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

Nicholas D.M. Hine

University of Warwick

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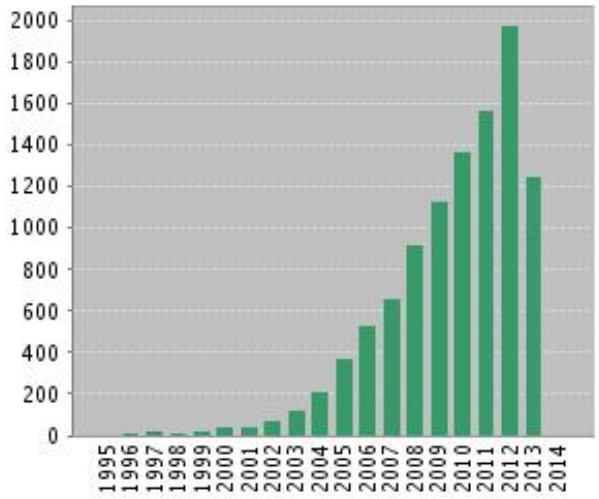
Outline

Why PAW?

Projector Augmented Waves:

- Best aspects of PWPSP & 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 psps
  (many similarities to Vanderbilt usps)

P. E. Blöchl, Phys. Rev. B 50, 17953 (1994)
($>$ 10000 citations)



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:

$$\hat{H}|\psi_n\rangle = \varepsilon_n |\psi_n\rangle$$
$$\tau^\dagger \hat{H} \tau |\widetilde{\psi}_n\rangle = \varepsilon_n \tau^\dagger \tau |\widetilde{\psi_n}\rangle$$

Modified orthogonality condition for PS wfns:

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

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:

$$E = \widetilde{E} + E^1 - \widetilde{E}^1 \,, \tag{1}$$

where:

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

Densities in PAW

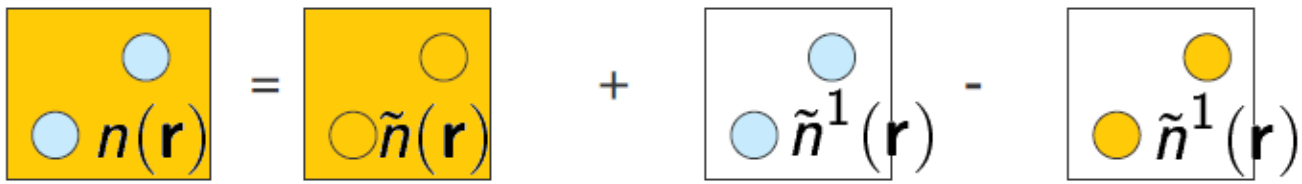
For the density, we write

$$n(\mathbf{r}) = \sum_n f_n |\psi_n(\mathbf{r})|^2 = \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r})$$

$$= \sum_n f_n |\tilde{\psi}_n(\mathbf{r})|^2 + \sum_{ij} \rho^{ij} \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) - \sum_{ij} \rho^{ij} \tilde{\varphi}_i(\mathbf{r}) \tilde{\varphi}_j(\mathbf{r})$$

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

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



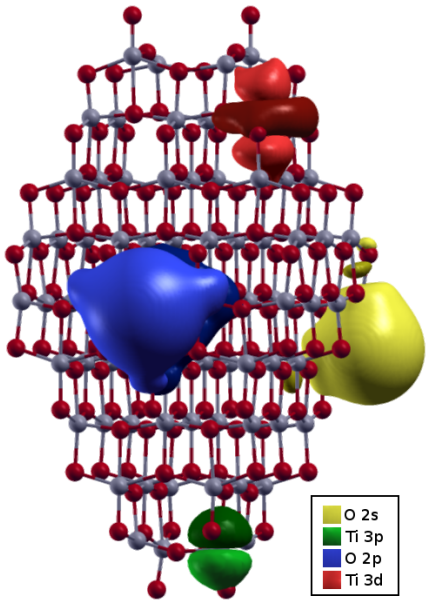
$\tilde{n}(\mathbf{r})$ can be treated on regular grid, but $n^1(\mathbf{r})$ and $\tilde{n}^1(\mathbf{r})$ must be treated on radial grid around each atom for high accuracy.

Outline

ONETEP

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

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



www.onetep.org

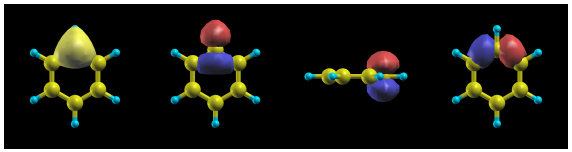
Energy: $E_T = \mathrm{Tr}(KH) - E_{\mathrm{dc}}$

- Local orbitals, $H_{\alpha\beta} = \langle \phi_\alpha | \hat{H} | \phi_\beta \rangle$ and $S_{\alpha\beta} = \langle \phi_\alpha | \phi_\beta \rangle$ and *sparse matrices*
- Density matrix *nearsighted* for insulators, so $K^{\alpha\beta}$ is *sparse*.
- Enforce normalisation and idempotency of DM while minimising energy E_T to optimise kernel $K^{\alpha\beta}$
- Optimise form of $\phi_\alpha(\mathbf{r})$ via systematic underlying basis

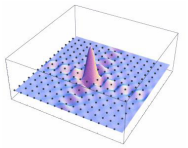
No use of eigenstates!

ONETEP

NGWF: in-situ optimisation



Psinc basis equivalent to plane-waves:

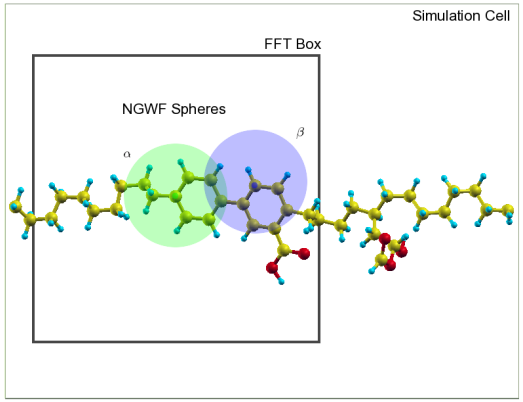


Minimal local orbital basis, systematic wrt real & recip-space cutoffs

FFT Box Approximation

Local $\phi_\alpha \Rightarrow$moving FFT box

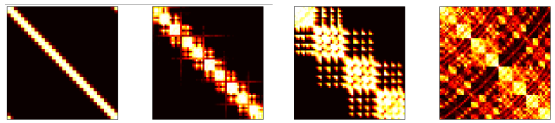
Kinetic/NL in recip-space



Strictly $O(N)$ $H_{\alpha\beta}$ and $n(\mathbf{r})$ evaluation

Sparse Matrix Algebra

Efficient parallelisation and load balance



Adaptive Kernel Optimisation

Purification / Penalty / LNV

$O(N)$ matrix algebra and kernel optimisation

Advantages of ONETEP

Accurate: equivalent to plane waves

Scales as $O(N)$ with system size

High parallel efficiency on thousands of cores

Vacuum is 'free'

