Overview of functionality in the ONETEP code

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ONETEP Masterclass 2017, Cambridge, 30th August 2017

Overview

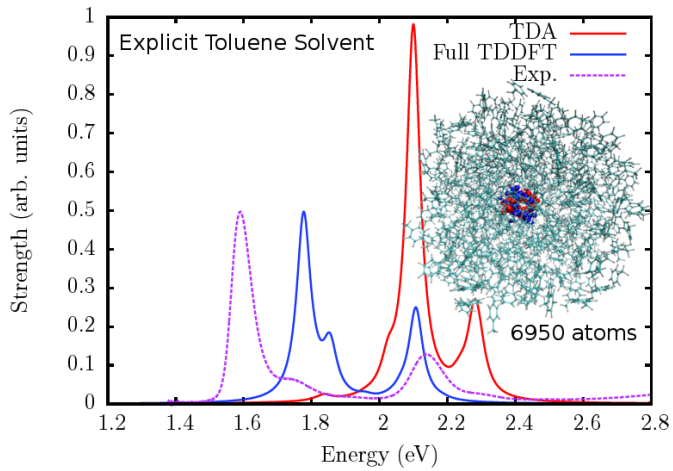
- LR-TDDFT
- Implicit Solvent
- van der Waals
- Metallic systems
- External Pressure
- PAW
- Hybrid Functionals
- Molecular Dynamics
- Transport
- Population Analysis
- Strong Correlations
- Constrained DFT
- Phonons
- Future Plans

Linear-Response TDDFT

Capability: Calculate localised excitations and optical spectra

People: Tim Zuehlsdorff, Jian-Hao Li, Peter Haynes, Nicholas Hine

- Linear-scaling time-dependent density-functional theory in the linear response formalism, T. J. Zuehlsdorff, N. D. M. Hine, J. S. Spencer, N. M. Harrison, D. J. Riley, and P. D. Haynes, J. Chem. Phys. 139, 064104 (2013).
- Linear-scaling time-dependent density-functional theory (TDDFT) beyond the Tamm-Dancoff approximation: obtaining efficiency and accuracy with in situ optimised local orbitals, T. J. Zuehlsdorff, N. D. M. Hine, M. C. Payne, P. D. Haynes, J. Chem. Phys. 143, 204107 (2015).



Quantified Natural Transition Orbitals:

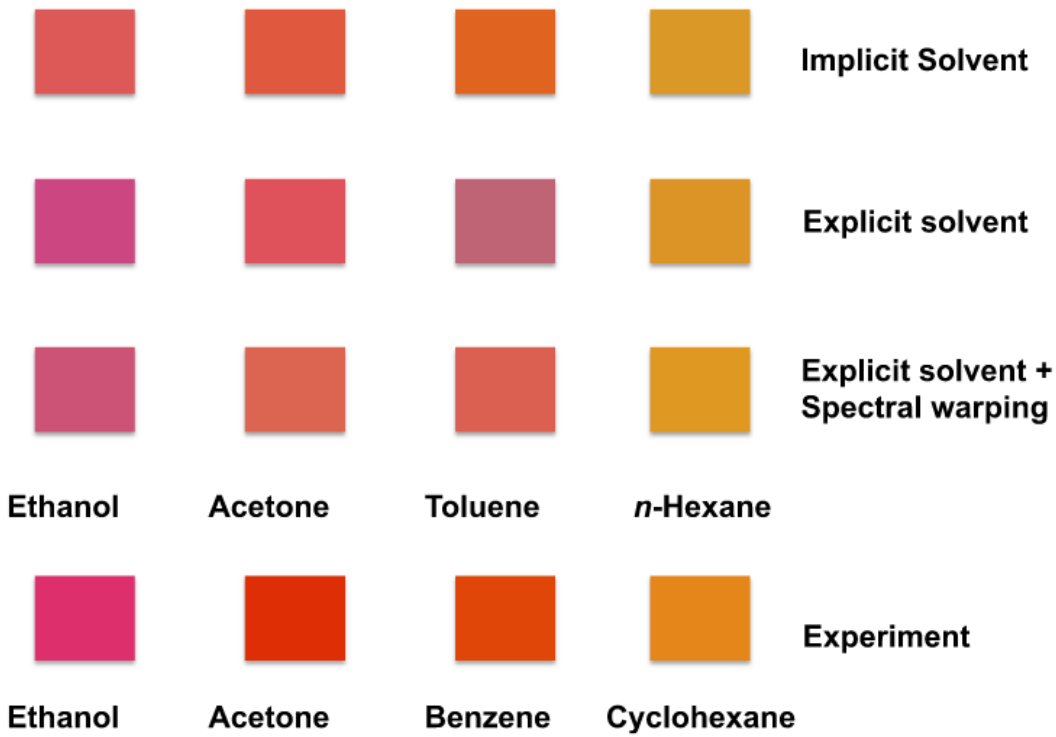
- Identifying and Tracing potential energy surfaces of electronic excitations via their transition origins: application to Oxirane, J.-H. Li, T.J. Zuehlsdorff, M. C. Payne, N. D. M. Hine, Phys. Chem. Chem. Phys. 17, 12065 (2015)

