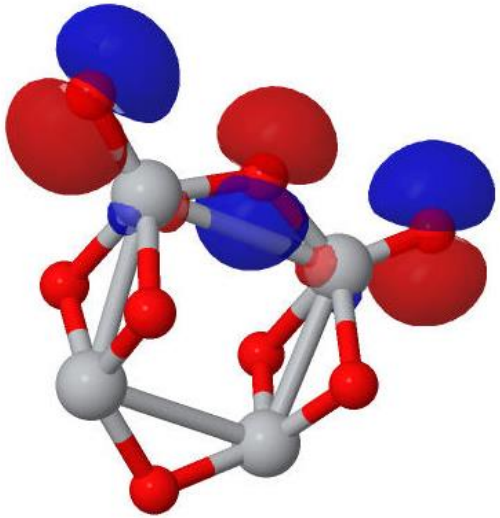
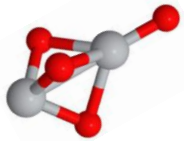
Hands-on Summer School: Electronic Structure Theory for Materials and (Bio)molecules

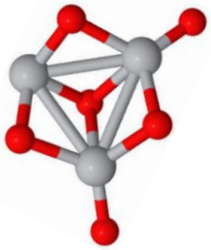
Los Angeles, July 21 - August 1, 2014

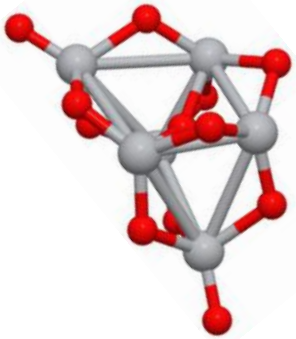


Tutorial 7: Integrating Concepts- Cluster Structure Prediction and Spectroscopy

Prepared by Noa Marom, Tulane University

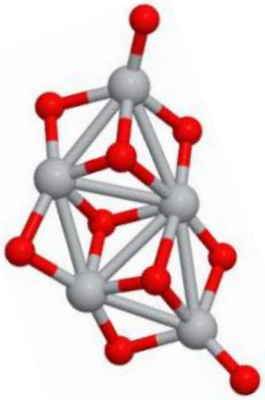


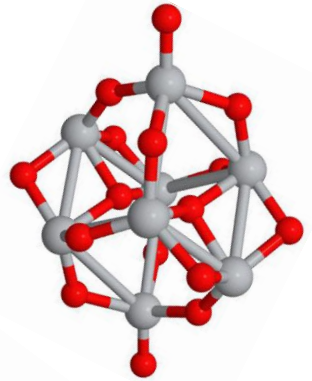




Aim:

Integrating some of the concepts learned in previous tutorials to solve the problem of assigning structures to spectroscopic data for TiO_2 clusters.

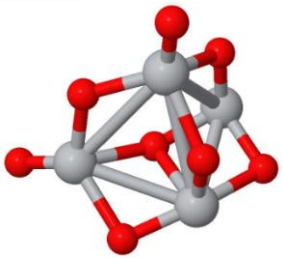


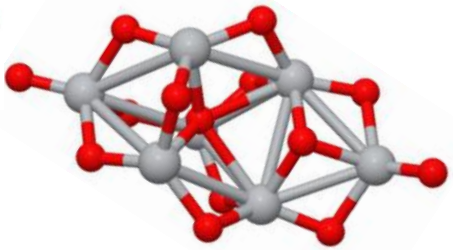


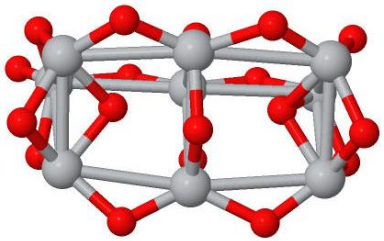
Flow:

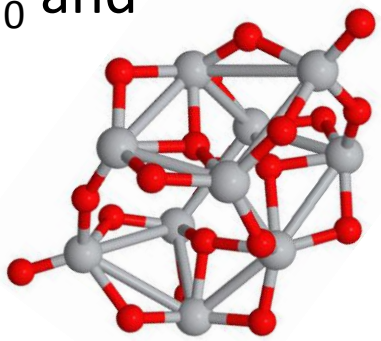
The tutorial has two main parts:

I. Structure search with basin hopping
II. Calculating vertical electron affinities of low lying isomers with G_0W_0 and comparing to photoemission experiments

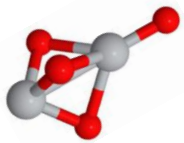


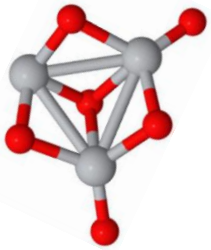


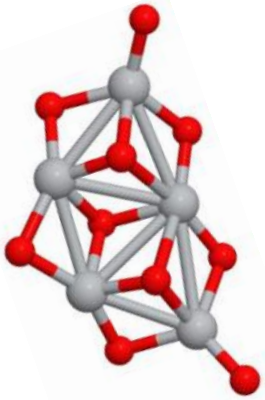


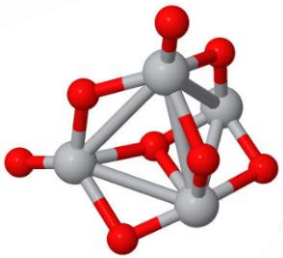


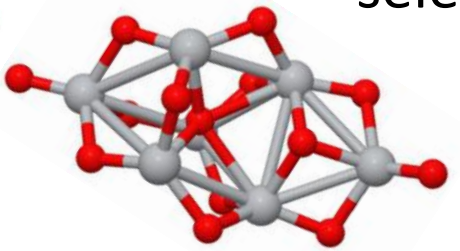
Atomic clusters:

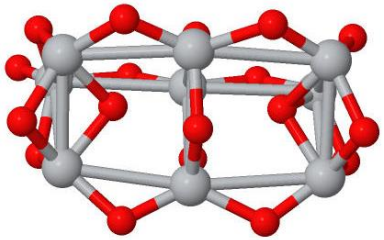


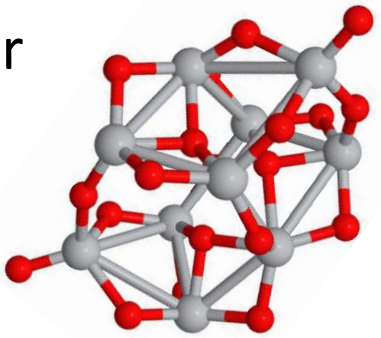


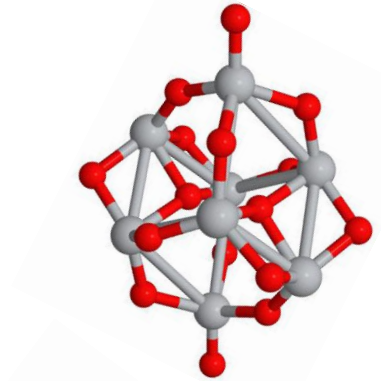


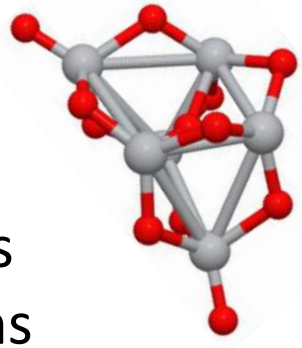












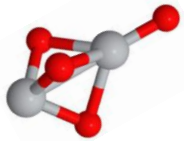
Atomic clusters are promising catalysts

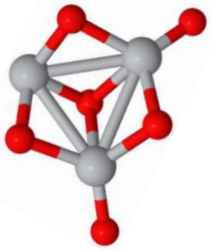
Even noble metals become highly reactive as clusters and can catalyze a variety of reactions

