

Time Dependent DFT (TDDFT)

Let us look the time dependent Schrödinger equation and also time dependent DFT. The mathematics is rather complex. Note that in this chapter we do not consider the atomic movement. Only the electrons time behavior (this is the Frank-Condon approximation).

The time dependent Schrödinger equation is

$$i \frac{\partial \psi(x, t)}{\partial t} = H(x, t) \psi(x, t)$$

The derivation of TD-DFT is again rather subtle but the final result is easy

$$\left[-\frac{1}{2} \sum_i \nabla_i^2 + 2 \int d^3 r_j \frac{\rho(r_j, t)}{|r_i - r_j|} - \sum_{I'} \frac{Z_I}{|r_i - R_I(t)|} + V_{xc}[\rho, t](r) + f(t) \right] \varphi_n^{KS}(r_i, t) = i \frac{\partial \varphi_n^{KS}(r_i, t)}{\partial t},$$

Note that there is an external time dependent functions $f(t)$ and the density and KS wave functions will depend on time. The external electric field can be written as $f(t) = \theta(t) r e \sin(\omega t)$, where ω is the frequency of the field, e is the polarization and θ tells when the field has switched on.

The density is

$$\rho(r, t) = \sum_n |\varphi_n^{KS}(r, t)|^2$$

The proof of the TD-DFT is more complex than in the standard DFT and it is based on the quantum mechanical action

$$A[\psi] = \int_{t_i}^{t_f} \left\langle \psi(t) \left| i \frac{\partial}{\partial t} - H(t) \right| \psi(t) \right\rangle dt$$

The $A[\psi]$ have a minimum when the ψ is the solution of the time dependent Schrödinger equation. Now one can argue that the A depend only on the density, $A[\rho(r, t)]$ (There is a review by Marques and Gross, but it is not easy.) As in the case of normal DFT it is not easy to find the V_{xc} (or $A[\rho(r, t)]$).

The simplest xc-approximation is the adiabatic LDA (ALDA)

$$A_{xc}^{ALDA}[\rho] = \int_{t_i}^{t_f} dt \int dr \rho(r,t) \varepsilon_{xc}^{LDA}(r,t)$$

Naturally all the common xc-approximations can be used adiabatically. There have been some ideas of TD- ϵ models but all practical calculations are done with common GGAs and adiabatic approximation.

Once the AGGA has been fixed the TD-DFT equations can be solved in two ways. One can use time propagation or linear response methods.

TD-DFT time propagation

In the time propagation method the direct time evolution of the wave function is computed. Note that the atoms do not move. Formally

$$\psi(t) = \exp \left[-i \int_0^t dt' H^{KS}(t') \right] \psi(0) \quad (\text{propagation})$$

This equation is not very useful since the KS Hamiltonian depend on time and it also depend on the density (and thus the wave functions). The (propagation) equation can be used in short times. Now the t is replaced with Δt and $\exp(x) \approx 1+x$, so

$$\psi^{(n)}(t + \Delta t) = \psi^{(0)}(t) - i \int_t^{t+\Delta t} dt' H^{KS}(\psi^{(n-1)}(t'), t') \psi^{(n-1)}(t')$$

The upper index in the wave function correspond to the self-consistent iteration.

Now the time evolution is related to electrons movement the time step is very small. The GPAW used time step of $8 \cdot 10^{-18}$ s (attosecond)!! (this is less than 1/100 of normal MD time step.)

The dynamic wave functions contain a lot of information. One important quantity is the dynamics density, $\rho(r,t)$. One of the main usage of TD-DFT is the estimation of the energies of the excited states. When the Hamiltonian do not depend much of the time one can write.

$$\Phi(t) = \sum_n C_n e^{-iE_n t} \varphi_n(0), \quad \Phi(0) = \sum_n C_n \varphi_n(0)$$

Now the time evolution of the contain information of the exited states. This information can be computed in many ways. One of the

most useful is the dynamical polarization. (It will also give information of the adsorption intensity)