TDDFT for Spectroscopy and Colour Prediction

Capability: Absorption spectra used to predict colours and exciton dynamics

People: Tim Zuehlsdorff, David Turban, Matt Turner, Peter Haynes, Nicholas Hine

- Solvent effects on electronic excitations of an organic chromophore, T. J. Zuehlsdorff, P. D. Haynes, F. Hanke, M. C. Payne, and N. D. M. Hine, J. Chem. Theory Comput., 12, 1853 (2016).
- Predicting solvatochromic shifts and colours of a solvated organic dye: The example of Nile Red, T. J. Zuehlsdorff, P. D. Haynes, M. C. Payne, and N. D. M. Hine, J. Chem. Phys. 146, 124504 (2017).



Electron Energy Loss Spectroscopy

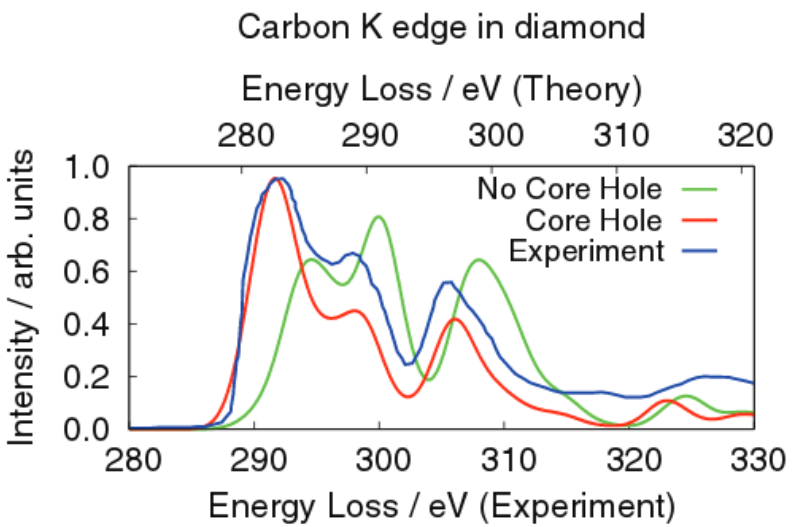
Capability: Predict spectra from EELS measurements

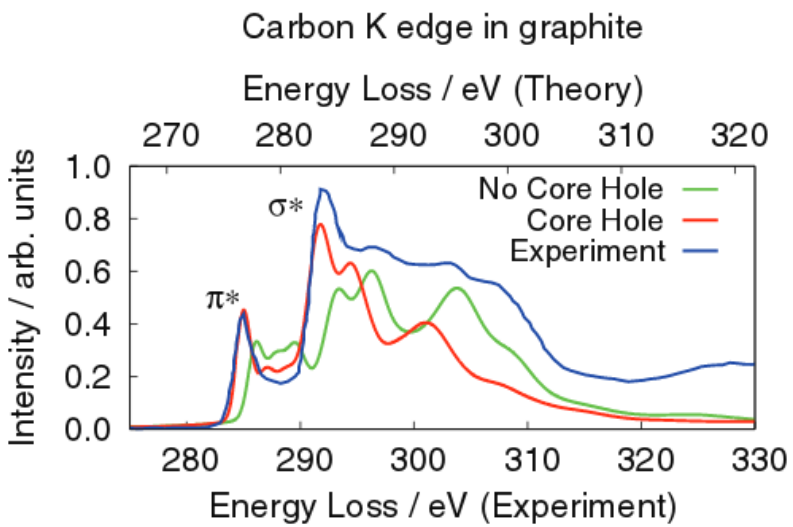
People: Edward Tait, Laura Ratcliff, Nicholas Hine

- Simulation of electron energy loss spectra of nanomaterials with linear-scaling density functional theory, E. W. Tait, L. E. Ratcliff, M. C. Payne, P. D. Haynes and N. D. M. Hine, J. Phys: Condens Matter, 28 195202 (2016).