... Problems

Only supports NCPPs: hard to treat transition metals, oxides etc

No use of eigenstates: how to apply PAW transformation?

www.onetep.org; CK Skylaris, PD Haynes, AA Mostofi and MC Payne, J. Chem. Phys. 122, 084119 (2005)

NDM Hine, PD Haynes, AA Mostofi, C-K Skylaris, MC Payne, Comput. Phys. Commun. 180, 1041 (2009)

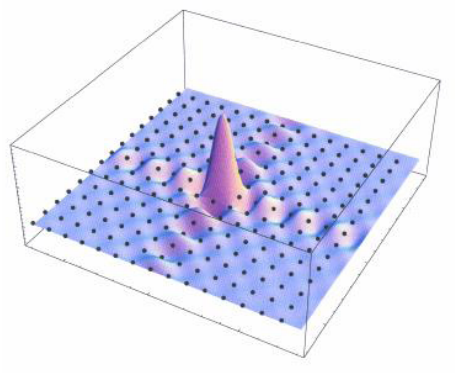
PAW with Density Matrices

Need equivalent PAW transformation on DM:

$$\rho = \widetilde{\rho} + \sum_{ij} \left(|\varphi_i\rangle\langle\widetilde{p}^i|\widetilde{\rho}|\widetilde{p}^j\rangle\langle\varphi_j| - |\widetilde{\varphi}_i\rangle\langle\widetilde{p}^i|\widetilde{\rho}|\widetilde{p}^j\rangle\langle\widetilde{\varphi}_j| \right)$$

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

$$D(\mathbf{r}) = \frac{1}{N_1 N_2 N_3} \sum_{K=-J_1}^{J_1} \sum_{L=-J_2}^{J_2} \sum_{M=-J_3}^{J_3} e^{i(K\mathbf{B_1} + L\mathbf{B_2} + M\mathbf{B_3}).\mathbf{r}}$$



Ideal for soft part of DM:

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

PAW with Density Matrices

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

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

and idempotent:

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

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 $S^{\mathrm{NC}}_{\alpha\beta} = \langle\phi_\alpha|\phi_\beta\rangle$

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

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

PAW with Density Matrices

We can use the PAW overlap operator

$$\widehat{S} = \widehat{1} + |\widetilde{p}^{i}\rangle(\langle\varphi_i|\varphi_j\rangle - \langle\widetilde{\varphi}_i|\widetilde{\varphi}_j\rangle)\langle\widetilde{p}^{j}|$$

to define an 'augmented' overlap matrix:

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

which can be constructed easily with sparse matrix algebra

Retain exact same algorithms for normalisation, LNV etc:

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

so LNV/Penalty algorithms remain the same.

PAW with Density Matrices

PS Hamiltonian retains same general form – obtained via $\mathrm{d}/\mathrm{d}\widetilde{\rho}$

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

Nonlocal energies are dependent on local electronic structure:

$$\widehat{D}_{ij}=\sum_{LM}\int\widetilde{v}_{\mathrm{H}}[\widetilde{n}+\widehat{n}+\widetilde{n}_{\mathrm{Zc}}](\mathbf{r})\widehat{Q}^{LM}_{ij}(\mathbf{r})d\mathbf{r}\,,$$

$$D^1_{ij}=\langle\varphi_i|\frac{-1}{2}\nabla^2+v^1_{\mathrm{eff}}|\varphi_j\rangle$$

$$\widetilde{D}^1_{ij}=\langle\widetilde{\varphi}_i|\frac{-1}{2}\nabla^2+\widetilde{v}^1_{\mathrm{eff}}|\widetilde{\varphi}_i\rangle+\sum_{LM}\int\widetilde{v}_{\mathrm{H}}[\widetilde{n}^1+\widehat{n}+\widetilde{n}_{\mathrm{Zc}}](\mathbf{r})\widehat{Q}^{LM}_{ij}(\mathbf{r})\mathrm{d}\mathbf{r}$$

PAW with Density Matrices

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

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

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

$$\widehat{n}(\mathbf{r}) = \mathscr{F}[\sum_{LM} \sum_{ij} \rho^{ij} \widehat{Q}_{ij}^{LM}(\mathbf{G}) e^{i\mathbf{G}.(\mathbf{R}_I - \mathbf{R}_{\mathrm{box}})}]$$

Augmenation box also used for screening of nonlocal energies

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

PAW optimisation of NGWFs

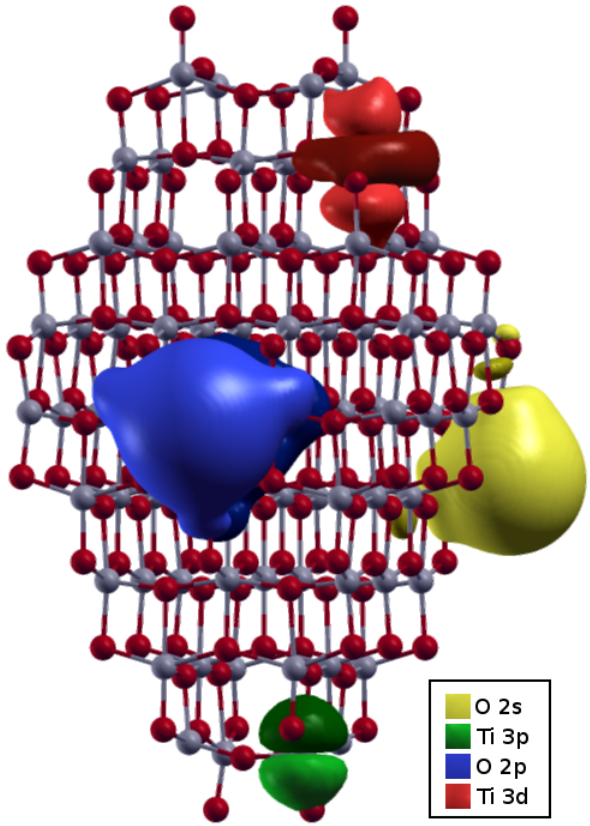
Initialise NGWFs to pseudoatomic orbitals of PAW dataset