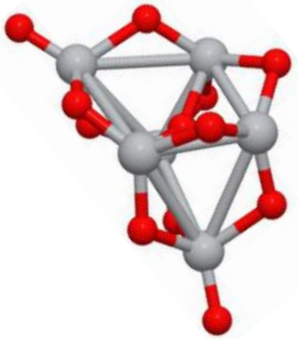
Unlike molecules and crystalline solids, atomic clusters do not have a fixed structure

The electronic properties of clusters depend strongly on their size and structure

This may be used for tailoring cluster catalysts with higher activity and selectivity



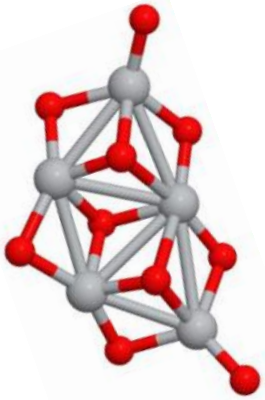


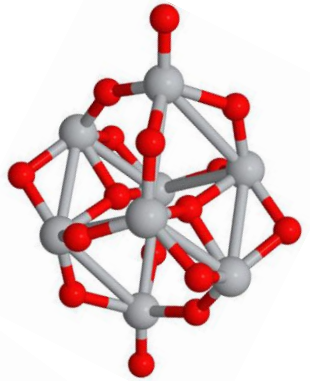


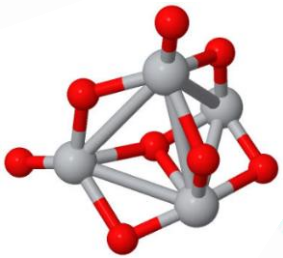
Atomic clusters:

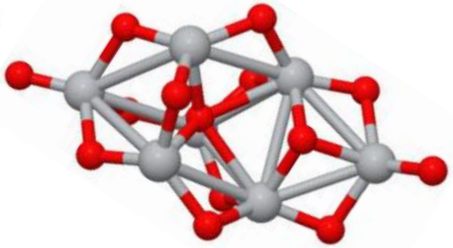
Clusters are too small to characterize their structure directly by x-ray diffraction

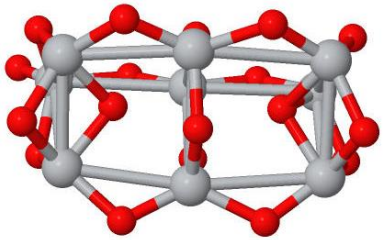
Their structure may be inferred by comparing first principles simulations with indirect spectroscopic measurements, such as photoemission spectroscopy (PES), x-ray spectroscopy, and IR/ Raman spectroscopy

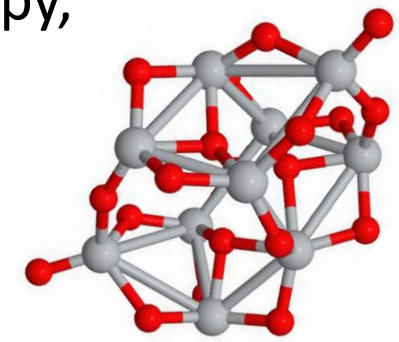




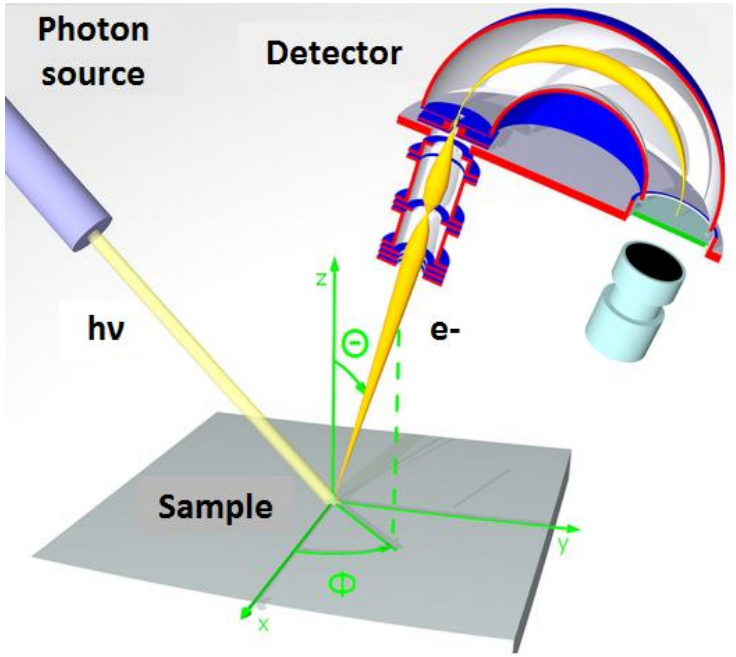




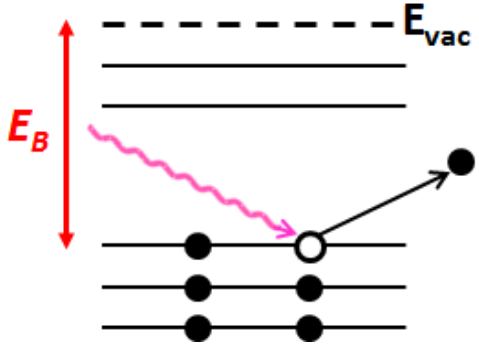


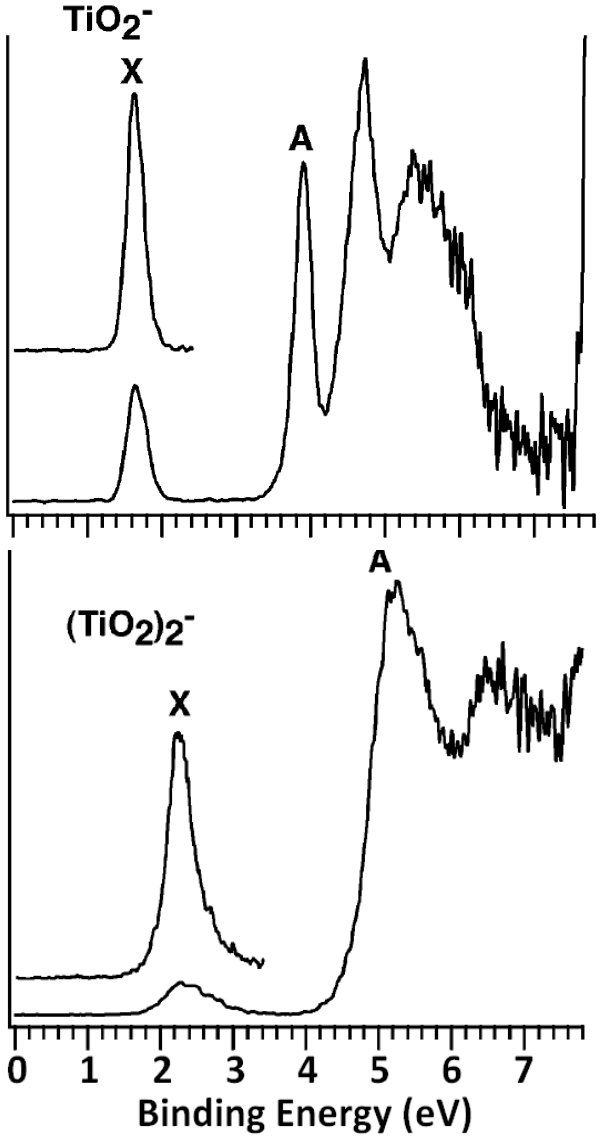


Photoemission Spectroscopy (PES)