$$\epsilon_2(\omega) = \frac{1}{\Omega}\sum_c\sum_i |\mathbf{q}\cdot\langle\psi_i|\mathbf{r}|\psi_c\rangle|^2\delta(E_i - E_c - \omega)$$

$$\langle\psi_i|\mathbf{r}|\psi_c\rangle = \langle\bar{\psi}_i|\mathbf{r}|\psi_c\rangle + \sum_{\nu} \langle\bar{\psi}_i|\bar{p}_\nu\rangle(\langle\varphi_\nu|\mathbf{r}|\psi_c\rangle - \langle\bar{\varphi}_\nu|\mathbf{r}|\psi_c\rangle)$$



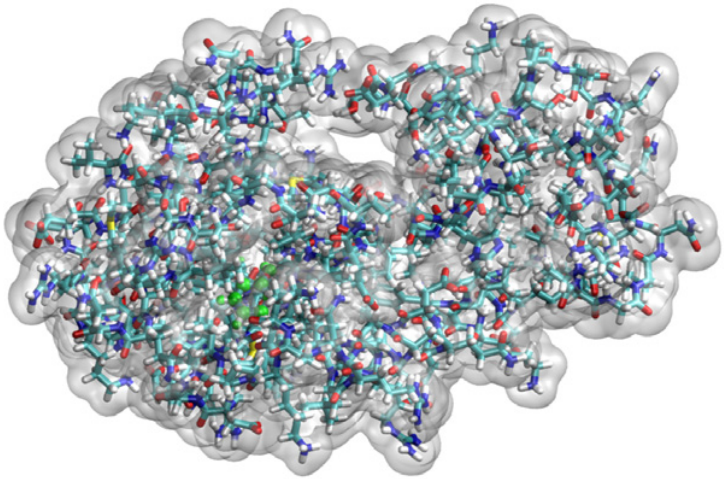


Implicit Solvent

Capability: Simulate molecules, nanostructures etc in a dielectric medium

People: Jacek Dziedzic, James Womack, Arash Mostofi, Chris Skylaris

- Minimal parameter implicit solvent model for ab initio electronic structure calculations, J. Dziedzic, H. H. Helal, C.-K. Skylaris, A. A. Mostofi, and M. C. Payne. Europhysics Letters 95, 43001 (2011).
- Large-scale DFT calculations in implicit solvent - a case study on the T4 lysozyme L99A/M102Q protein, J. Dziedzic, S. J. Fox, T. Fox, C. S. Tautermann, and C.-K. Skylaris, Int. J. Quantum Chem 113, 771, (2013).

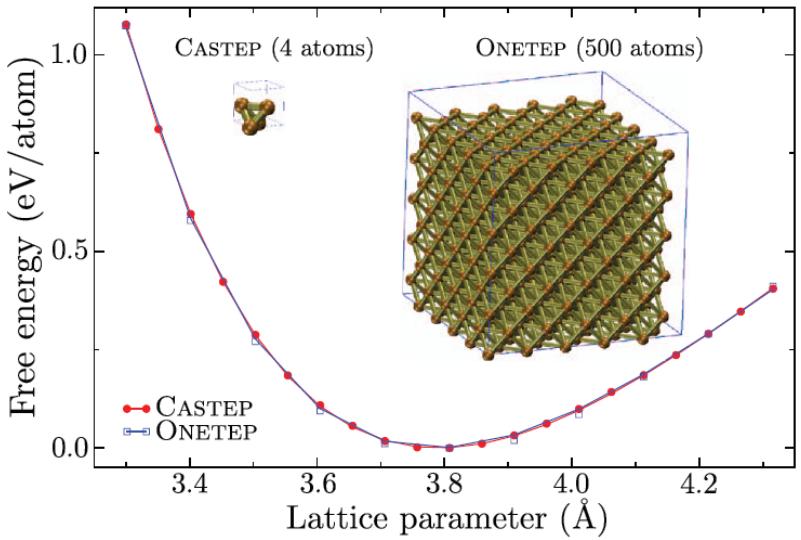


Metallic Systems

Capability: Treatment of large metallic systems eg metallic nanoparticles (Asymptotic Cubic-Scaling, but near-linear for medium/large systems)

People: Alvaro Ruiz-Serrano, Chris Skylaris

- A variational method for density functional theory calculations on metallic systems with thousands of atoms, A. Ruiz-Serrano and C.-K. Skylaris, J. Chem. Phys. 139, 054107 (2013).
- Perspective: Methods for large-scale density functional calculations on metallic systems, J. Aarons, M. Sarwar, D. Thompsett, and C.-K. Skylaris, J. Chem. Phys. 145 220901 (2016).
- Predicting the oxygen binding properties of platinum nanoparticle ensembles by combining high-precision electron microscopy & DFT, J. Aarons et al Nano Letters 17, 4003 (2017).