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

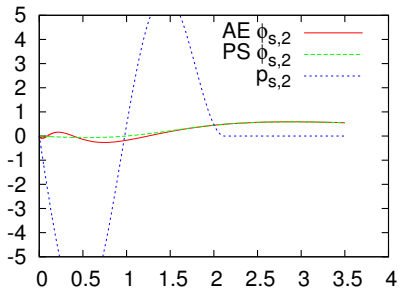
$$
\begin{aligned}
\mathbf{F}_I &= -\frac{\partial E}{\partial \mathbf{R}_I} - \left\{ \frac{\partial E}{\partial |\phi_\alpha\rangle} \frac{d|\phi_\alpha\rangle}{d\mathbf{R}_I} + \frac{\partial E}{\partial \langle\phi_\alpha|} \frac{d\langle\phi_\alpha|}{d\mathbf{R}_I} \right\} \\
&= -\frac{\partial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

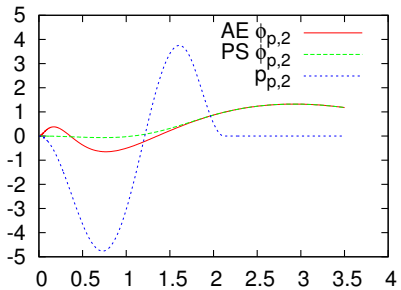
$$
\begin{aligned}
\mathbf{F}_I^{\mathrm{loc}} &= -\int (\widetilde{n}(\mathbf{r}) + \widehat{n}(\mathbf{r})) \frac{\partial v_{\mathrm{H}}[\widetilde{n}_{\mathrm{Zc}}](\mathbf{r})}{\partial \mathbf{R}_I} \,\mathrm{d}\mathbf{r} \,, \qquad (2) \\
\mathbf{F}_I^{\mathrm{nlcc}} &= -\int v_{\mathrm{xc}}[\widetilde{n} + \widetilde{n}_{\mathrm{c}}] \frac{\partial \widetilde{n}_{\mathrm{c}}(\mathbf{r})}{\partial \mathbf{R}_I} \,\mathrm{d}\mathbf{r} \\
\widehat{\mathbf{F}}_I &= -\int \widetilde{v}_{\mathrm{H}}[\widetilde{n} + \widehat{n} + \widetilde{n}_{\mathrm{Zc}}](\mathbf{r}) \frac{\partial \widehat{n}(\mathbf{r})}{\partial \mathbf{R}_I} \,\mathrm{d}\mathbf{r} \\
\mathbf{F}_I^{\mathrm{nl}} &= \sum_{\nu \in I} \Big[- D_{\nu\mu} \langle \widetilde{p}^\mu | \phi_\alpha \rangle K^{\alpha\beta} \left\langle \phi_\beta \middle| \frac{\partial \widetilde{p}^\nu}{\partial \mathbf{R}_I} \right\rangle \\
&\qquad - \left\langle \frac{\partial \widetilde{p}^\nu}{\partial \mathbf{R}_I} \middle| \phi_\alpha \right\rangle K^{\alpha\beta} \langle \phi_\beta | \widetilde{p}^\mu \rangle D_{\mu\nu} \\
&\quad + O_{\nu\mu} \langle \widetilde{p}^\mu | \phi_\alpha \rangle K^{\alpha\gamma} H_{\gamma\delta} S^{\delta\beta} \left\langle \phi_\beta \middle| \frac{\partial \widetilde{p}^\nu}{\partial \mathbf{R}_I} \right\rangle \\
&\quad + \left\langle \frac{\partial \widetilde{p}^\nu}{\partial \mathbf{R}_I} \middle| \phi_\alpha \right\rangle K^{\alpha\gamma} H_{\gamma\delta} S^{\delta\beta} \langle \phi_\beta | \widetilde{p}^\mu \rangle O_{\mu\nu} \Big] \,.
\end{aligned}
$$

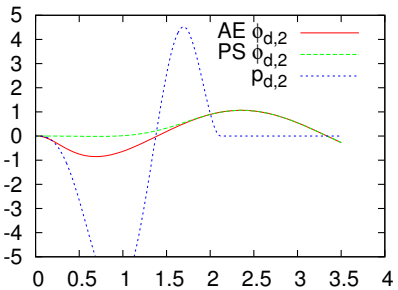
PAW Datasets

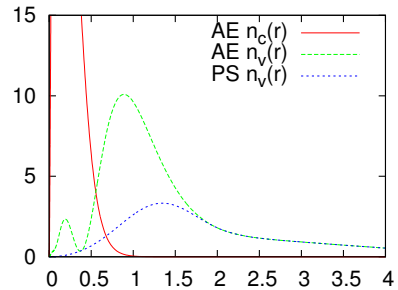
Precalculate $|\varphi_i\rangle$, $|\tilde{\varphi}_i\rangle$, $|\tilde{p}^i\rangle$, $n_c(r)$, $\tilde{n}_c(r)$, D^0_{ij}, $v_{\mathrm{H}}[\tilde{n}_{Zc}](r)$

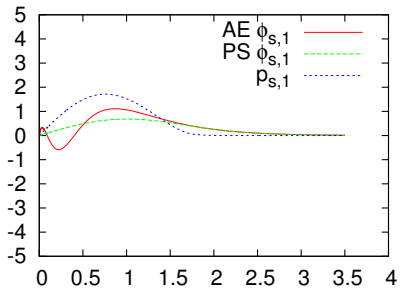
- AtomPAW or Vanderbilt uspp datasets, in same format as ABINIT
- Important that projectors not be too large, or NGWF gradient suffers
- Convergence properties equivalent to ABINIT