$$E_K = h\nu + E_B$$



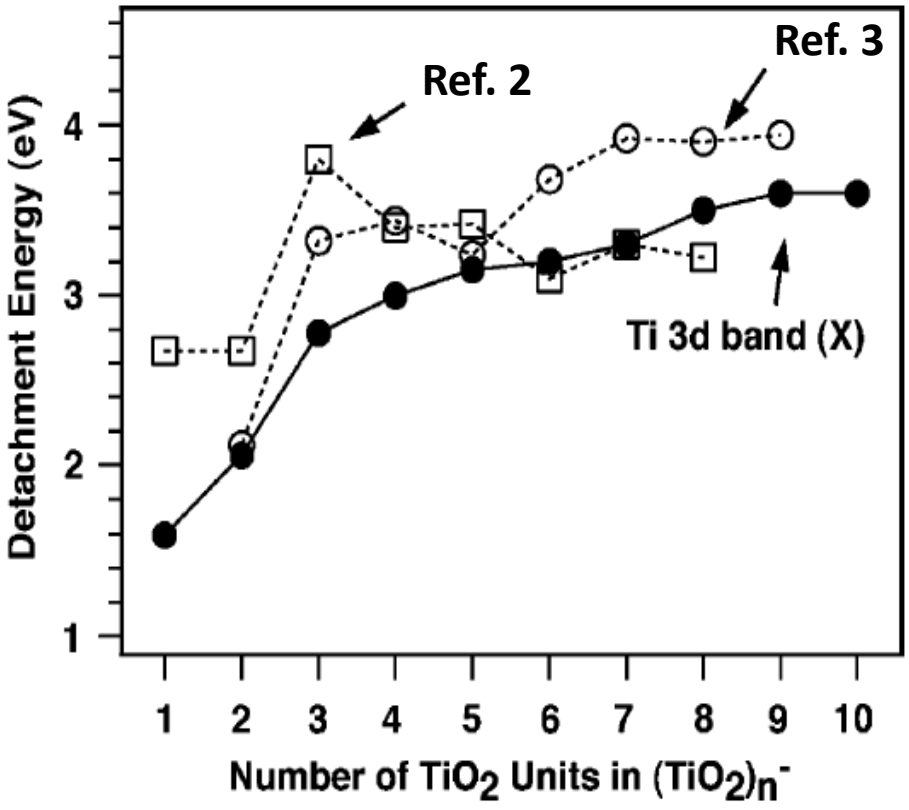


Zhai and Wang *JACS* 129, 3022 (2007)

The Problem:

Zhai and Wang measured the vertical electron affinities (VEAs) and vertical detachment energies (VDEs) of negatively charged $(TiO_2)_{1\text{-}10}$ clusters by PES

The structures of the clusters were not assigned, as two different DFT calculations did not agree with experiment quantitatively or qualitatively



Zhai and Wang *JACS* 129, 3022 (2007)

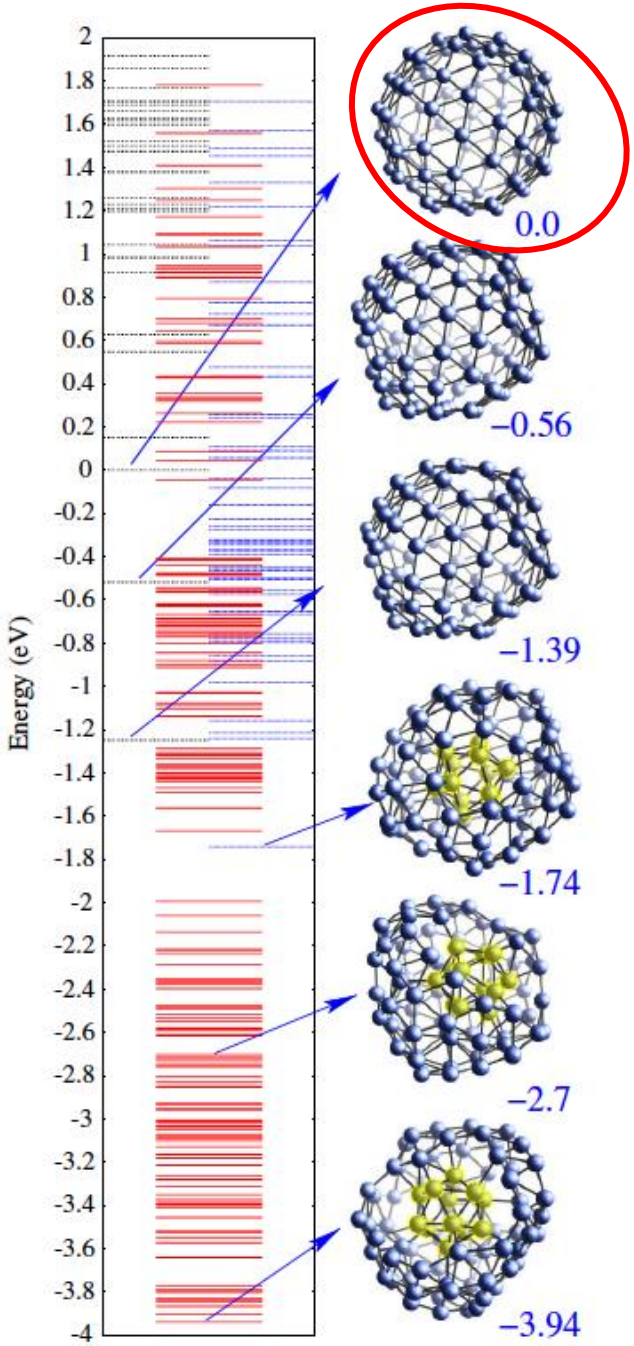
Cluster Structure Search:

It is important to perform an unbiased structure search because intuition can be misleading

For example, in PRL 98, 166804 (2007) the existence of a B_{80} fullerene was proposed, based on intuition

Later, two different groups performed global optimization and showed that the B_{80} fullerene is in fact high above the global minimum of and thus unlikely to exist [JPCA 114, 9969 (2010); PRL 106, 225502 (2011)]

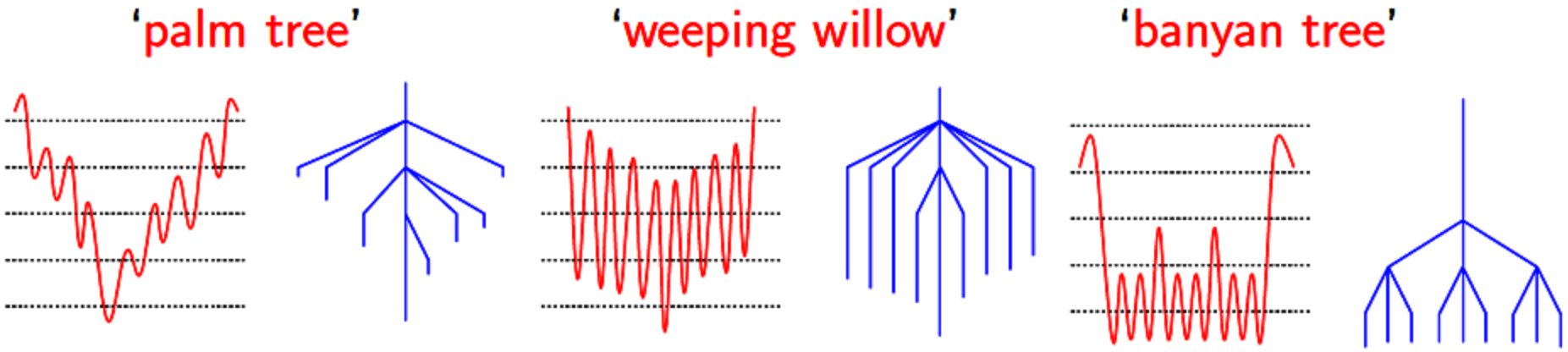
There are several ways to search for the global minimum of a multidimensional potential energy surface



Global Optimization:

The challenge: finding the global minimum of a multidimensional potential energy surface (PES) with many local minima, without exposing the whole PES

Different global optimization methods employ different strategies for escaping from local minima and sampling the PES



Disconnectivity graphs are a way to visualize the structure of a potential energy surface

David Wales "*Energy Landscapes*" Cambridge University Press (2003)

Global Optimization: Simulated Annealing

A molecular dynamics simulation is performed, in which the cluster is heated to a high temperature, at which it essentially melts, and then slowly cooled down.