Dynamic polarization

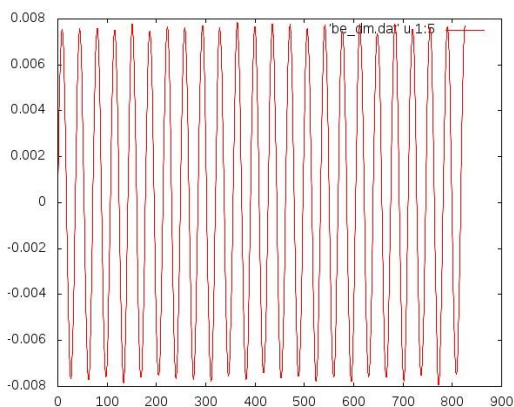
If there is an oscillating external field in x (or y, z) direction $f(t)=E \times \sin(\omega t)$ the electron density will change as $\delta\rho(r,t) = \rho(r,t) - \rho(r,0)$. Now we can determine the dynamical polarization

$$\alpha_x(\omega) = -\frac{1}{E} \int d^3r x \delta\rho(r, \omega)$$

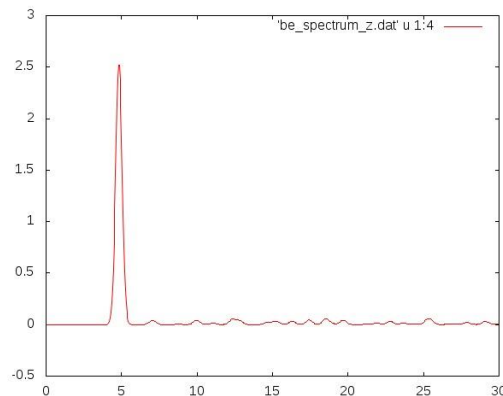
Where $\delta\rho(r, \omega)$ is the Fourier transformation of $\delta\rho(r, t)$. Now photoadsorption spectra can be obtained as the imaginary part of the dynamical polarization:

$$S(\omega) = \frac{2\omega}{3\pi} \text{Im} \sum_i \alpha_i(\omega)$$

GPAW TD-DFT data for Be atom.



Time dependent data



frequency data

TD-DFT linear response

Often the time dependent simulations of the KS equations are slow due to the very small time step. So there is another possibility to use the linear response model. (It works for small perturbations.)

We can write perturbation that depend with one frequency (monochromatic radiation)

$$\delta V(r, t) = v^+(r) \exp(i\omega t) + v^-(r) \exp(-i\omega t)$$

This change the potential as

$$\delta V_{eff}(r, t) = \delta V(r, t) + \delta V_{SCF}(r, t)$$

And after Fourier transformation

$$\delta V_{eff}(r, \omega) = \delta V(r, \omega) + \delta V_{SCF}(r, \omega)$$

Where

$$\delta V_{SCF}(r, \pm\omega) = \int dr' \left\{ \frac{1}{|r - r'|} + \frac{\delta^2 E_{xc}}{\delta\rho(r)\delta\rho(r')} \right\} \delta\rho(r', \pm\omega)$$

and

$$\delta\rho(r, \pm\omega) = 2 \sum_i^{occ} [\delta\varphi_i^\pm(r)\varphi_i(r) + \varphi_i(r)\delta\varphi_i^\pm(r)]$$

the $\delta\varphi_i^\pm(r)$ is the KS wave function change due to the perturbation. Also $\int dr \delta\varphi_i^\pm(r)\varphi_i(r) = 0$. These wave functions can be solved from:

$$\sum_j^{occ} [H^{KS} \delta_{ij} - \epsilon_{ij}] |\delta\varphi_j^\pm\rangle + Q \delta V_{SCF}(\pm\omega) |\varphi_i\rangle = \mp\omega |\delta\varphi_i^\pm\rangle \quad (\text{lin resp})$$

where $Q = 1 - \sum_i^{occ} |\varphi_i\rangle\langle\varphi_i|$. The Q project from the wave functions to the unoccupied unperturbed states. (Note: $1 = \sum_i^{all} |\varphi_i\rangle\langle\varphi_i|$, so $Q|\varphi_{i=occ}\rangle = 0$, but $Q|\varphi_{i=unocc}\rangle = |\varphi_{i=unocc}\rangle$).

The equation (lin resp) is solvable but the main problem is that there are much more empty states than occupied ones. This limits the linear response calculation of very large systems. The well converged calculations will take enormous amount of memory. The linear response method is very general and it can be applied to almost any small perturbation.

Exited states

The most common application of TDDFT is the exited states. The pure DFT will give too low HOMO-LUMO gap. The main problem is the single particle picture, the eigenvalues. The TDDFT will give much more realistic results. There are some examples in the exercises.