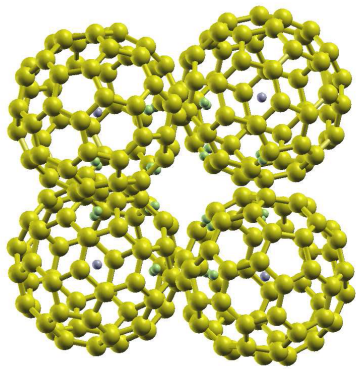
van der Waals

Capability: Fully non-local van der Waals Density Functionals, using functionals eg Dion et al, and fast method of Roman-Perez & Soler.

People: Lampros Andrinopoulos, Gabriel Constantinescu, Fabiano Corsetti, Nicholas Hine, Arash Mostofi

- Article in Preparation: L. Andrinopoulos, F. Corsetti, N. Hine, A. Mostofi
- Used in: Energy landscape and band-structure tuning in realistic MoS2/MoSe2 heterostructures G. C. Constantinescu, N. D. M. Hine Phys. Rev. B 91, 195416 (2015).

$$E_c^{\mathrm{nl}} = \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})\phi(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}') \Rightarrow E_c^{\mathrm{nl}} = \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})\phi(q,q',r)\rho(\mathbf{r}')$$



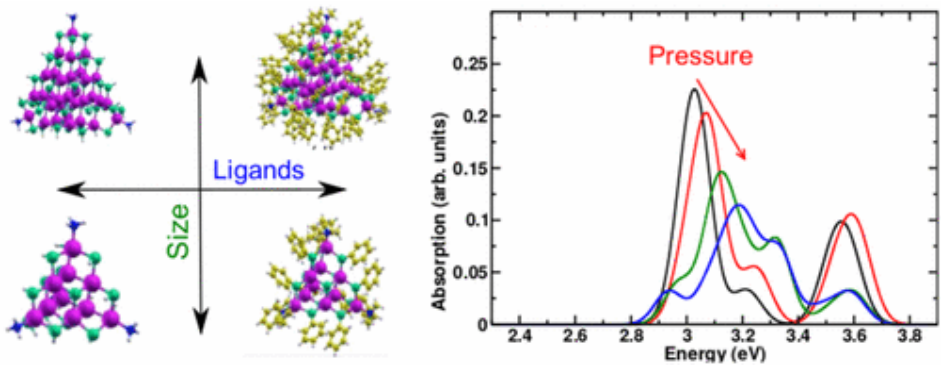
Update: Now have VDW-DF1, VDW-DF2, OPTPBE, OPTB88, C09, etc

External Pressure

Capability: Simulated systems under external pressure, via enthalpy method

People: Niccolo Corsini, Nicholas Hine, Peter Haynes

- Simulations of Nanocrystals Under Pressure: Combining Electronic Enthalpy and Linear-Scaling Density-Functional Theory, N. R. C. Corsini, A. Greco, N. D. M. Hine, C. Molteni, P. D. Haynes, J. Chem. Phys., 139, 084117 (2013).
- Pressure-induced amorphisation and a new high density amorphous metallic phase in matrix-free Ge nanoparticles, N. R. C. Corsini et al, Nano Letters 15, 7334 (2015).
- Unravelling the Roles of Size, Ligands and Pressure in the Piezochromic Properties of CdS Nanocrystals, N. R. C. Corsini, N. D. M. Hine, P. D. Haynes and C. Molteni, Nano Letters 17, 1042 (2017).



Projector Augmented Wave

Capability: Use PAW treatment of core electrons rather than norm-conserving pseudos. Effectively an all-electron treatment, enabling accurate calculations on high-Z elements & transition metals.

People: Nicholas Hine

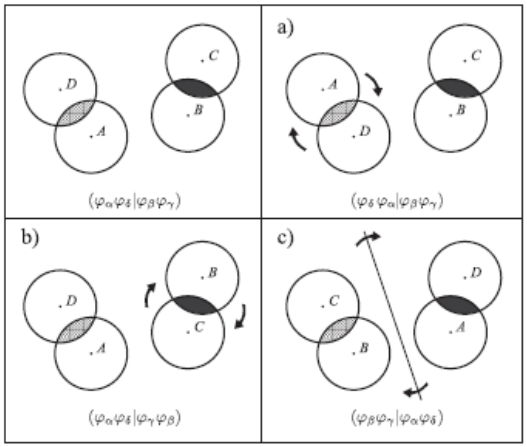
- Linear-Scaling Density Functional Theory using the Projector Augmented Wave Method, N. D. M. Hine, J. Phys. Condens. Matter 29, 024001 (2017).
- Used in: Energy landscape and band-structure tuning in realistic MoS2/MoSe2 heterostructures G. C. Constantinescu, N. D. M. Hine Phys. Rev. B 91, 195416 (2015).