The purpose of simulated annealing is not necessarily to perform realistic dynamics but to adequately sample the potential energy surface to obtain a realistic global minimum structure.

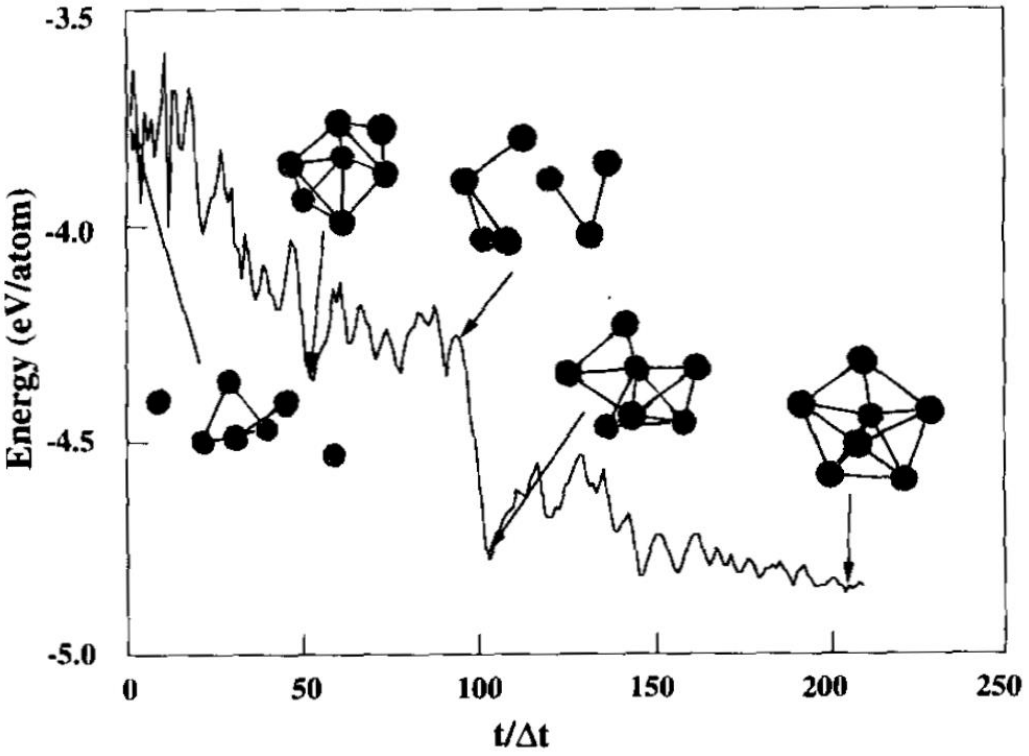
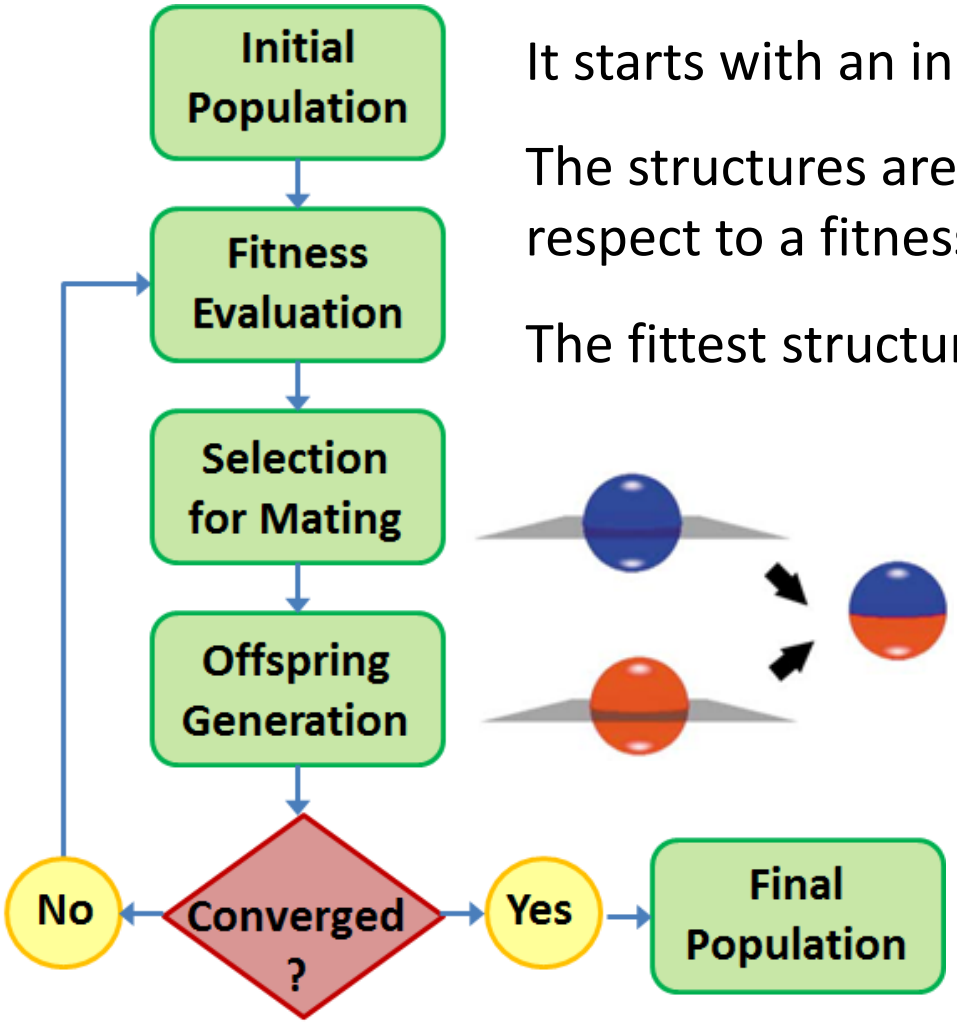


Fig. 1. Simulated anneal for a Si_7 cluster. The binding energy per atom is illustrated as function of the simulation time. The initial temperature of the simulation is 3000 K; the final temperature is 300 K. Also shown are the intermediary structures which occur as the simulation proceeds. The time step Δt is 300 a.u.

J. R. Chelikowsky et al. Computer Physics Communications 85, 325 (1995)

Global Optimization: Genetic Algorithm



A genetic algorithm mimics an evolutionary process.

It starts with an initial population of trial structures.

The structures are locally optimized and evaluated with respect to a fitness function (e.g., the total energy).

The fittest structures are selected for mating.

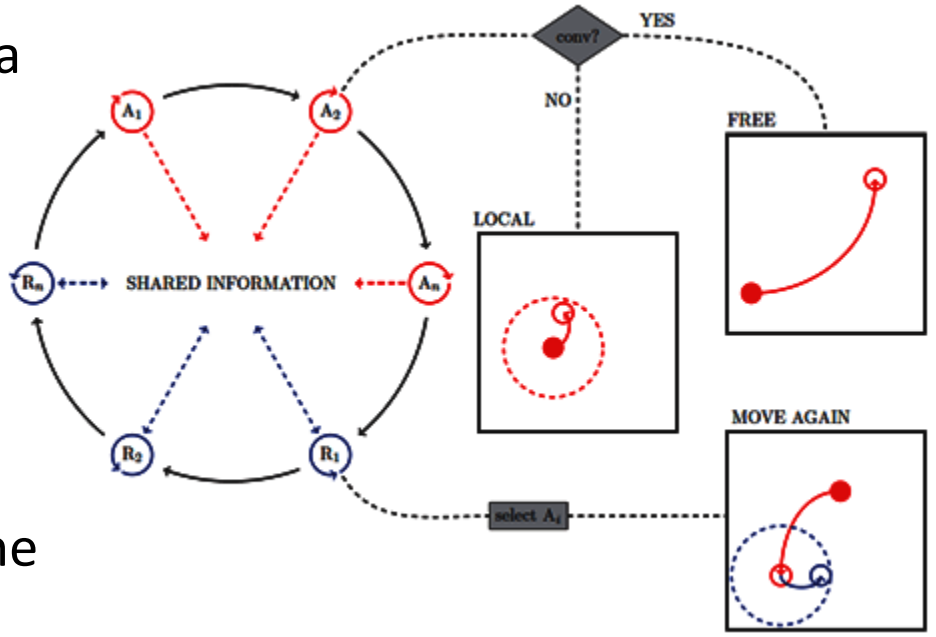
Occasionally, a "bad" structure is selected to maintain the diversity of the population (mutation).