For water the transitions are nicely between single states

```
STATE 1: E= 0.258460 au      7.033 eV   56725.4 cm**-1
  4a -> 5a : 0.998680 (c= -0.99933995)
STATE 2: E= 0.327736 au      8.918 eV   71929.8 cm**-1
  4a -> 6a : 0.999693 (c= 0.99984673)
STATE 3: E= 0.343375 au      9.344 eV   75362.2 cm**-1
  3a -> 5a : 0.983370 (c= 0.99165009)
STATE 4: E= 0.414838 au     11.288 eV   91046.5 cm**-1
  3a -> 6a : 0.981217 (c= -0.99056406)
STATE 5: E= 0.487355 au     13.262 eV  106962.0 cm**-1
  2a -> 5a : 0.980963 (c= -0.99043565)
```

This is not very far from CCSD computations

```
IROOT= 1: 0.283525 au      7.715 eV   62226.6 cm**-1
  Amplitude  Excitation
 -0.999502   4 -> 5
IROOT= 2: 0.360423 au      9.808 eV   79103.8 cm**-1
  Amplitude  Excitation
 0.975525   4 -> 6
 0.217756   4 -> 7
IROOT= 3: 0.376303 au     10.240 eV   82589.1 cm**-1
  Amplitude  Excitation
 -0.991910   3 -> 5
```

but for anthracene much more states are included (tddft)

```
STATE 1: E= 0.114956 au      3.128 eV   25229.9 cm**-1
  43a -> 50a : 0.017133 (c= 0.13089165)
  44a -> 49a : 0.032653 (c= 0.18070047)
  45a -> 48a : 0.025425 (c= -0.15945094)
  46a -> 47a : 0.889338 (c= -0.94304696)
  46a -> 50a : 0.010924 (c= 0.10451737)
STATE 2: E= 0.132730 au      3.612 eV   29130.9 cm**-1
  45a -> 47a : 0.501213 (c= 0.70796412)
  46a -> 48a : 0.497676 (c= -0.70546121)
STATE 3: E= 0.143041 au      3.892 eV   31393.8 cm**-1
  44a -> 47a : 0.537031 (c= -0.73282412)
  46a -> 49a : 0.462394 (c= 0.67999540)
```

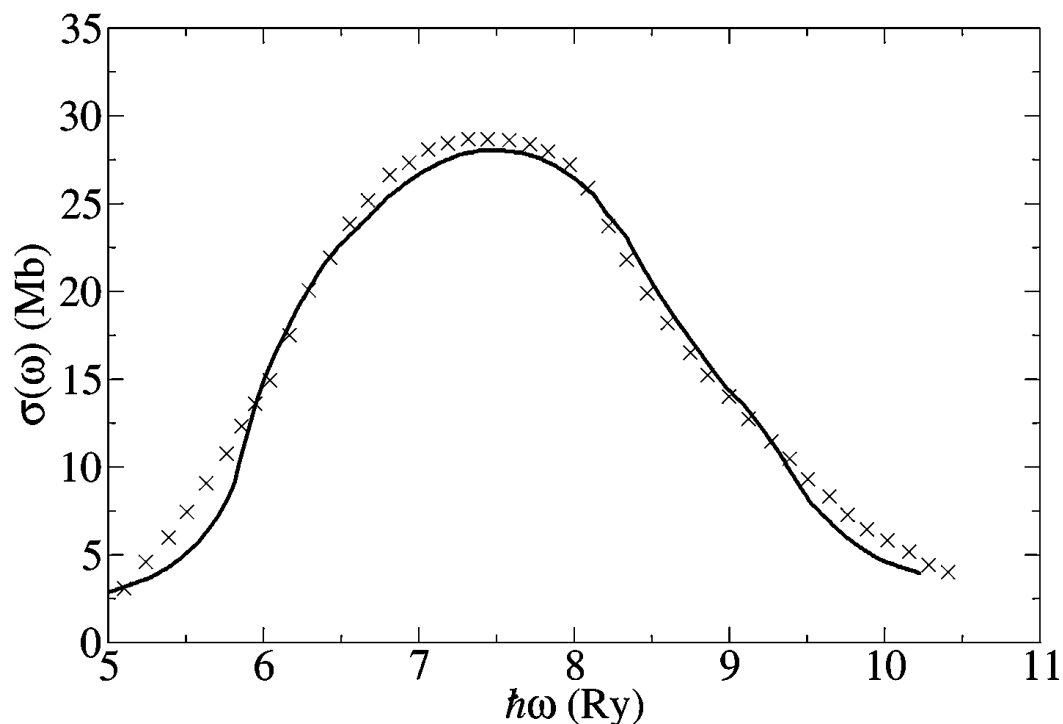
the picture is similar with CCSD

```
IROOT= 1: 0.126075 au      3.431 eV   27670.3 cm**-1
  Amplitude  Excitation
 0.120315   42 -> 49
 -0.118325   44 -> 54
 0.706223   45 -> 47
 0.676794   46 -> 48
IROOT= 2: 0.145959 au      3.972 eV   32034.3 cm**-1
  Amplitude  Excitation
 0.170369   45 -> 48
 -0.976808   46 -> 47
IROOT= 3: 0.193406 au      5.263 eV   42447.7 cm**-1
  Amplitude  Excitation
 0.394940   42 -> 47
 0.116646   43 -> 54
 0.612319   44 -> 48
 0.593317   45 -> 49
 -0.284490   46 -> 54
```