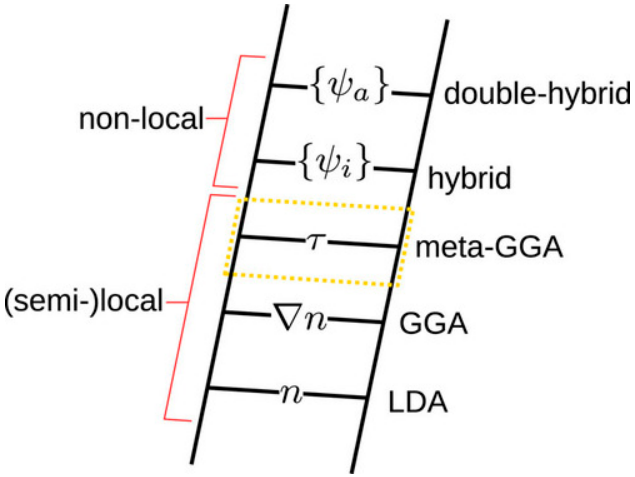
Hybrid Functionals and MetaGGAs

Capability: Functionals including exact exchange (eg B3LYP)

People: Jacek Dziedzic, James Womack, Chris Skylaris

- Linear-Scaling calculation of Hartree-Fock exchange energy with Non-Orthogonal Generalised Wannier functions, J. Dziedzic, Q. Hill, C. K. Skylaris, J. Chem. Phys., 139, 214103 (2013).
- Self-consistent implementation of meta-GGA functionals for the ONETEP linear-scaling electronic structure package, J. C. Womack, N. Mardirossian, M. Head-Gordon, and C.-K. Skylaris, J. Chem. Phys. 145, 204114 (2016).



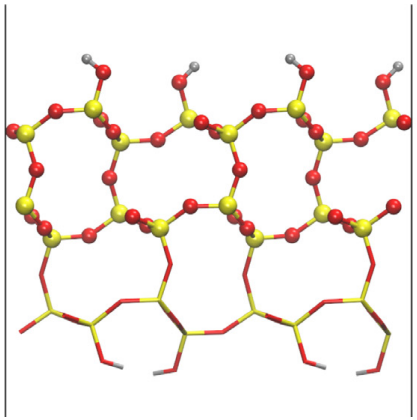


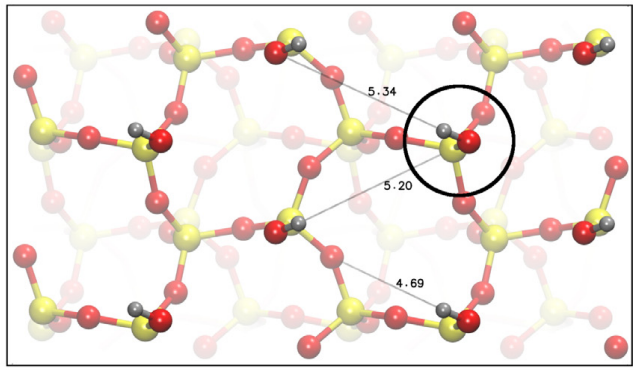
Molecular Dynamics

Capability: Perform Dynamics on large systems, with density matrix extrapolation

People: Valerio Vitale, Simon Dubois, Chris Skylaris

- Anharmonic infrared spectroscopy through the Fourier transform of time correlation function formalism in ONETEP, V. Vitale, J. Dziedzic, S. M. M. Dubois, H. Fangohr, C.-K. Skylaris, J. Chem. Theor. Comput. 11, 3321 (2015).
- Acid-base dissociation mechanisms and energetics at the silica–water interface: An activationless process, B. M. Lowe, , C.-K. Skylaris, N. G. Green, Journal of Colloid and Interface Science 451, 231 (2015).





$$1: \quad \mathbf{v}' = \mathbf{v}_n + \frac{\Delta t}{2m} * \mathbf{F}_n \tag{2}$$