This process propagates structural features associated with, e.g., a lower energy until the global minimum is found

R. L. Johnston, *Dalton Transactions* 2003, 4193 (2003)

Global Optimization: Swarm Algorithm

The optimization is performed via the collective behavior of a population (or a swarm) of random walkers that simultaneously evaluate the fitness function at different positions on the PES with an intelligent communication scheme



For example, the artificial bee colony algorithm has three types of random walkers:

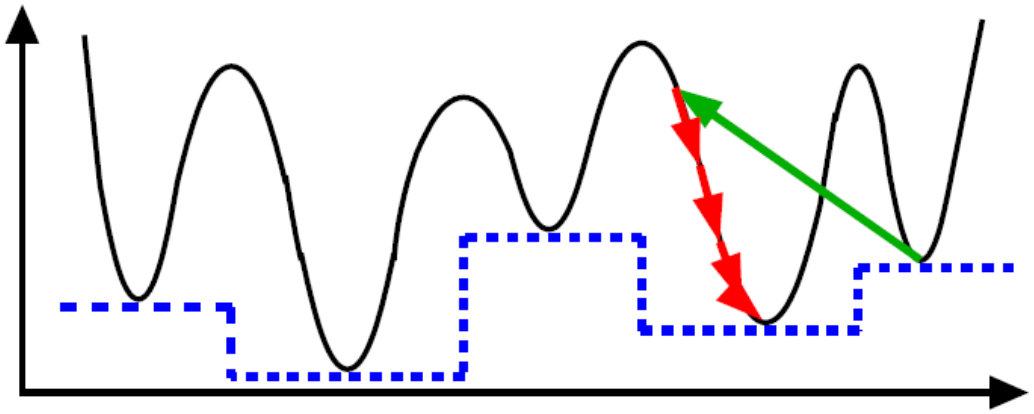
- Scouts sample the PES in a random and unconditional manner.
- Employees move randomly and accept only new positions with a lower function value.
- Onlookers randomly probe the environment of Employees to locally accelerate the sampling frequency in promising areas.

C. Wehmeyer *et al*. *JCP* 137, 194110 (2012)

Global Optimization: Basin Hopping

The potential energy surface (PES) is explored by performing consecutive jumps from one local minimum to another.

In each BH step the positions of the atoms in the cluster are randomly perturbed.



Gehrke and Reuter *PRB* 79, 085412 (2009)

Then, a local geometry optimization is performed to bring the system into a local minimum.

This transforms the PES into a series of plateaus, representing basins of attraction corresponding to the set of configurations that relax to a given minimum.

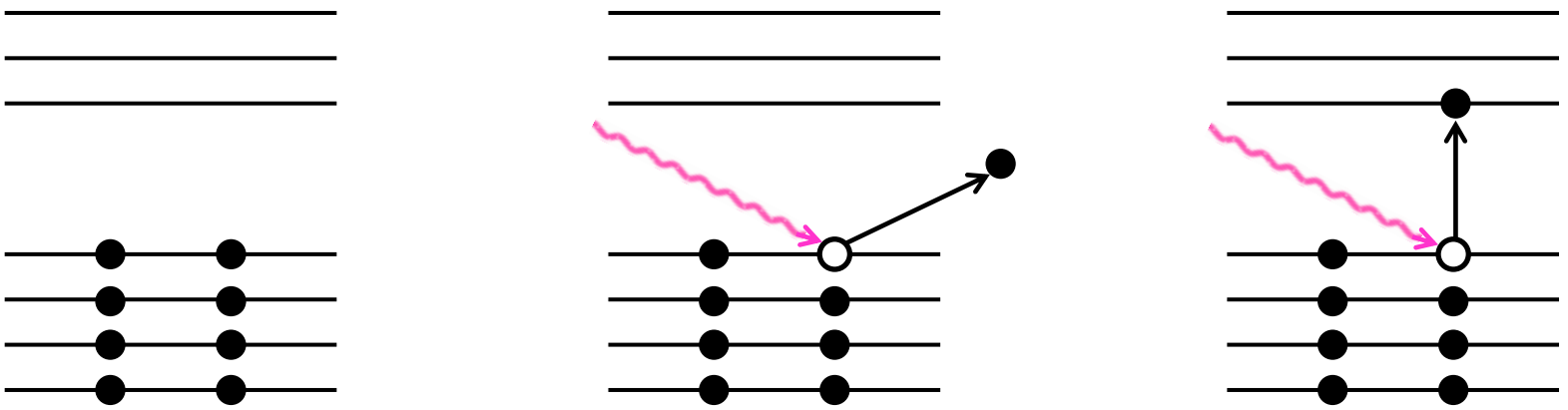
Overview of Electronic Structure Methods:

Structure
Mechanical properties
Vibrational spectrum

Ionization potential (IP)
Electron Affinity (EA)
Fundamental gap
Defect/dopant charge transition levels

Absorption spectrum
Optical gap
Exciton binding energy

Ground State | **Charged Excitation** | **Neutral Excitation**

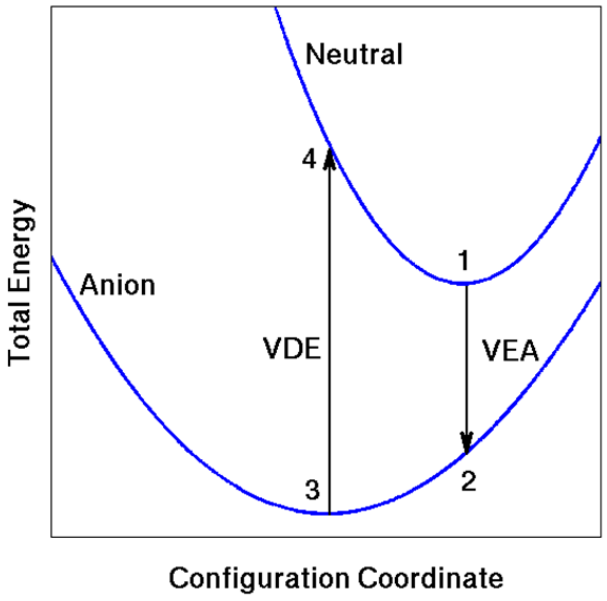


DFT → (+ electronic relaxation) → **GW** → (+ electron-hole interaction) → **BSE**

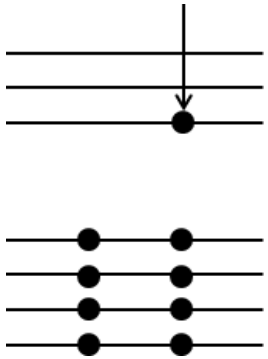
DFT → **TDDFT**

Theoretical Spectroscopy for TiO_2 clusters with GW:

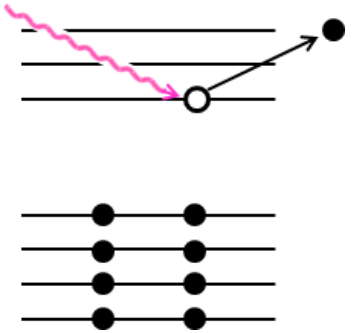
In this tutorial we will use GW to calculate the vertical electron affinities (VEA) and vertical detachment energies (VDE) of TiO_2 clusters because both properties correspond to charged excitations