Overall, the TD-DFT works rather well even when the adiabatic GGA's are used. To my knowledge the non-adiabatic DFT models are not really used. In Orca there are CCSD based methods that can be used for testing the TD-DFT methods. A fast implementation of excited state CCSD is STEOM-CCSD. One can also use CIS (or HF-CIS) methods for excited states but this is not very accurate. In Orca there is also a very fast approximate TD-DFT methods: stddft. This is convenient for very large systems.

To summarize: again the first choice is TD-DFT, with medium size molecules the STEOM-CCSD is more accurate but it become rather quickly very time consuming.

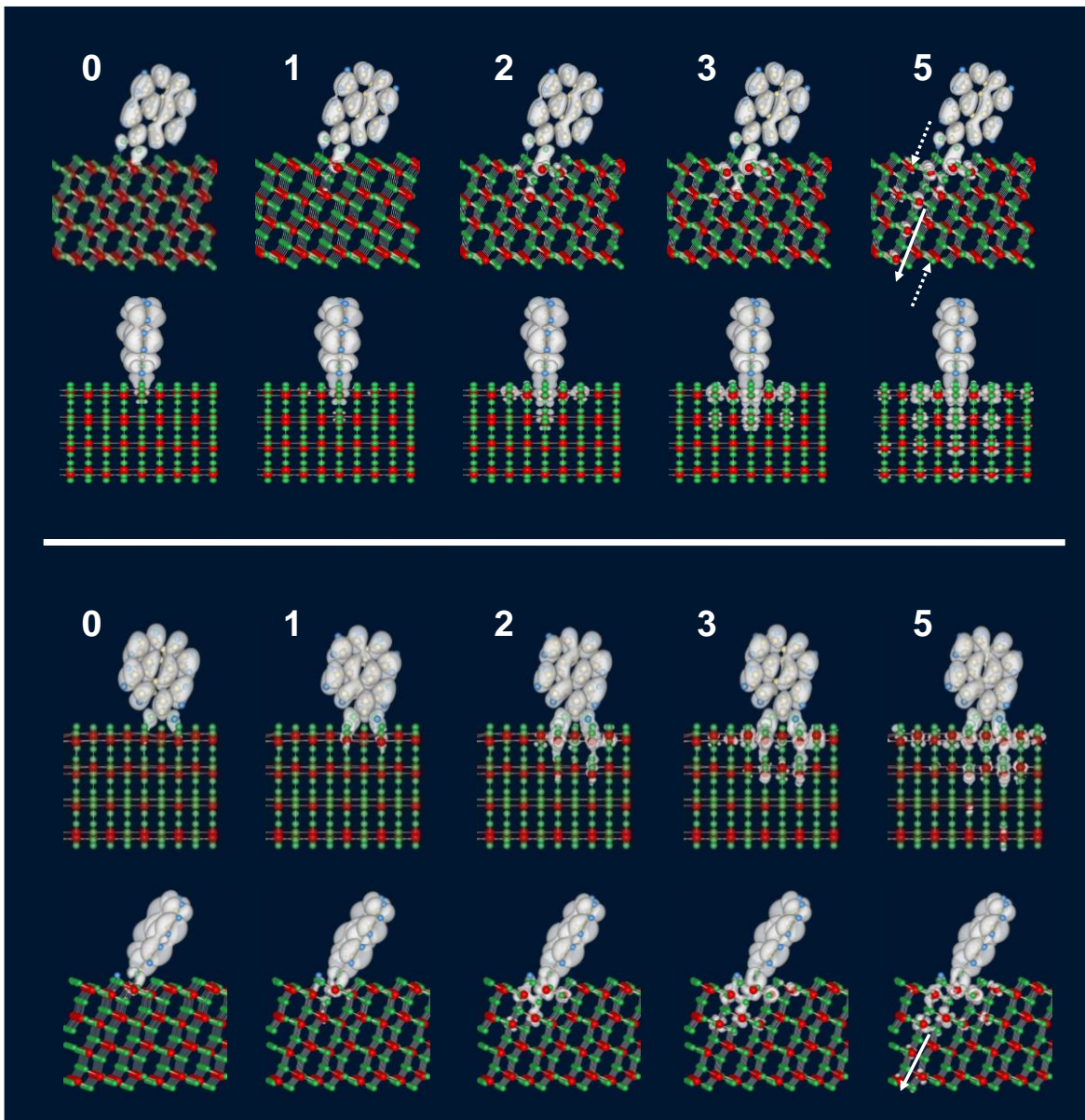
Example: Computed (line) and measured (x) Xenon adsorption spectra.



