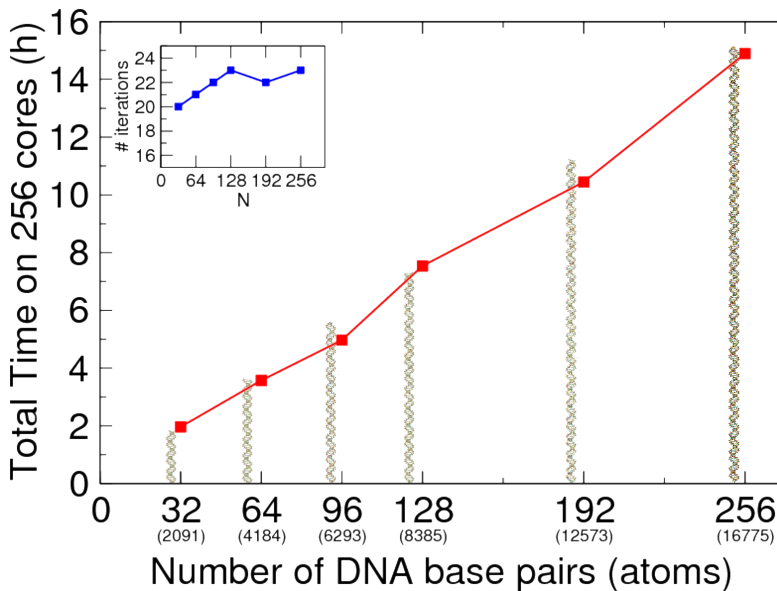


Calculation times

Overhead of PAW is very low:



Calculation times



Augmentation

Augmentation of a matrix is a very general concept in LS-PAW

For traditional $O(N^3)$ PAW implementations, one calculates expressions like:

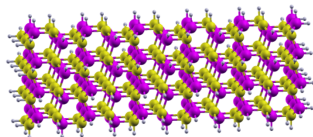
$$\langle A \rangle = \sum_n f_n \langle \psi_n | \hat{A} | \psi_n \rangle = \sum_n f_n \langle \tilde{\psi}_n | \hat{A} | \tilde{\psi}_n \rangle + \sum_n f_n \langle \tilde{\psi}_n | \tilde{\rho}^i \rangle (\langle \varphi_i | \hat{A} | \varphi_j \rangle - \langle \tilde{\varphi}_i | \hat{A} | \tilde{\varphi}_j \rangle) \langle \tilde{\rho}^j | \tilde{\psi}_n \rangle$$

For LS-PAW, we can 'augment' the matrix elements in terms of local orbitals:

$$\langle \phi_\alpha | \hat{A} | \phi_\beta \rangle^{\text{aug}} = \langle \phi_\alpha | \hat{A} | \phi_\beta \rangle + \langle \phi_\alpha | \tilde{\rho}^i \rangle (\langle \varphi_i | \hat{A} | \varphi_j \rangle - \langle \tilde{\varphi}_i | \hat{A} | \tilde{\varphi}_j \rangle) \langle \tilde{\rho}^j | \phi_\beta \rangle$$

So eg for dipole moment:

$$\begin{aligned} d_{\text{el}} &= K^{\beta\alpha} [\langle \phi_\alpha | r | \phi_\beta \rangle \\ &\quad + \langle \phi_\alpha | \tilde{\rho}^i \rangle (\langle \varphi_i | r | \varphi_j \rangle - \langle \tilde{\varphi}_i | r | \tilde{\varphi}_j \rangle) \langle \tilde{\rho}^j | \phi_\beta \rangle] \\ &= K^{\beta\alpha} \langle \phi_\alpha | r | \phi_\beta \rangle^{\text{aug}} \end{aligned}$$

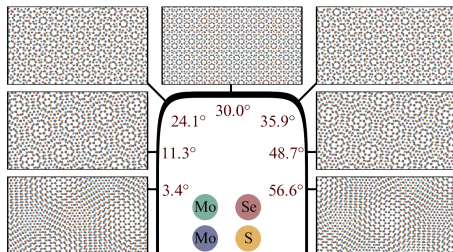
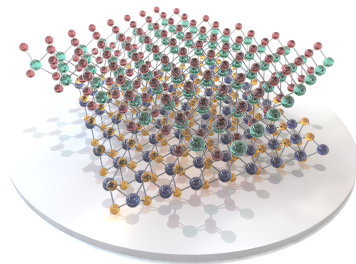


PW Avraam, NDM Hine, P Tangney, and PD Haynes, Phys. Rev. B 83, 241402(R) (2011); PW Avraam, NDM Hine, P Tangney, PD Haynes, Phys. Rev. B 85 115404 (2012); NDM Hine, PW Avraam, P Tangney, and PD Haynes, Phys. J. Phys. Conf. Ser. 367, 012002 (2012).

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Example: $\text{MoS}_2/\text{MoSe}_2$ heterostructure – 4-5% lattice mismatch produces incommensurate interface. Interlayer interactions may depend on lattice mismatch angle:

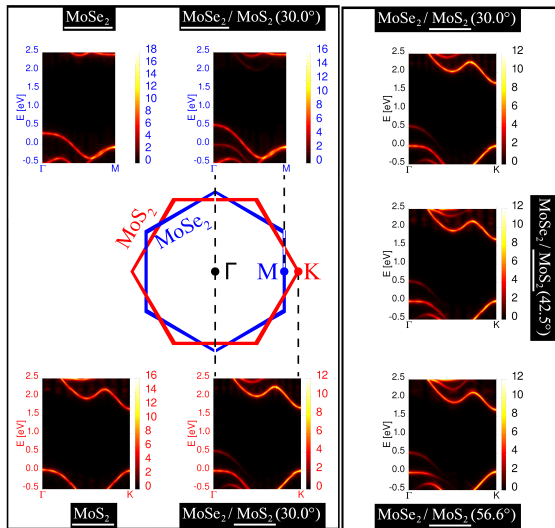


(images by G. Constantinescu)

These structures contain Mo, W, Se etc → PAW very useful

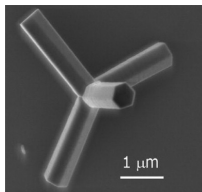
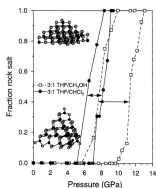
TMDC Heterostructures: Bandstructure Projection

- Reduces spectral weight for $\Gamma \rightarrow K$ transitions, allowing for improved Photoluminescence.
- Indirect transitions redshifted compared to monolayers, as shown in $\text{MoS}_2/\text{WSe}_2$ bilayers
- Hole mass near Γ varies with angle (increases towards 60°) due to different portions of the BZ coming to momentum alignment.

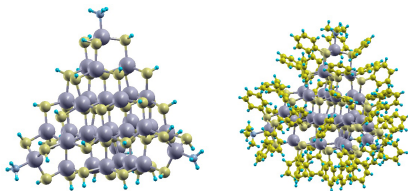


Pressure-Induced Phase Transformations in Nanomaterials

Pressure causes phase transformations (eg ZB to RS) in CdS, CdSe nanocrystals



Optical properties of resulting nanoparticles important for sensor & photovoltaics applications



Many interesting effects of ligands, size, shape, etc.

Conclusions

- PAW Framework integrates well into ONETEP: similarity of underlying psinc basis to plane-waves
- Minimal overhead compared to equivalent NCPP calculation (somewhat higher complexity of code!)