Vertical electron affinity (VEA) = GW LUMO of the neutral species



Vertical detachment energy (VDE) = GW HOMO of the relaxed anion

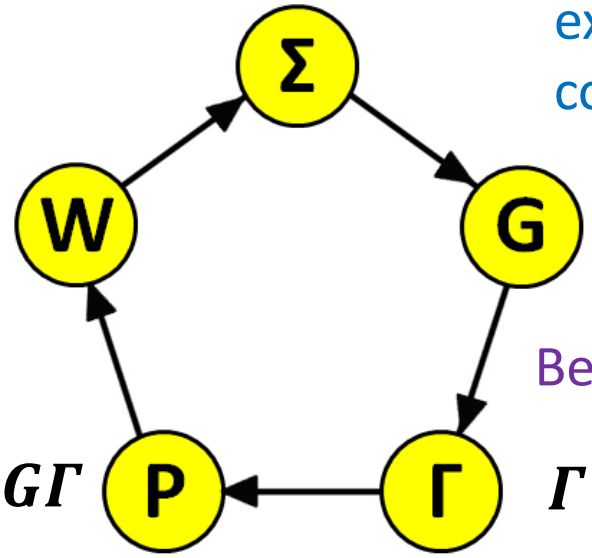


N. Marom, M. Kim, and J. R. Chelikowsky, *PRL* 108, 106801 (2012)

Many-Body Perturbation Theory: Hedin's Equations

An exact closed set of 5 equations for finding the interacting one particle Green's function:

Σ is expanded in terms of the screened coulomb potential, *W*: $\Sigma = iGW\Gamma$



Dyson equation: obtain *G* from the non-interacting G_0 and the self-energy operator, Σ, which contains all the exchange and correlation contributions

$$G = G_0 + G_0 \Sigma G$$

$$W = v + vPW$$

Bethe-Salpeter equation:

$$\Gamma = 1 + \frac{\delta \Sigma}{\delta G} GG\Gamma$$

Polarization: $P = -iGG\Gamma$ response to particle addition/ removal

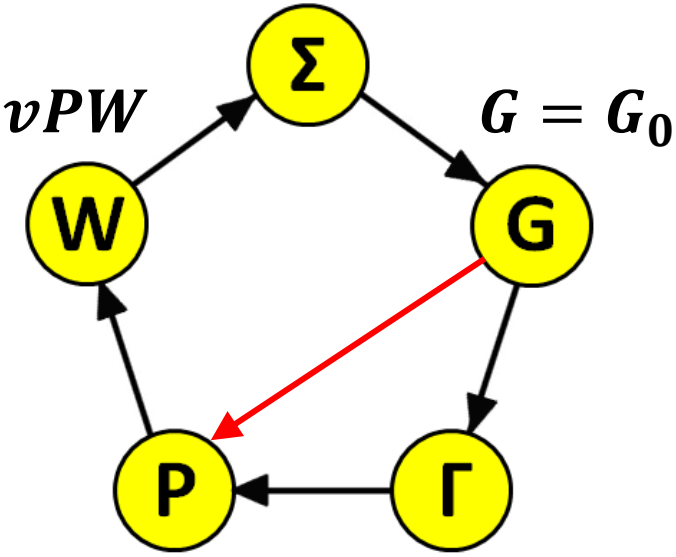
Vertex: contains interactions between quasiparticles

L. Hedin, Phys. Rev. 139, A796 (1965)

The *GW* Approximation:

The (self-consistent) *GW* approximation amounts to neglecting the vertex in the self-energy and the polarization, i.e. neglecting the interactions between quasi-particles

$$\Sigma = iGW\Gamma$$



$$W = v + vPW \qquad G = G_0 + G_0\Sigma G$$

$$P = -iGG\Gamma \qquad \Gamma = 1 + \frac{\delta\Sigma}{\delta G}GG\Gamma$$

The random phase approximation (RPA) for the polarization

L. Hedin, Phys. Rev. 139, A796 (1965)

Non-Self-Consistent G_0W_0:

The Kohn-Sham orbitals and eigenvalues from a DFT calculation are assumed to be a good approximation for the many-body wave-function and QP energies

The QP energies are calculated non-self-consistently as perturbative corrections to the DFT eigenvalues by solving the linearized quasi-particle equation in the diagonal approximation:

$$E_i^{G_0W_0} = \varepsilon_i^{KS} + \left\langle \varphi_i \left| \Sigma^{G_0W_0} - V_{xc} \right| \varphi_i \right\rangle$$

Hybertsen and Louie, *PRB* 34, 5390 (1986)

Basis Set Convergence of G_0W_0:

The Kohn-Sham eigenvalues and eigenfunctions from a DFT calculation are used to evaluate G_0 and W_0

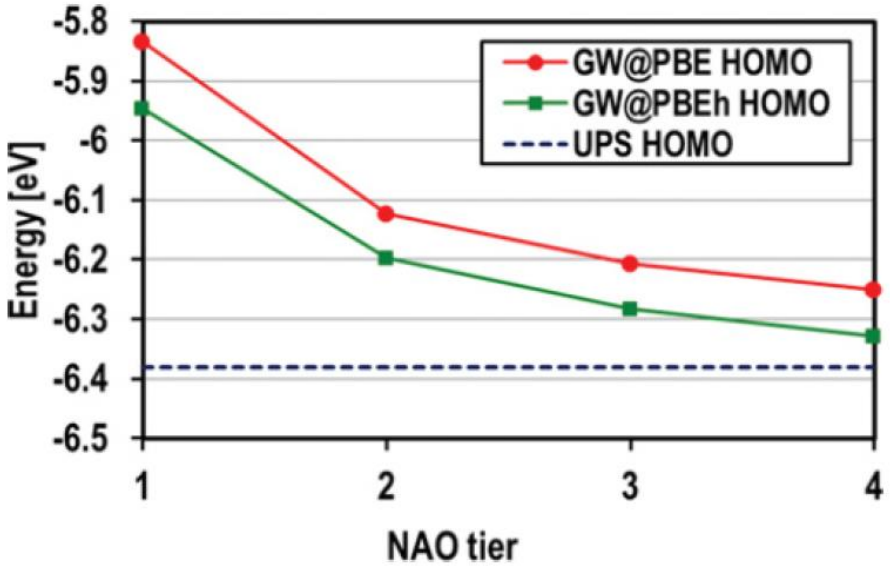
The expressions for the Green's function and the density response function (used to calculate *W*) contain infinite sums over states:

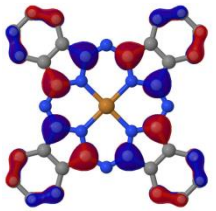
$$G_0(\boldsymbol{r},\boldsymbol{r}',\omega) = \sum_n \frac{\psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}')}{\omega - \varepsilon_n - i\eta\, sgn(\varepsilon_F - \varepsilon_n)}$$

$$\chi_0(\boldsymbol{r},\boldsymbol{r}',i\omega) = \sum_m^{occ}\sum_a^{unocc} \frac{\psi_m^*(\boldsymbol{r})\psi_a(\boldsymbol{r})\psi_a^*(\boldsymbol{r}')\psi_m(\boldsymbol{r}')}{i\omega-\varepsilon_a+\varepsilon_m} + \text{c.c.}$$