Mostly the usage of TD-DFT is simple and it is implemented to most of the quantum chemical programs

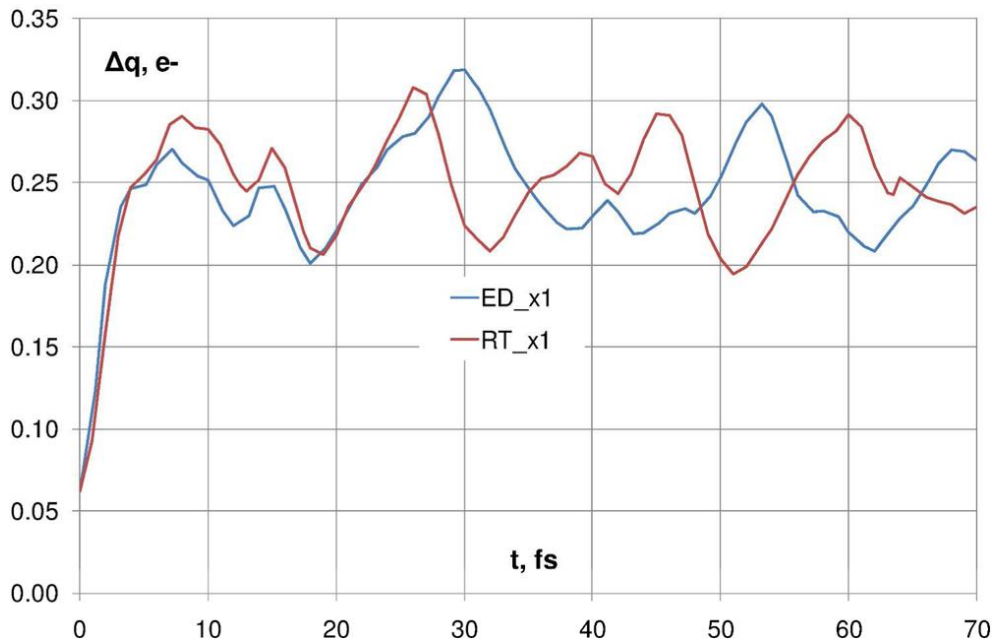
Example: Electron transfer from antenna molecule to TiO₂ surface. A model calculation of the Grätzell solar cell. Note that this is so large system that the linear response calculation are not possible. The simulation was done with time propagation. The time step was 8 as.

Ref. O. Syzgantseva M.Puska, K.L. Physical Factors Affecting Charge Transfer at the Pe-COOH-TiO₂ Anatase Interface, JPCC (2104)



Total charge transfer during time. The RT is the real time propagation and ED is the Ehrenfest dynamics where also the atoms

move. If the excitation is non-dissociative the Ehrenfest dynamics usually is not relevant for heavy atoms.