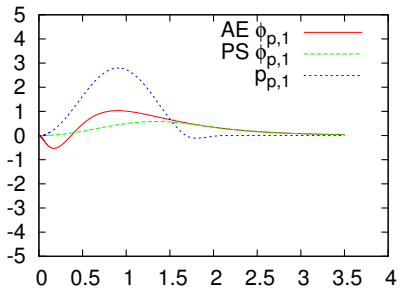


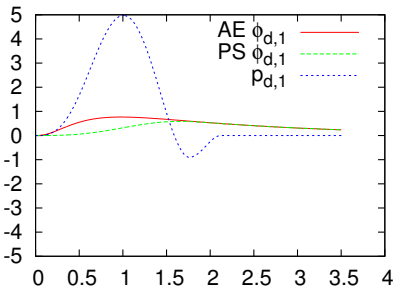


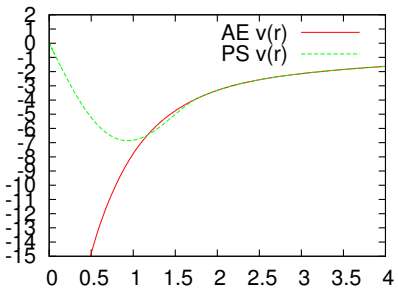




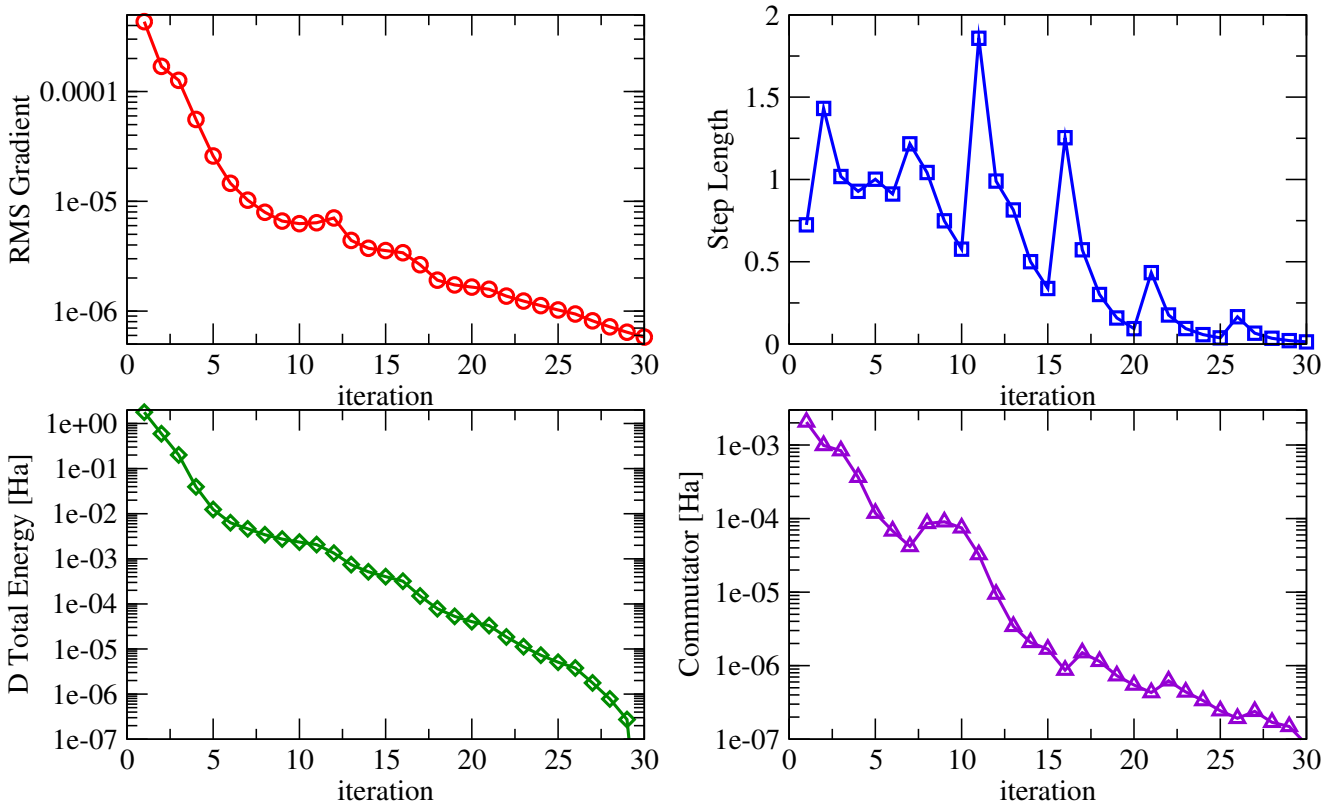








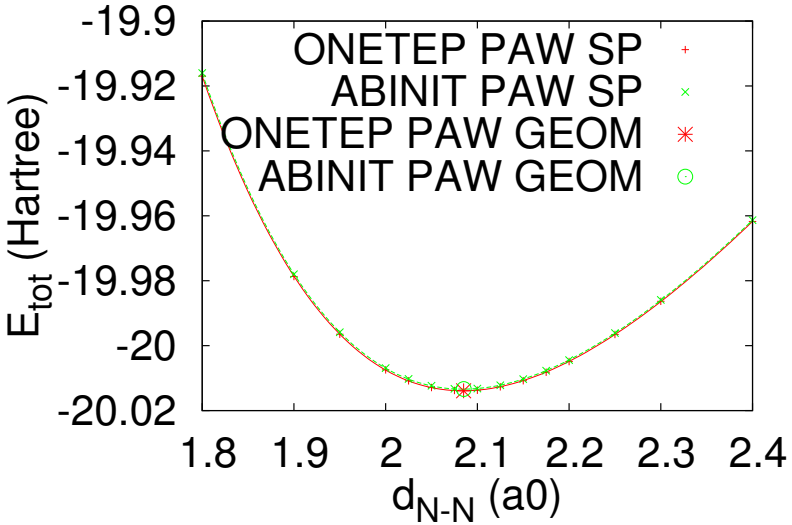
Convergence - Silicon 64-atom cell

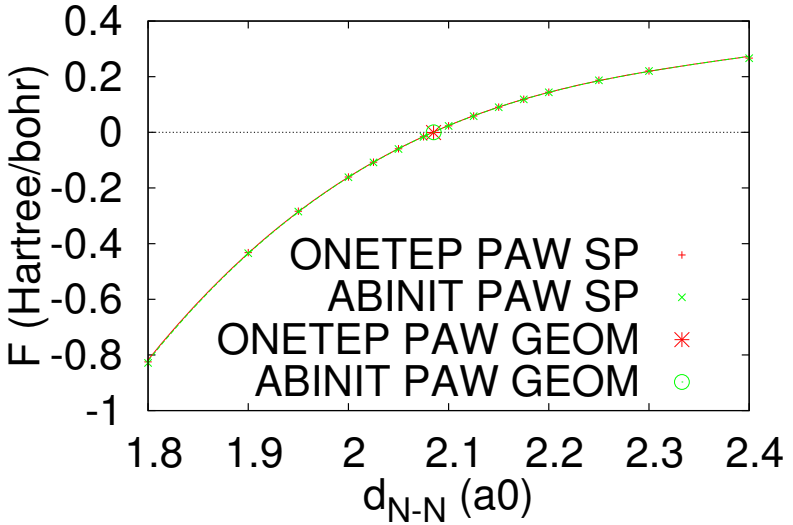


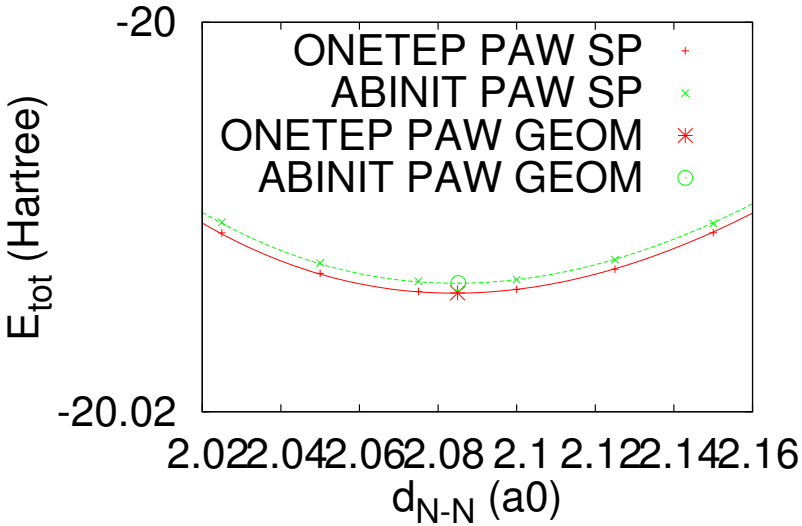
- Converges well by all standard measures (step length goes to zero)