This leads to a slow convergence with the number of basis functions

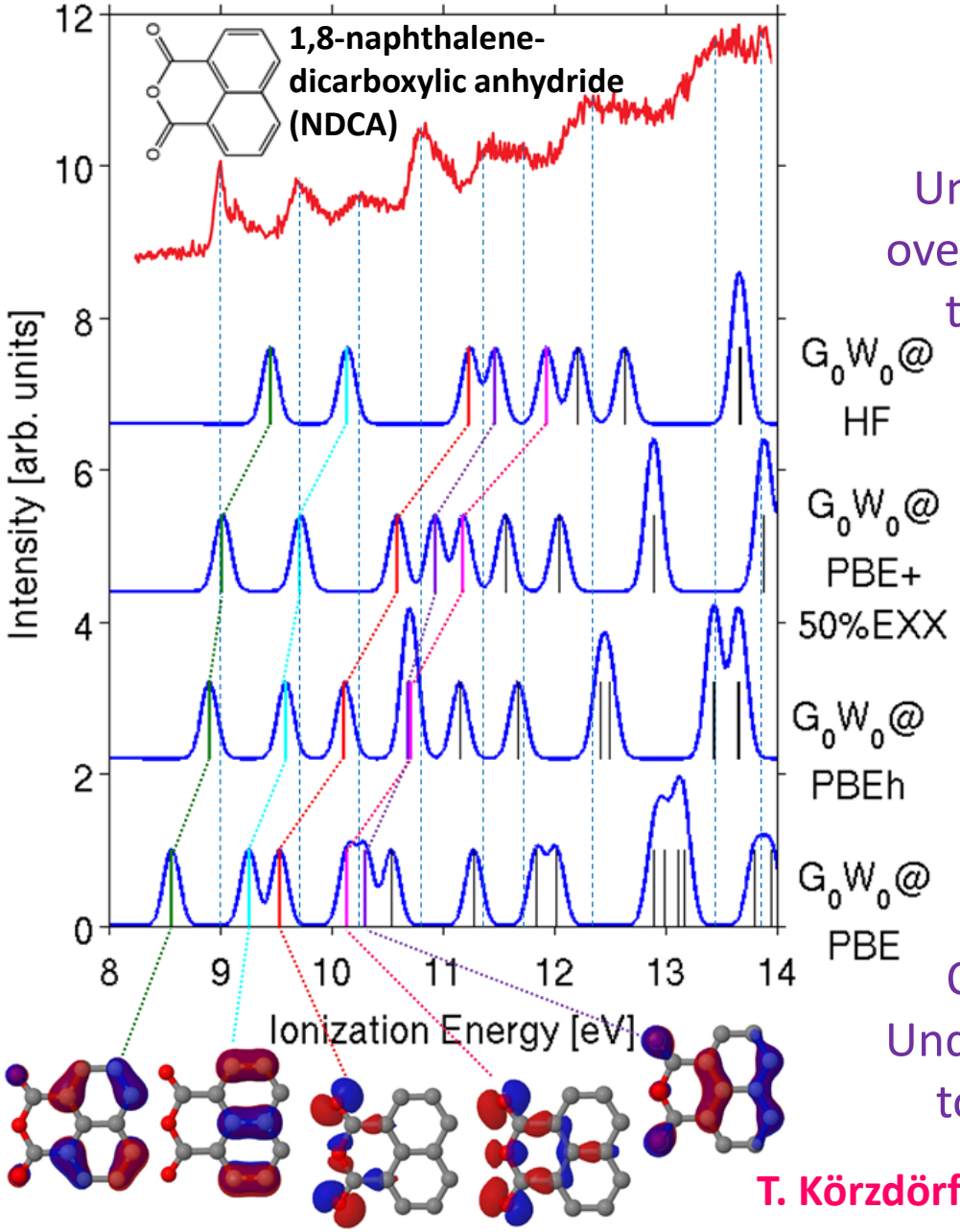
A tier 4 basis set is typically converged to below 0.1 eV





N. Marom *et al. PRB* 84 195143 (2011)

The Starting Point Dependence of G_0W_0:



Screening

Underscreened: overestimated gap too stretched

100

% Fock Exchange (EXX)

0

Overscreened: Underestimated gap too compressed

Self-interaction error (SIE)

Spurious Coulomb repulsion of an electron from itself

Affects highly localized orbitals more strongly

Causes qualitative changes in the orbital ordering that propagate from DFT to G_0W_0

Mitigated by addition of EXX

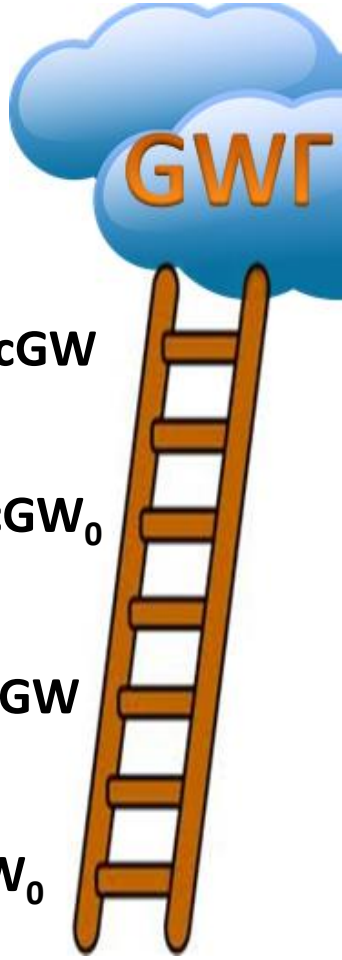
T. Körzdörfer & N. Marom, PRB 86, 041110(R) (2012)

Benchmark of GW Methods for Azabenzenes:

A higher level of self-consistency does not always result in a higher accuracy!

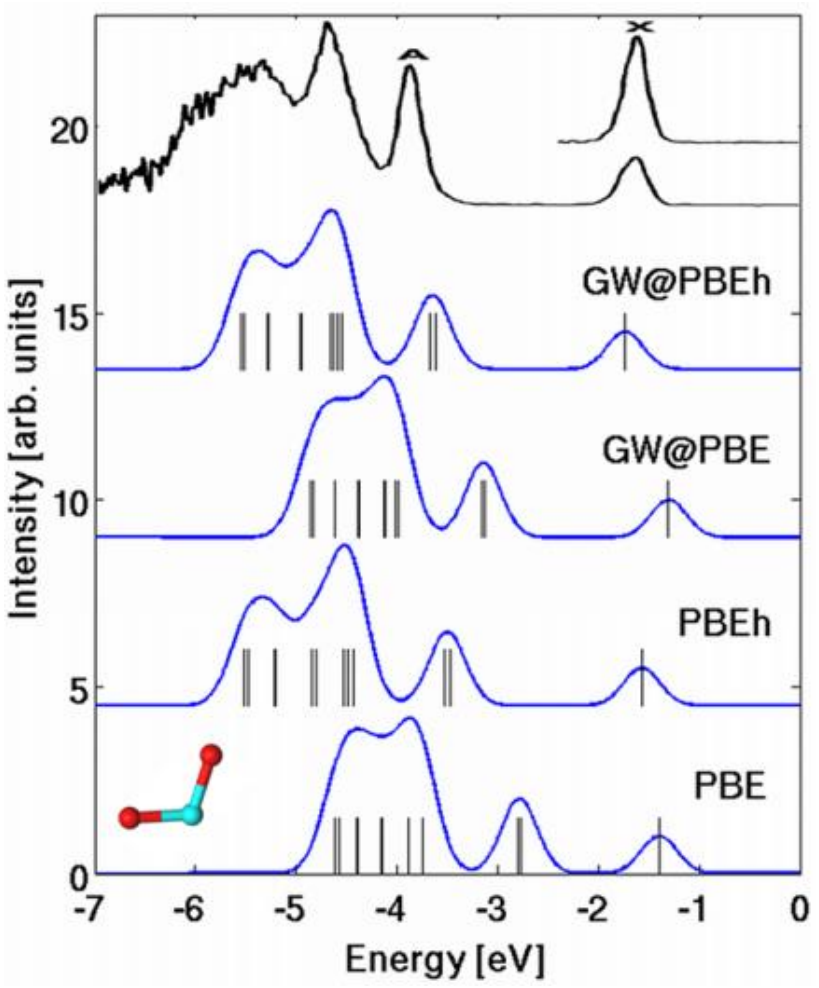
Finding a G_0W_0 or $scGW_0$ starting point with the "right amount" of overscreening can compensate for neglecting the vertex in the GW approximation