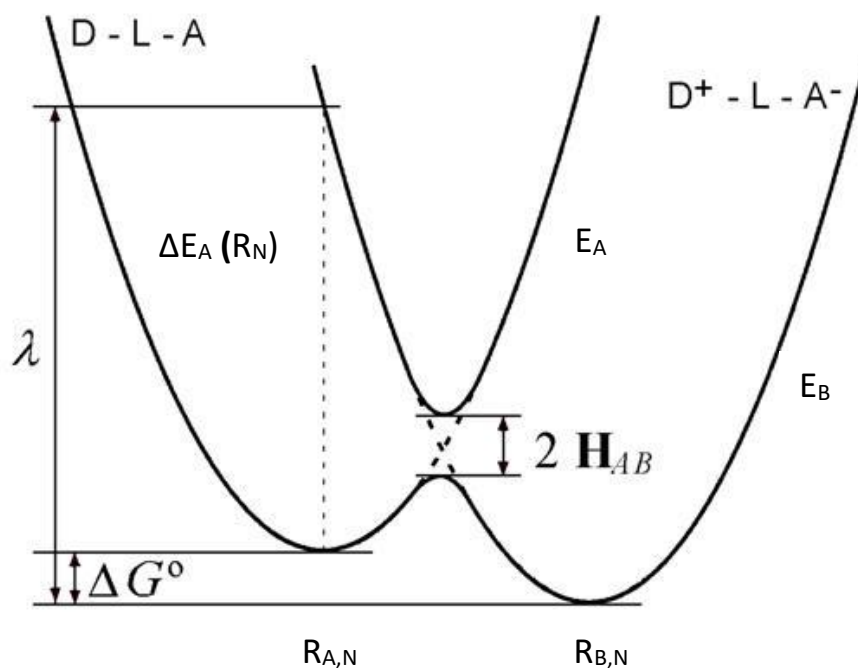


Constraint DFT (CDFT)

The DFT is a ground model and not suitable for charge transfer reactions. In case of symmetric charge transfer the DFT ground state contains both of the states whereas the real ground state is usually unsymmetric.

The standard model for charge transfer is the Marcus theory. The two minima, normal state and the zwitterionic state, are described as two parabolas. The minima are separated with free energy ΔG , the reorganization free energy is λ and the coupling parameter is H_{AB}

$$k_{et} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left(-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda k_b T}\right)$$



The normal DFT often favors the non-zwitterionic state. To model both of the states we need a method to force the charge to localize in one region of the system. We can use so called Constraint DFT methods.

The formal CDFT equation is simple:

$$F[\rho, \lambda] = \max_{\lambda} \min_{\rho} (E_{KS}[\rho] + \sum_c \lambda_c \{ \int w_c(r) \rho(r) dr - N_c \})$$

The w_c is the weight function that determines the charge localization. In the zwitterion case we need to define the donor and acceptor atoms of the molecule and force their total charges to be +1 or -1. The mathematical solution is not simple but that is not important.

The CDFT can be used for both static and dynamical systems. With this approach the Marcus parameters can be computed by doing two AIMD simulation with same atomic positions but the electron in minima A (electron localized to minima A) and another one with electron minima B. The key quantity is the vertical energy gap, the energy difference of the two electron transfer states with the same coordinates:

$$\Delta E_A(R_{A,N}) = E_A(R_{A,N}) - E_B(R_{A,N})$$

Now

$$\lambda = \frac{\langle \Delta E_A \rangle_T + \langle \Delta E_B \rangle_T}{2}, \quad \Delta G = \frac{\langle \Delta E_A \rangle_T - \langle \Delta E_B \rangle_T}{2}$$

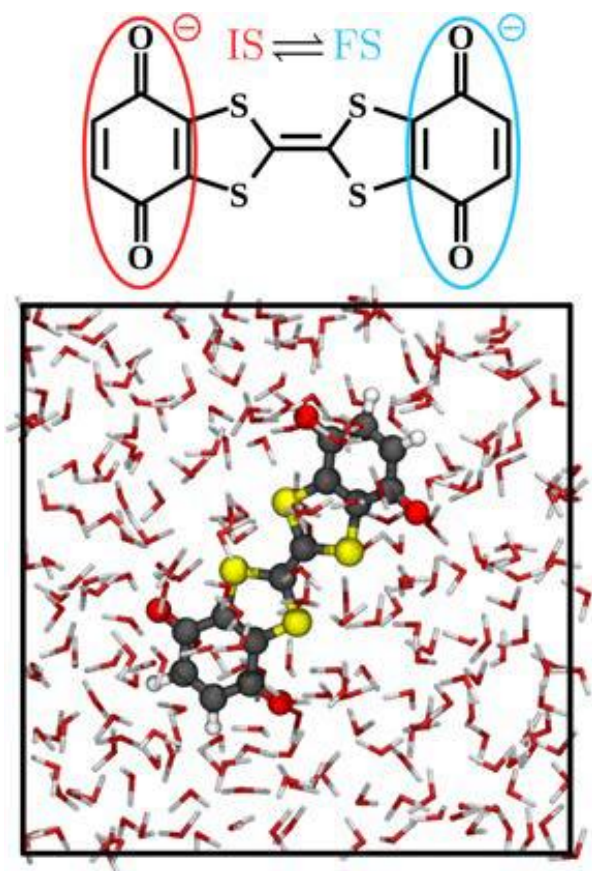
Here the $\langle \rangle_T$ means the MD time average of the simulations.