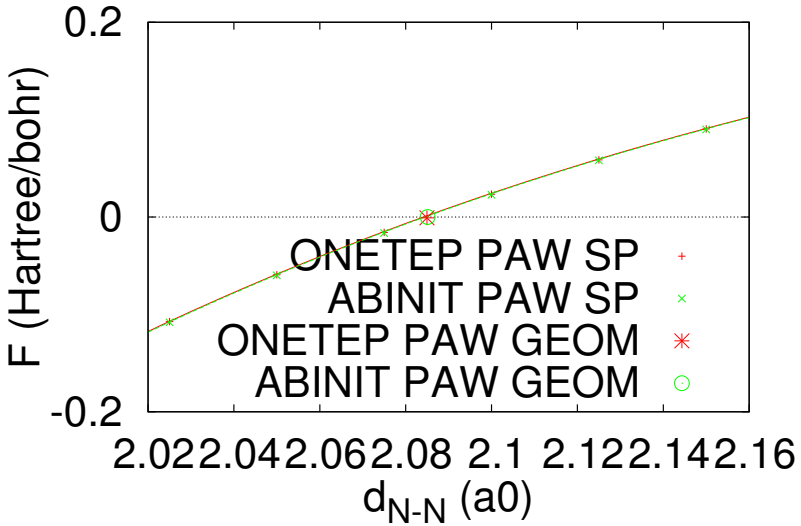
Agreement with ABINIT

Nitrogen molecule: N_2



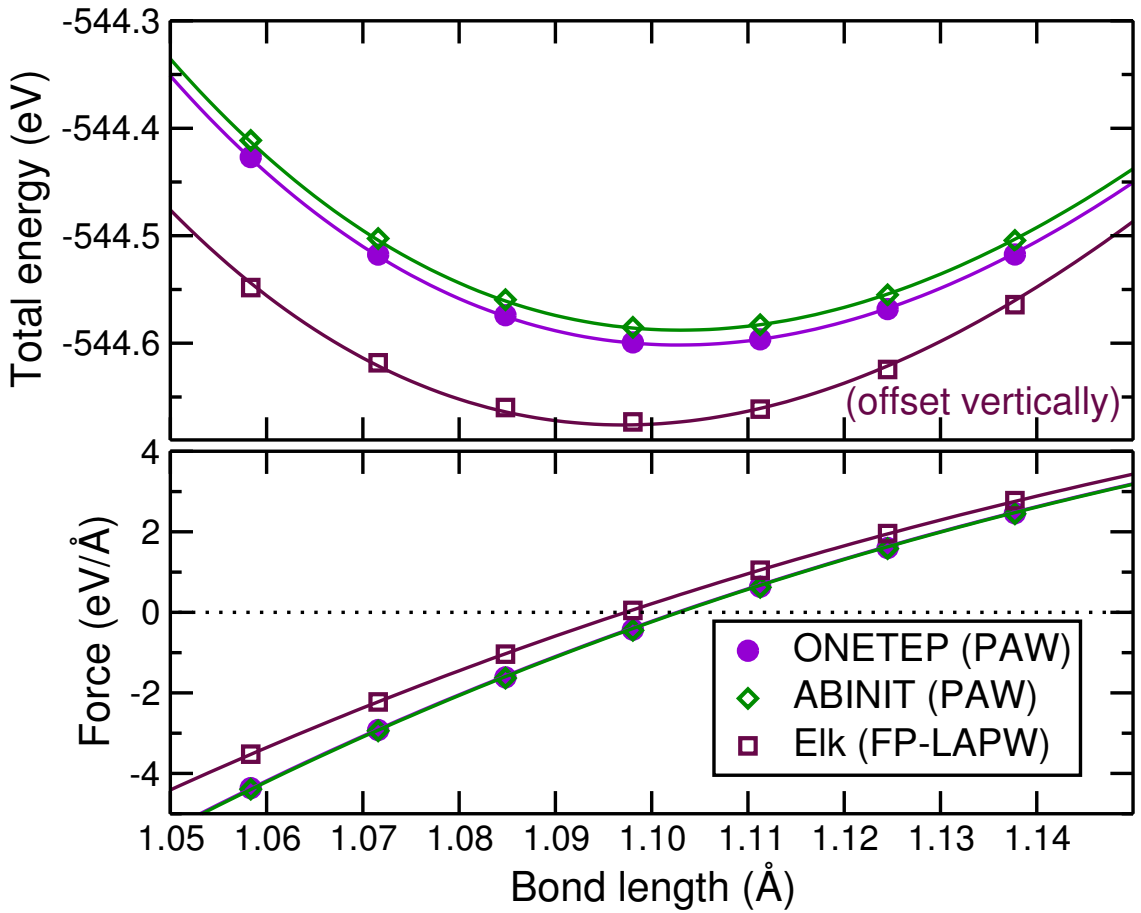






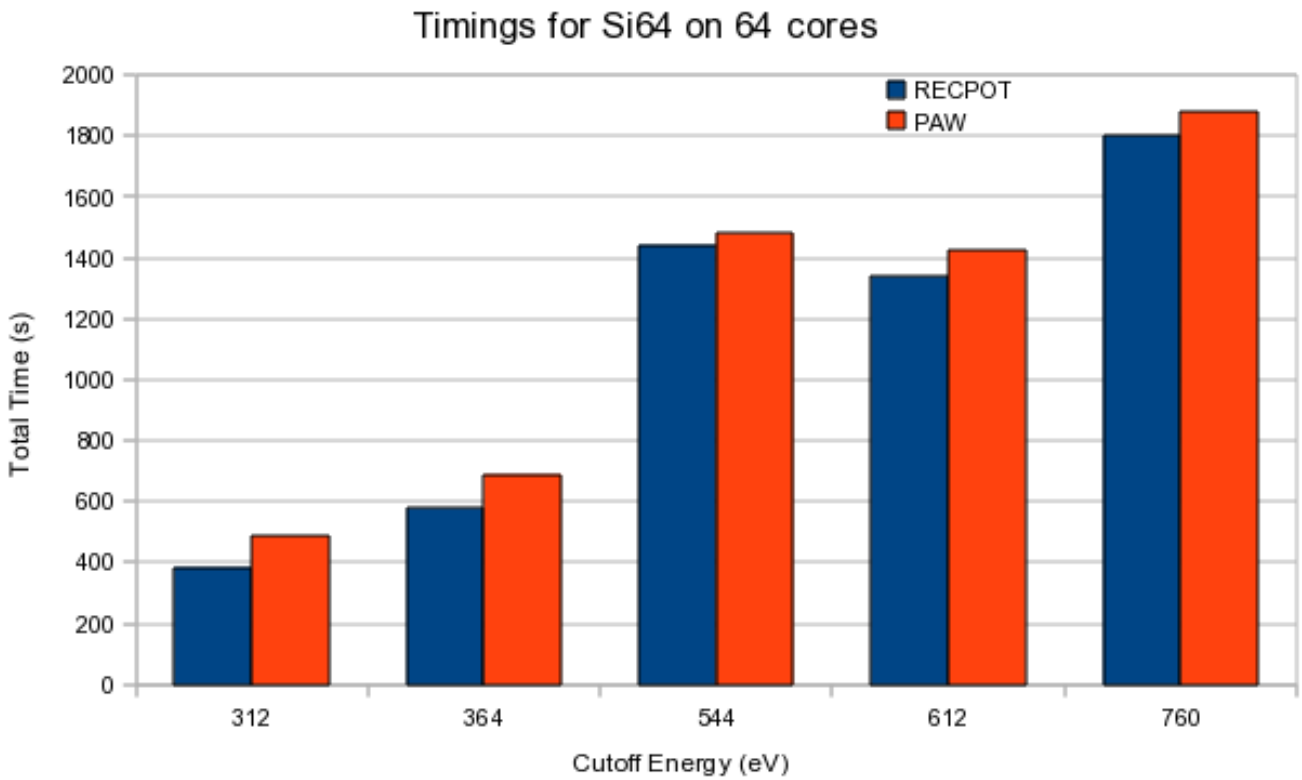