$$2: \quad \mathbf{r}_{n+1} = \mathbf{r}_n + \Delta t * \mathbf{v}' \tag{3}$$

$$3: \quad \text{Compute ionic forces } \mathbf{F}_{n+1} \tag{4}$$

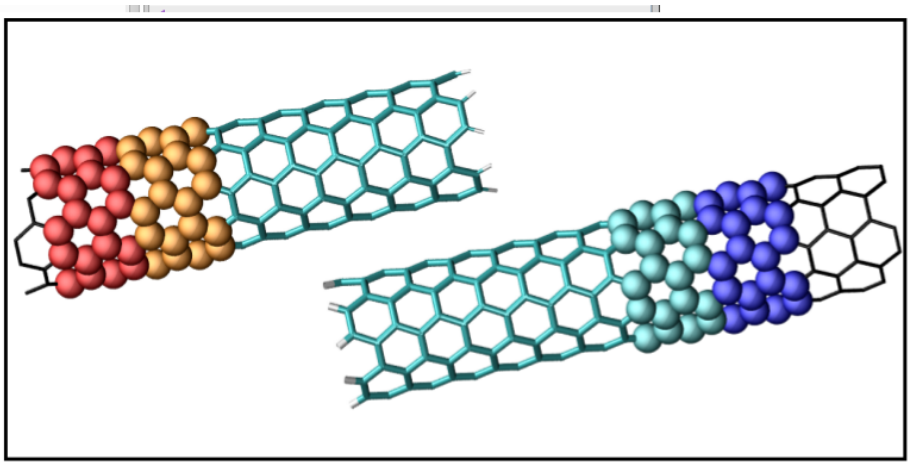
$$4: \quad \mathbf{v}_{n+1} = \mathbf{v}' + \frac{\Delta t}{2m} * \mathbf{F}_{n+1} \tag{5}$$

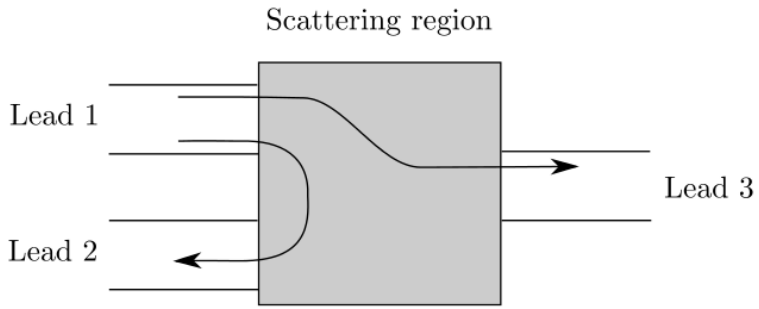
Transport

Capability: Perform Dynamics on large systems, with density matrix extrapolation

People: Simon Dubois, Rob Bell, Arash Mostofi

- Electronic transport calculations in the onetep code: Implementation and applications, R. A. Bell, S.M.M. Dubois, M. C. Payne, A. A. Mostofi, Comput. Phys. Commun. 193, 78 (2015).



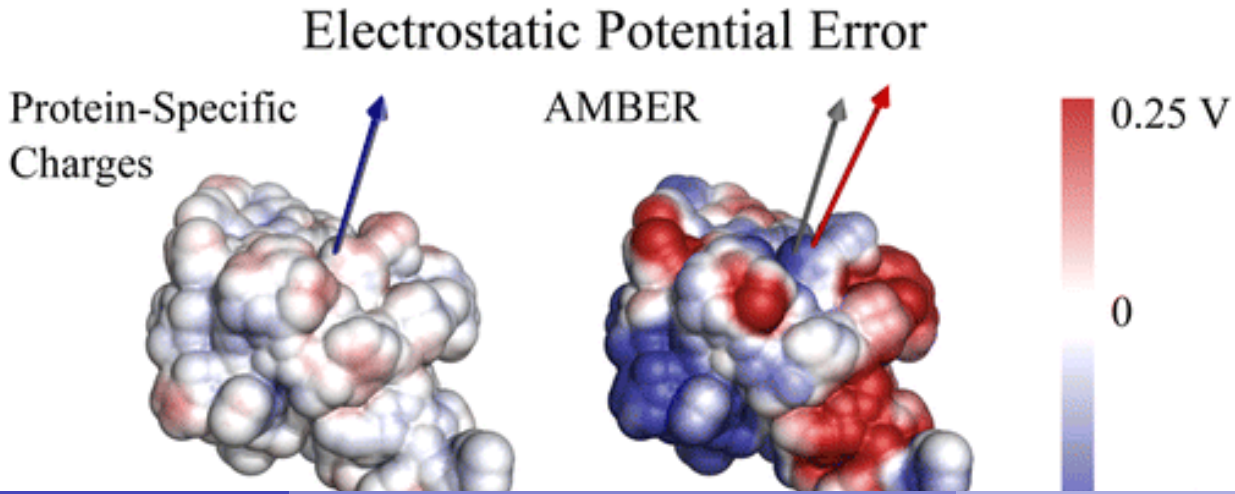


Population Analysis & Energy Decomposition

Capability: Natural Population Analysis, Hirschfeld, DDEC, etc, for forcefield fitting and electrostatics

