

# Density Functional Theory III

Nicholas M. Harrison

*Department of Chemistry, Imperial College London, &  
Computational Materials Science, Daresbury Laboratory*

[nicholas.harrison@ic.ac.uk](mailto:nicholas.harrison@ic.ac.uk)

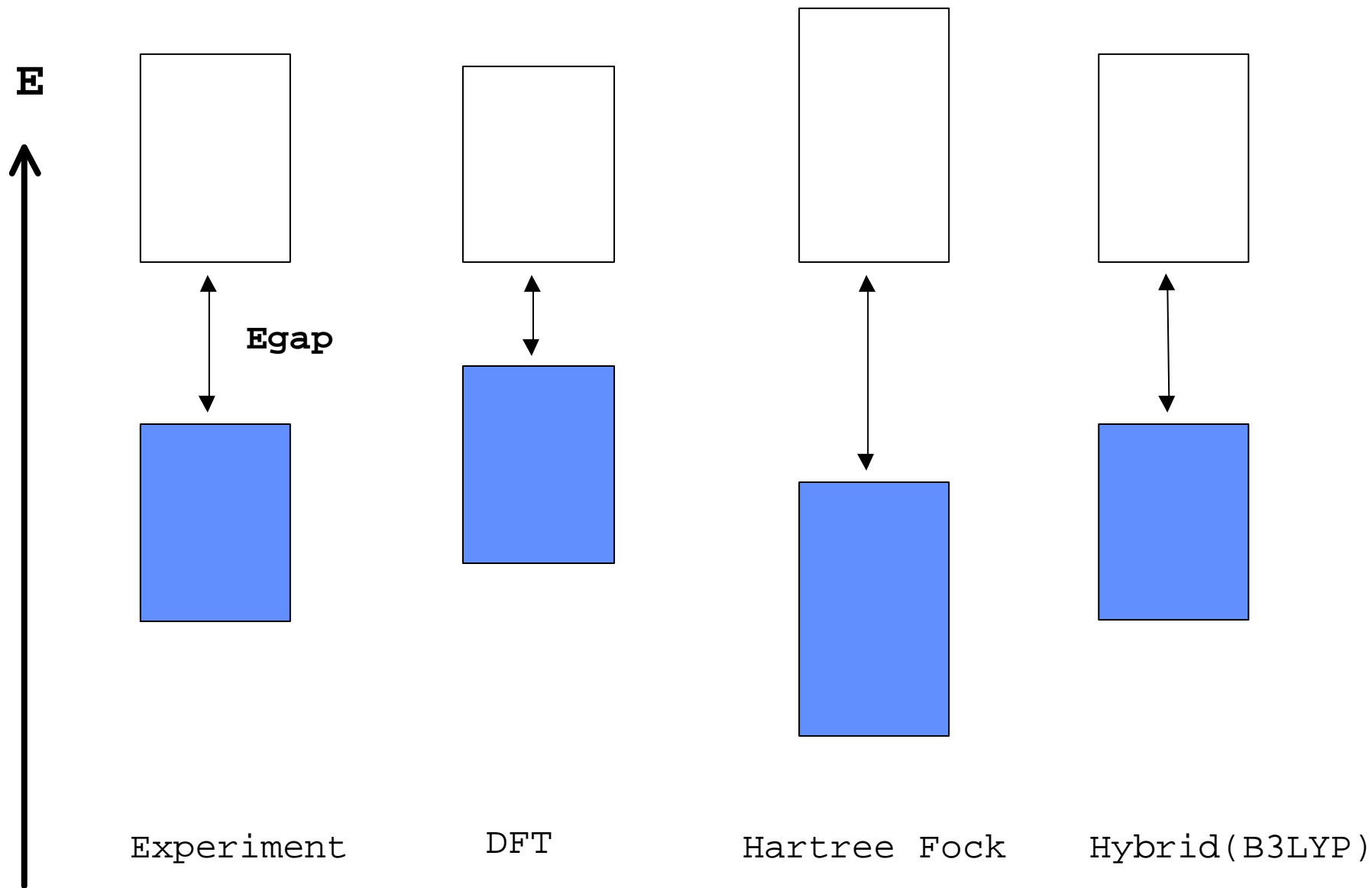
## Conclusions II

- Approximations to DFT are currently the state of the art for materials simulation but do not provide a systematic approach to the exact result.
- With a judicious choice of functional atomisation energies are *typically* accurate to 3-5 kcal/mol, structures to 0.01 Ang., frequencies to 40-60  $\text{cm}^{-1}$
- Much larger errors are possible in ‘difficult’ systems
- Heavily parameterised functionals gain a little for the training set but appear to be less transferable
- Hybrid and meta-GGA look very promising.

# Band Gaps !

- The band gap determines many properties: optical, dielectric, electronic....
- Formally DFT yields the total energy and density – the eigenvalues are **NOT** excitation energies
- The DFT eigenvalues do have some correspondence with the observed adsorbtion spectra...

# DFT Band Structures – Qualitative Guide !



# Self Interaction.. I

The potential in DFT is computed from the TOTAL density.

$$\left[ -\frac{1}{2} \nabla^2 + v_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) \right] \mathbf{f}_i(\mathbf{r}) = \epsilon_i \mathbf{f}_i(\mathbf{r})$$

$$V_{xc}(\mathbf{r}) = \frac{\partial E_{xc}[\rho]}{\partial \rho(\mathbf{r})} \quad \rho(\mathbf{r}) = \sum_{i=1}^N |\mathbf{f}_i(\mathbf{r})|^2$$

As each individual electron contributes to this density – an electron interacts with itself !

Or..

## Self Interaction II

- An electron in an occupied orbital interacts with  $N$  electrons –  $V(N)$  when it should interact with  $N-1$  ie:  $V(N-1)$  – this is the *self interaction*.
- DFT: All occupied bands are pushed up in energy by this interaction – essentially an on-site/diagonal Coulomb/Exchange repulsion. DFT band gaps are TOO SMALL..
- Hartree Fock theory... Exchange and Coulomb cancel exactly – no self interaction. In fact over corrected – GAPS TOO BIG.
- Hybrid – 20% HF and 80% DFT .... Gaps are pretty good !!!

# Hybrid Functionals and Band Gaps

	Expt (eV)	Hybrid (eV)
Si	~3.5	3.8
Diamond	5.5	5.8
GaAs	1.4	1.5
ZnO	3.4	3.2
Al <sub>2</sub> O <sub>3</sub>	~9.0	8.5
Cr <sub>2</sub> O <sub>3</sub>	3.3	3.4
MgO	7.8	7.3
MnO	3.6	3.8
NiO	3.8	3.9
TiO <sub>2</sub>	3.0	3.4
FeS <sub>2</sub>	1.0	2.0
ZnS	3.7	3.5

# The Band Structure of Silicon