The H_{AB} is bit trickier but also that can be computed.

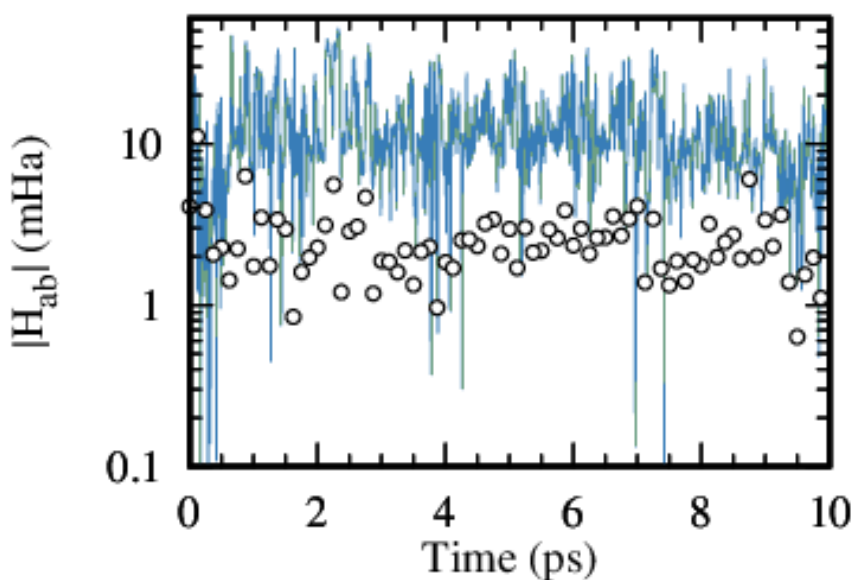
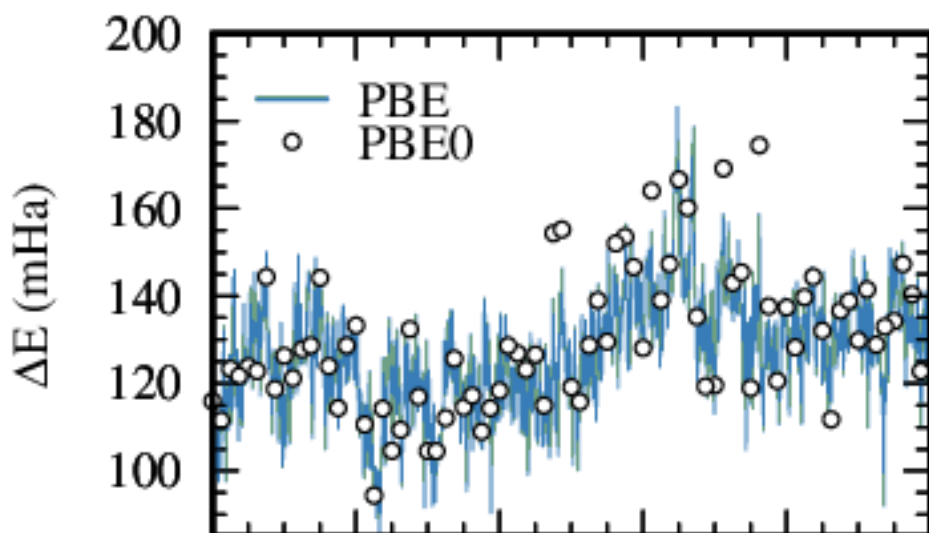
More details

Holmberg, N.; Laasonen, K.; *J. Chem. Theory Comp.*, 13 (2017), 587-601, DOI: 10.1021/acs.jctc.6b01085