People: Louis Lee, Danny Cole, Chris Skylaris

- Polarized Protein-Specific Charges from Atoms-in-Molecule Electron Density Partitioning, L. P. Lee , D. J. Cole , C.-K. Skylaris, W. L. Jorgensen , and M. C. Payne, J. Chem. Theory Comput. 9, 2981 (2013).
- Natural bond orbital analysis in the ONETEP code: Applications to large protein systems, L. P. Lee, D. J. Cole, M. C. Payne, and C.-K. Skylaris, J. Comp.Chem. 34, 429 (2013).
- Biomolecular Force Field Parameterization via Atoms-in-Molecule Electron Density Partitioning, D. J. Cole, J. Z. Vilseck, J. Tirado-Rives, M. C. Payne, and W. L. Jorgensen, J. Chem. Theory Comput. 12, 2312 (2016).
- Intuitive Density Functional Theory-Based Energy Decomposition Analysis for Protein\u2013Ligand Interactions, M. J. S. Phipps, T. Fox, C. S. Tautermann, and C.-K. Skylaris, J. Chem. Theor. Comput. 13, 1837(2017).

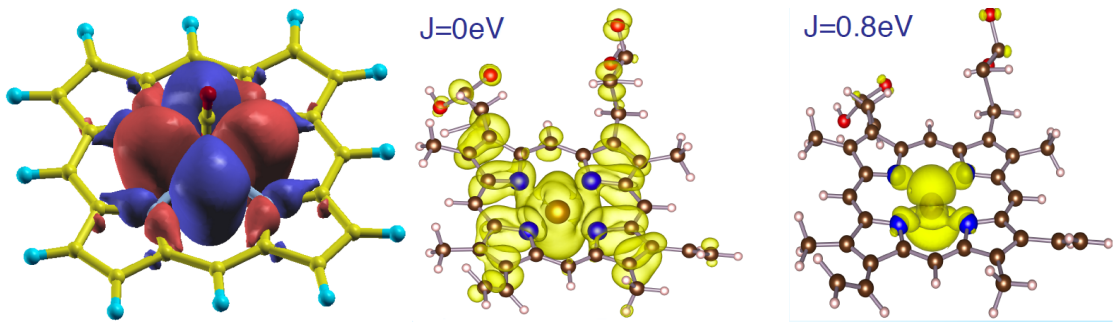


Strong Correlations

Capability: DFT+U (penalise non-integer occupations); Dynamical Mean Field Theory

People: David O'Regan, Cedric Weber, Nicholas Hine, Arash Mostofi

- Inapplicability of exact constraints and a minimal two-parameter generalization to the DFT+U based correction of self-interaction error, G. Moynihan, G. Teobaldi, and D. D. O'Regan, Phys. Rev. B 94, 220104(R) (2016).
- Renormalization of myoglobin–ligand binding energetics by quantum many-body effects, C. Weber, D. J. Cole, D. D. O'Regan, M. C. Payne, PNAS 111, 5790 (2014).
- Importance of many body effects in the kernel of hemoglobin for ligand binding, C. Weber, D. D. O'Regan, N. D. M. Hine, P. B. Littlewood, G. Kotliar and M. C. Payne, Physical Review Letters, 110, 106402 (2013).
- Vanadium dioxide : A Peierls-Mott insulator stable against disorder, C. Weber, D. D. O'Regan, N. D. M. Hine, M. C. Payne, G. Kotliar and P. B. Littlewood, Physical Review Letters 108, 256402 (2012).
- Ligand Discrimination in Myoglobin from Linear-Scaling DFT+U, D. J. Cole, D. D. O'Regan, and M. C. Payne, J. Phys. Chem. Lett. 3, 1448 (2012).
- Linear-scaling DFT+U with full local orbital optimization, D. D. O'Regan, N. D. M. Hine, M. C. Payne and A. A. Mostofi, Phys. Rev. B 85, 085107 (2012).