	MAE (eV)	Orbital ordering	SPD (eV)
scGW	0.31	1/4	0
$scGW_0$ @PBE	0.27	3/4	0.70
ev-scGW @PBE	0.57	2/4	0.40
G_0W_0@ PBEh	0.17	3/4	1.38



N. Marom, F. Caruso, X. Ren, O. T. Hofmann, T. Körzdörfer, J. R. Chelikowsky, A. Rubio, M. Scheffler, P. Rinke, PRB 86 245127 (2012)

The spectrum of TiO_2^-



Broadening: Gaussian convolution simulates experimental resolution

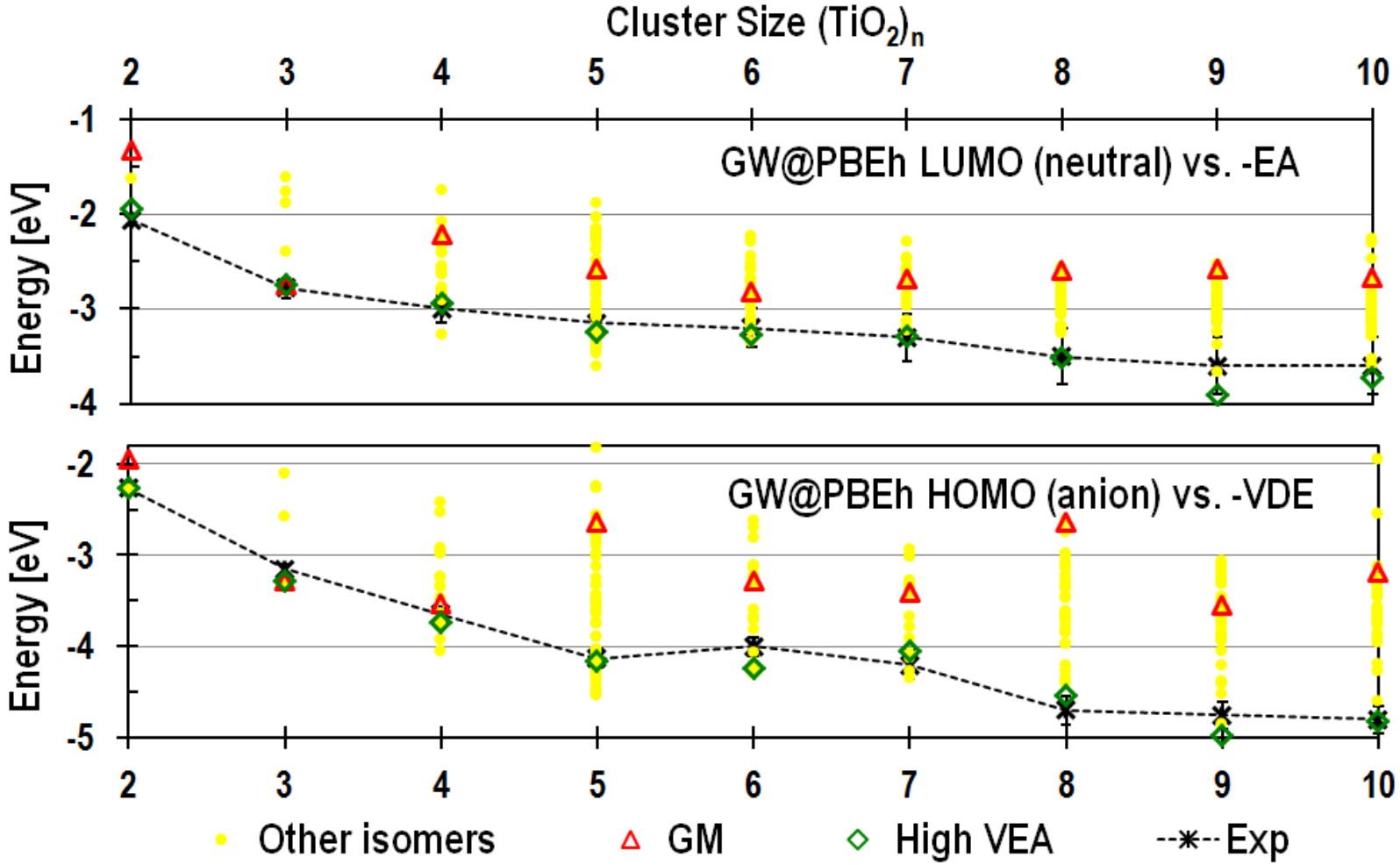
DFT spectra are shifted to align the HOMO with the IP from total energy differences (because KS eigenvalues are not QP excitation energies)

G_0W_0@PBEh/t4 is in good agreement with experiment and will be used in this tutorial to calculate VEAs and VDEs

N. Marom, J. E. Moussa, X. Ren, A. Tkatchenko, and J. R. Chelikowsky, *PRB* 84, 245115 (2011)

VEA and VDE of $(TiO_2)_{2\text{-}10}$ Clusters:

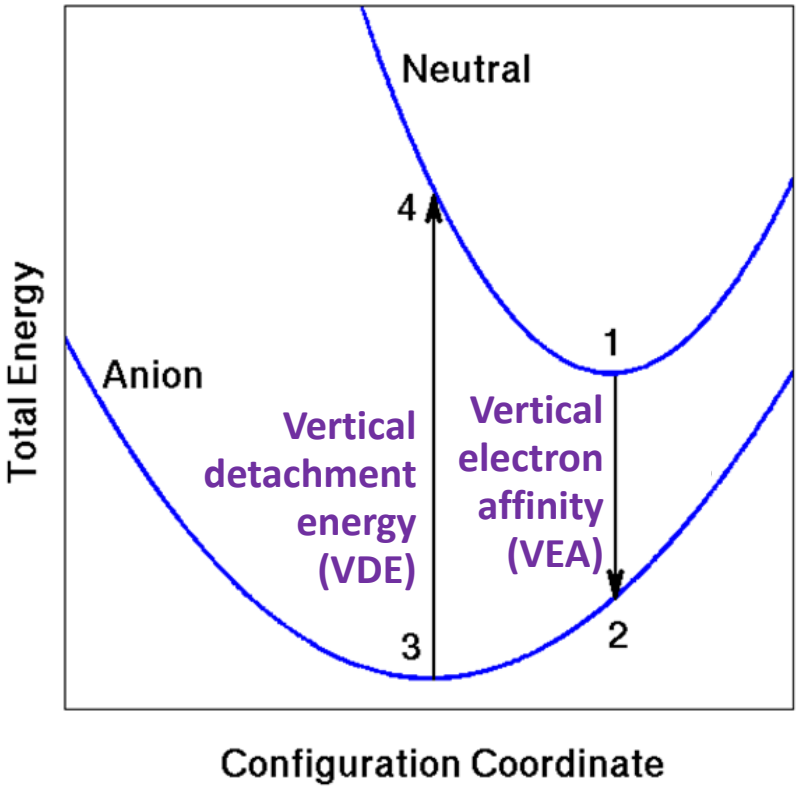
Isomers with a high vertical electron affinity (VEA) are in agreement with experiment… unlike the global minimum (GM) isomers!



N. Marom, M. Kim, and J. R. Chelikowsky, *PRL* 108, 106801 (2012)

Selection Mechanism for High Electron Affinity:

- The clusters initially form as neutrals
- Several low-energy isomers form
- The clusters acquire an electron from the plasma (process 1→2)
- The cluster with the highest vertical electron affinity (VEA) "wins" the electron via charge transfer reactions
- Only the charged clusters go through mass spectrometry



- The anions cool down and relax to the meta-stable state of the high VEA isomer (process 2→3)
- The vertical detachment energy (VDE) is then measured by PES (process 3→4)

L. Kronik et al. *Nature Materials* 1, 49 (2002)