Agreement with All-Electron Calculations

Comparison with Elk FP-LAPW code:

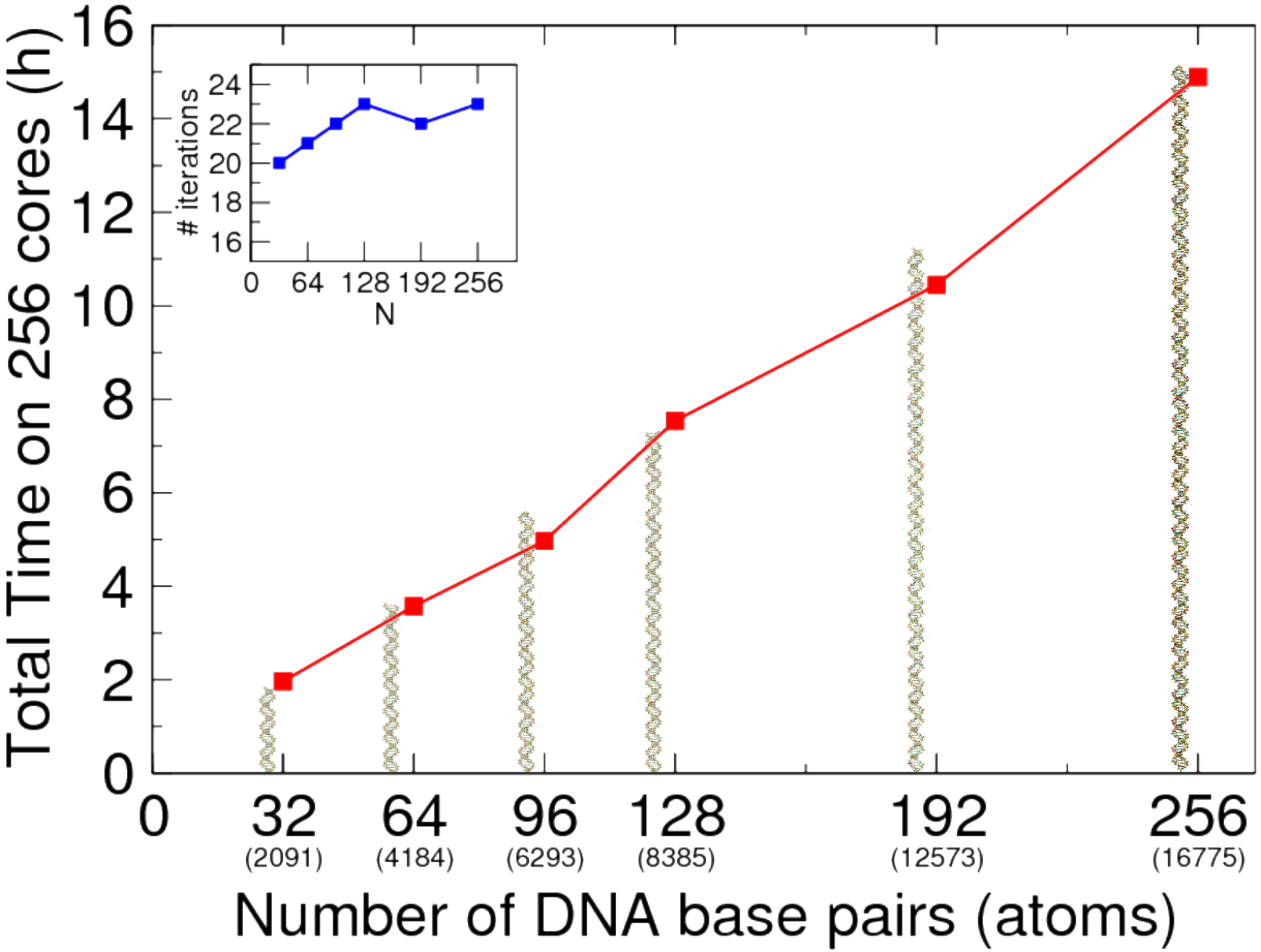


Calculation times

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:

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

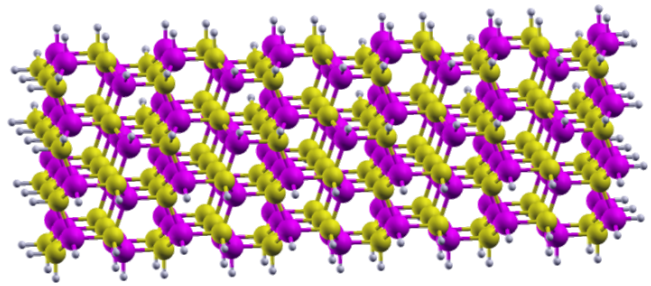
For LS-PAW, we can 'augment' the matrix elements in terms of local orbitals:

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

So eg for dipole moment:

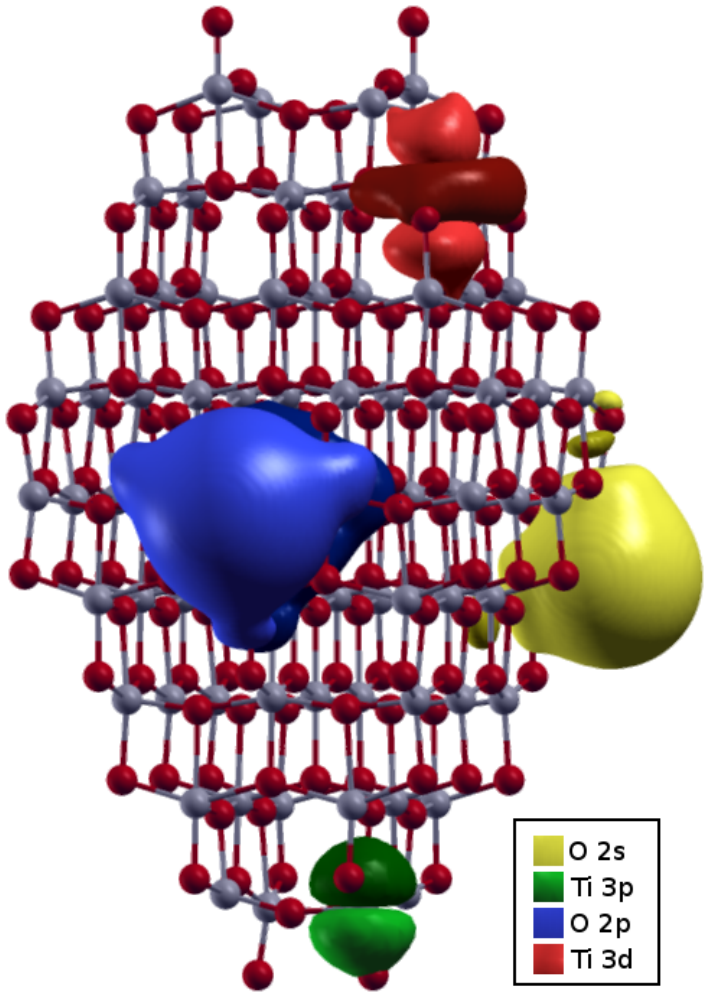
$$\begin{aligned} \mathbf{d}_{\text{el}} &= K^{\beta\alpha} [\langle \phi_\alpha | \mathbf{r} | \phi_\beta \rangle \\ &\quad + \langle \phi_\alpha | \widetilde{p}^i \rangle (\langle \varphi_i | \mathbf{r} | \varphi_j \rangle - \langle \widetilde{\varphi}_i | \mathbf{r} | \widetilde{\varphi}_j \rangle)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

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).



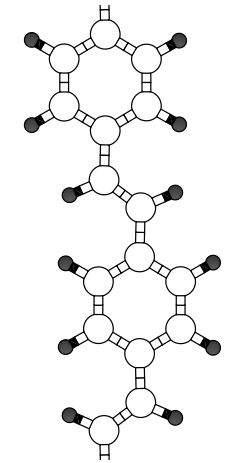
Outline

Anatase TiO2 Nanocrystals

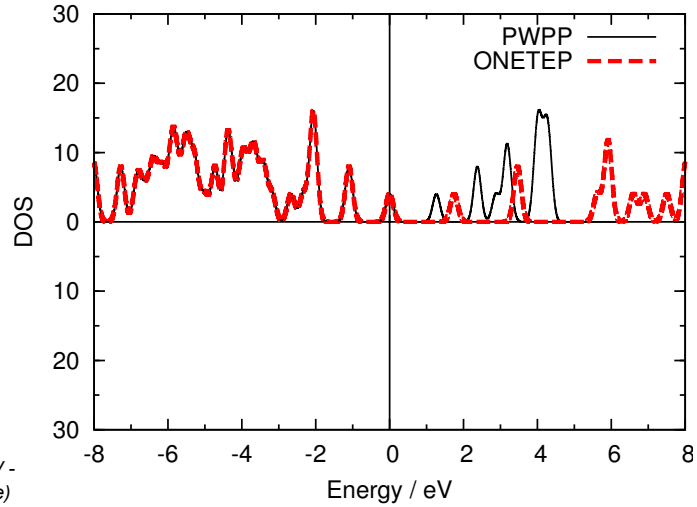


Theoretical Spectroscopy

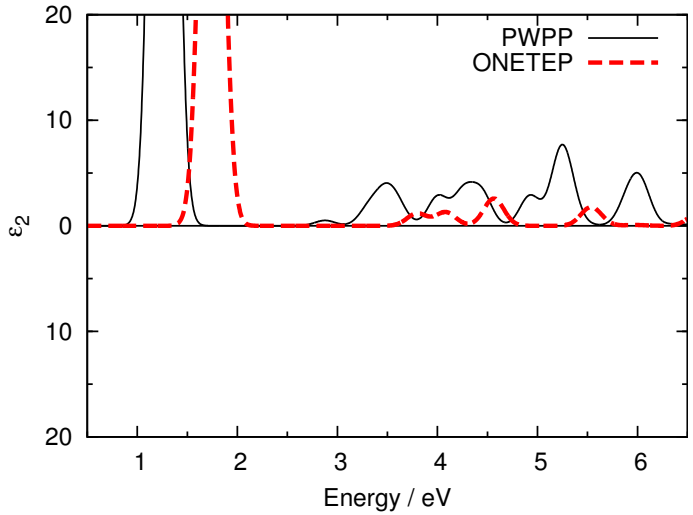
Unoccupied states are not well-represented in valence NGWF representation:



The conjugated polymer PPV - poly(para-phenylene vinylene)



Consequently, optical spectra are similarly poor:



Construct new set of NGWFs and new 'conduction state' kernel to describe ψ_c
Project out and shift valence states so that conduction states are lowermost

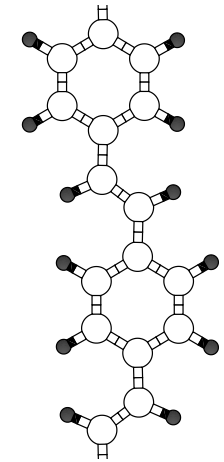
Optical spectra employ Fermi Golden Rule with dipole approximation:

$$\varepsilon_2(\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{v,c} |\langle \psi_c | \hat{\mathbf{q}}.\mathbf{r} | \psi_v \rangle|^2 \delta(\varepsilon_c - \varepsilon_v - \hbar\omega)$$

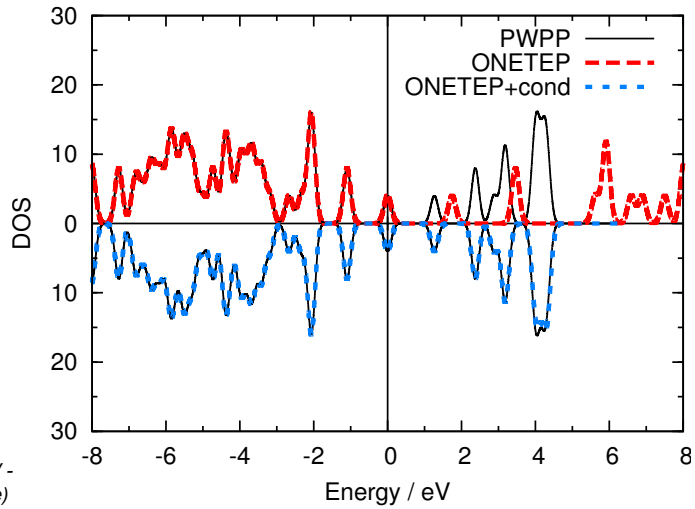
$O(N)$ diagonalisation only in *minimal basis*

Theoretical Spectroscopy

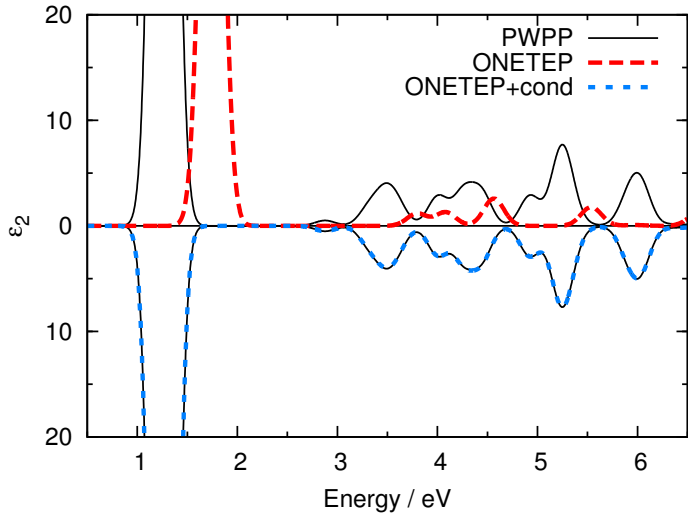
With joint basis of valence and conduction NGWFs, DOS agrees well with PWPP result:



The conjugated polymer PPV - poly(para-phenylene vinylene)



Consequently, optical spectra are similarly improved:



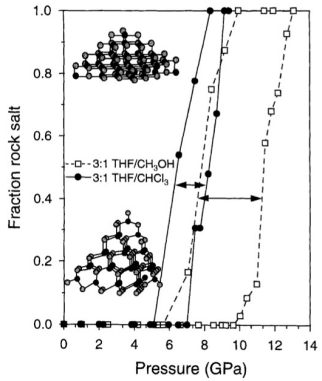
Optimised conduction NGWFs can describe all localised states of a molecule (but not vacuum states)

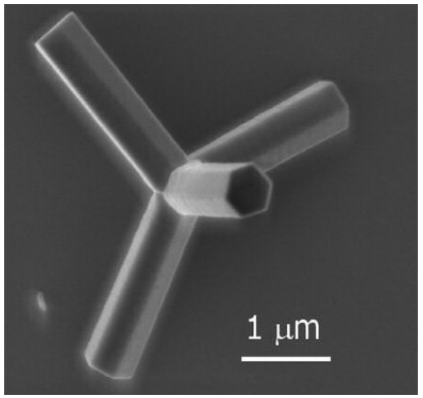
However, spectra is still subject to the fundamental limitations of DFT: bandgaps severely underestimated!

L. E. Ratcliff, N.D.M. Hine, P.D. Haynes, Phys. Rev. B **84**, 165131 (2012)

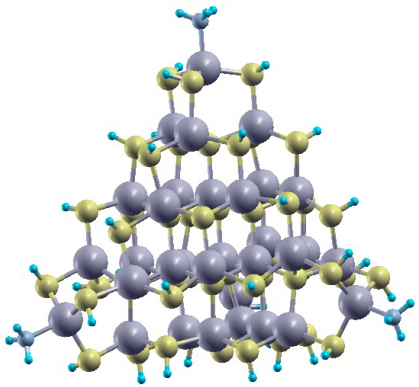
Pressure-Induced Phase Transformations in Nanomaterials

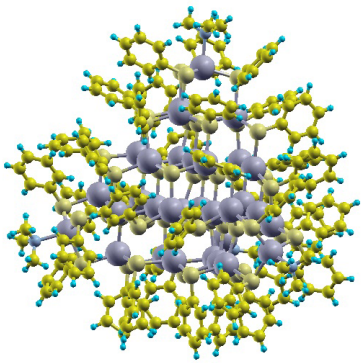
Pressure causes phase transformations (eg ZB to RS) in CdS, CdSe nanocrystals





Optical properties of resulting nanoparticles important for sensor & photovoltaics applications





Many interesting effects of ligands, size, shape, etc: See poster by Niccolo Corsini

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!)
- Enables low-cost treatment of transition metal oxides
- Development of core-level spectroscopy in-progress
- Future extensions to NMR, EFG, etc;

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