The test system

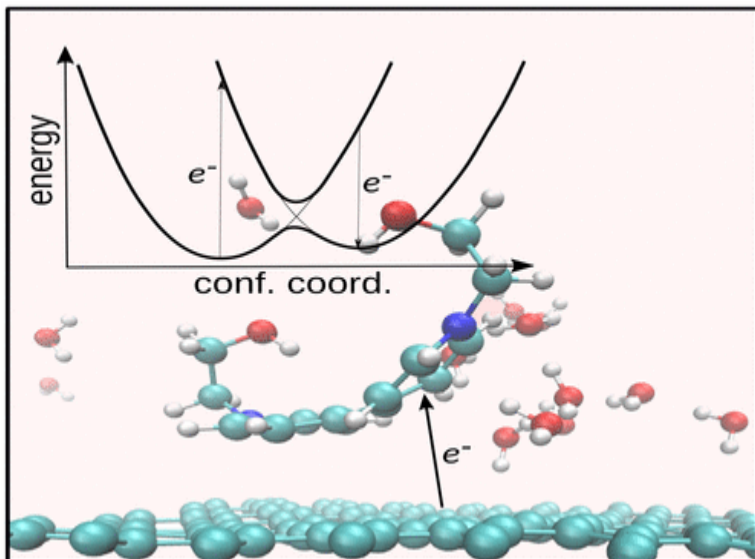


Key results. The system was simulated with PBE-D3 and several static geometries were computed with PBE0

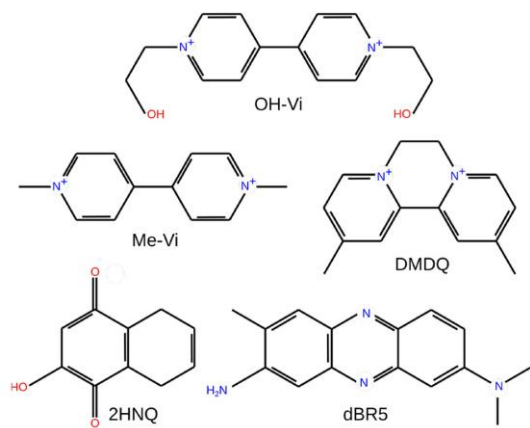


The key application of cDFT is the electron transfer and we have recently apply it to electron transfer form graphite electrode to some molecules. (Hashemi, Peljo, and Laasonen, *J. Phys. Chem. C* 2023, 127, 7, 3398–3407)

Understanding Electron Transfer Reactions Using Constrained Density Functional Theory: Complications Due to Surface Interactions



Molecules



Results

reaction	$\langle \Delta E^J[R_i] \rangle$	$\langle \Delta E^J[R_j] \rangle$	ΔA_{ij}^0	λ	ΔA_{ij}^\ddagger	$\langle H_{ij}^0 \rangle$	ΔA_{ij}^{ad}
DMDQ ^{+2/+1}	0.46 ± 0.15	0.80 ± 0.14	-0.17	0.63	0.08	0.58 ± 0.17	BL
DMDQ ^{+1/0}	1.89 ± 0.12	-0.59 ± 0.15	1.24	0.64	1.37	0.64 ± 0.09	0.73
OH-Vi ^{2+/1+}	0.40 ± 0.13	0.57 ± 0.14	-0.09	0.49	0.08	0.58 ± 0.18	BL
OH-Vi ^{+1/0}	2.27 ± 0.17	-0.59 ± 0.17	1.43	0.84	1.53	0.74 ± 0.09	0.79
Me-Vi ^{2+/1+}	0.16 ± 0.13	0.99 ± 0.22	-0.41	0.58	0.01	0.78 ± 0.21	BL
Me-Vi ^{+1/0}	1.72 ± 0.19	-0.68 ± 0.20	1.20	0.52	1.42	0.61 ± 0.09	0.81
dBR5 ^{0/-1}	1.87 ± 0.21	-0.43 ± 0.19	1.15	0.72	1.21	0.41 ± 0.19	0.80
dBR5 ^{-1/-2}	3.73 ± 0.17	-2.33 ± 0.25	3.03	0.70	4.96	0.64 ± 0.16	4.32
2HNQ ^{0/-1}	-0.06 ± 0.14	0.88 ± 0.17	-0.47	0.41	0.00	0.73 ± 0.23	BL
2HNQ ^{-1/-2}	2.88 ± 0.28	-0.60 ± 0.18	1.74	1.14	1.81	1.08 ± 0.15	0.73