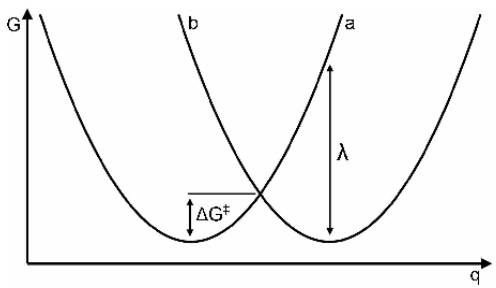


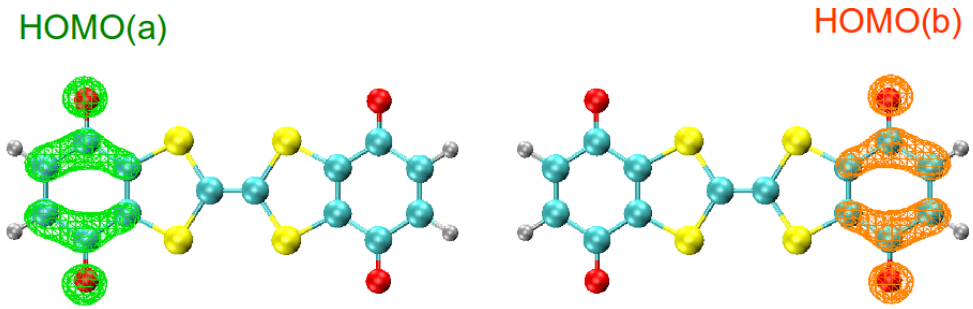
Constrained DFT

Capability: Constrain populations & spins of certain regions of a system (eg for studying charge transfer reactions)

People: Gilberto Teobaldi, David O'Regan, David Turban, Nicholas Hine

- Supercell convergence of charge-transfer energies in pentacene molecular crystals from constrained DFT, D. H. P. Turban, G. Teobaldi, D. D. O'Regan, N. D. M. Hine, Phys. Rev. B 93, 165102 (2016).
- Optimization of constrained density functional theory, D. D. O'Regan and G. Teobaldi, Phys. Rev. B 94, 035159 (2016).



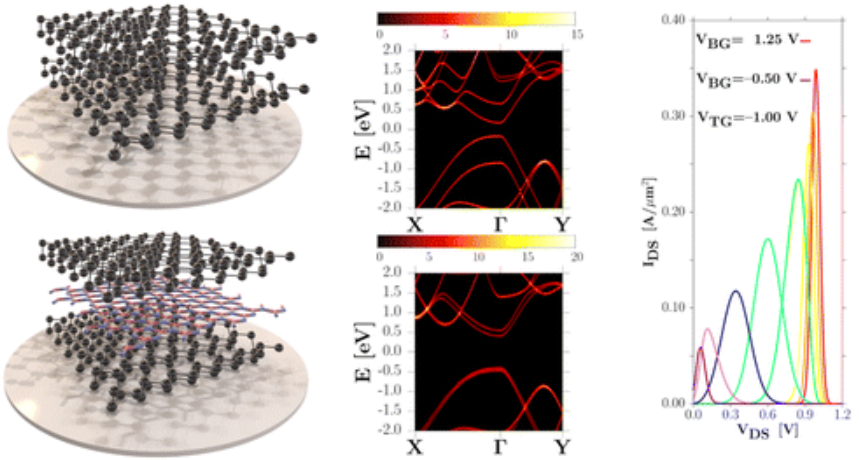


Spectral Function Projection

Capability: Perform Supercell Calculation, Project result onto Primitive Bandstructure

People: Gabriel Constantinescu, Nicholas Hine

- Energy landscape and band-structure tuning in realistic MoS2/MoSe2 heterostructures, G. C. Constantinescu and N. D. M. Hine, Phys. Rev. B 91, 195416 (2015).
- Multi-purpose Black-Phosphorus/hBN heterostructures, G. C. Constantinescu, N. D. M. Hine, Nano Letters, 16, 2586 (2016).
- Determination of band offsets, hybridization and exciton binding in 2D semiconductor heterostructures, N. R. Wilson et al, Science Advances 3, e1601832 (2017)



Phonons

Capability: Calculate vibrational frequencies, free energies, phonon modes etc, via a) finite-difference approach, b) linear-response methods

People: Fabiano Corsetti, Gabriel Constantinescu

- Article(s) in Preparation

$$E^{\mathrm{tot}} = E^{\mathrm{eq}} + \frac{1}{2} \sum_{a,\alpha,\kappa,a',\alpha',\kappa'} u_{a,\alpha,\kappa} \phi^{\alpha,\alpha'}_{\kappa,\kappa'}\left(a,a'\right) u_{a',\alpha',\kappa'},$$

$$\phi^{\alpha,\alpha'}_{\kappa,\kappa'}\left(a,a'\right) = \frac{\partial^2 E}{\partial u_{a,\alpha,\kappa} \partial u_{a',\alpha',\kappa'}}.$$

$$D^{\alpha,\alpha'}_{\kappa,\kappa'}\left(\mathbf{q}\right) = \frac{1}{\sqrt{M_\alpha M_{\alpha'}}} \sum_a \phi^{\alpha,\alpha'}_{\kappa,\kappa'}\left(a,0\right) \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{R}_a},$$

Future Plans

- TD-hybrid Functional
- Linear Response Phonons
- Spin Orbit
- Many-body Methods

Conclusions

- Many exciting new developments!
- **Long-term vision:** a simulation toolset enabling computational discovery with true predictive power for nanomaterials.