Time Dependent DFT (TDDFT)

Let us look the time dependent Schrödinger equation and also time dependent DFT. The mathematics is rather compex. Note that in this chapter we do not concider 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 results is easy

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 + 2\int d^3r_j \frac{\rho(r_j,t)}{|r_i - r_j|} - \sum_{iJ}\frac{Z_I}{|r_i - R_J(t)|} + V_{xc}[\rho,t](r) + f(t)\right]\varphi_n^{KS}(r_i,t) = i\frac{\partial\varphi_n^{KS}(r_i,t)}{\partial t},$$

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)= θ(t)r e sin(ωt), 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

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

The A[ψ] have a minima when the phi is the solution of the time dependent Schrödinger equation. Now one can argue that the A depend only on the density, A[ρ(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 Vxc (or A[ρ(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 has been some ideas of TD-xc 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

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

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)=1+x, so

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

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 $8*10^{-18}$ 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

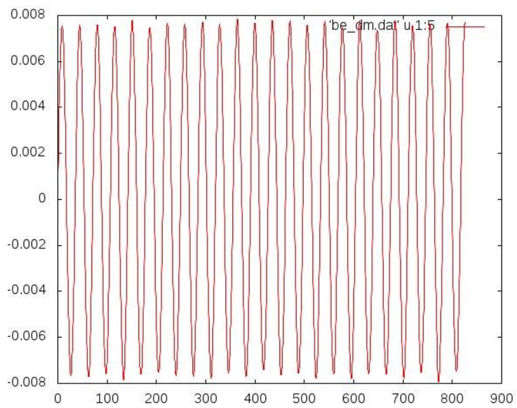
If there is an oscillating external field in x (or y, z) direction f(t)=E x sin(ωt) the electron density will change as $\delta\rho(r,t) = \rho(r,t) - \rho(r,0)$. Now we can determine the dynamical polarization

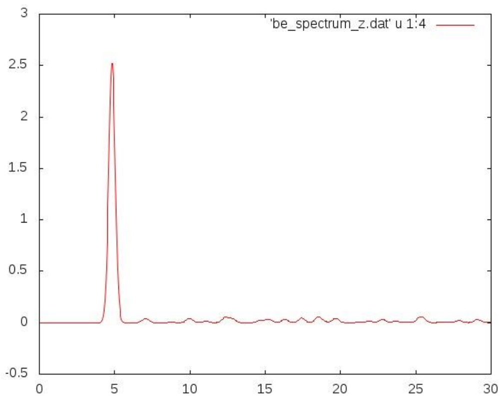
$$\alpha_x(\omega) = -\frac{1}{E}\int d^3r\, x\delta\rho(r,\omega)$$

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:

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

GPAW TD-DFT date for Be atom.





Time dependent data

frequency data

TD-DFT linear responce

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

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

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:

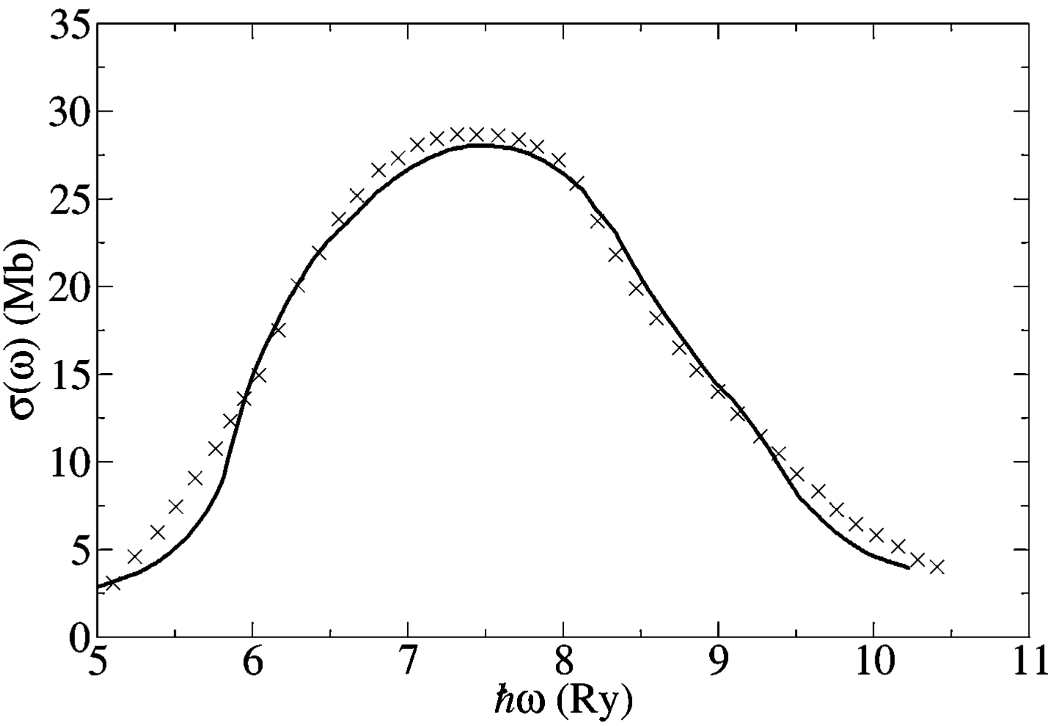
$$\textstyle\sum_j^{occ}\left[H^{KS}\delta_{ij} - \epsilon_{ij}\right]|\delta\varphi_j^{\pm}\rangle + Q\,\delta V_{SCF}(\pm\omega)|\varphi_i\rangle = \mp\omega|\delta\varphi_i^{\pm}\rangle \qquad \text{(lin resp)}$$

where $Q = 1 - \sum_i^{occ}|\varphi_i\rangle\langle\varphi_i|$. The Q project from the wave functions the accupied 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 not easy but it is solvable. The main problem is that there are much more empty states than occupied ones. This limit the linear response calculation of very large systems. The well converged calculations will take enormous amount of memory. The linear response methods is very general and it can be applied to almost any small perturbation.

Overall the TD-DFT works rather well even when the adiabastic GGA's are used. TO my knowledge there are very few non-adiabatic DFT models.

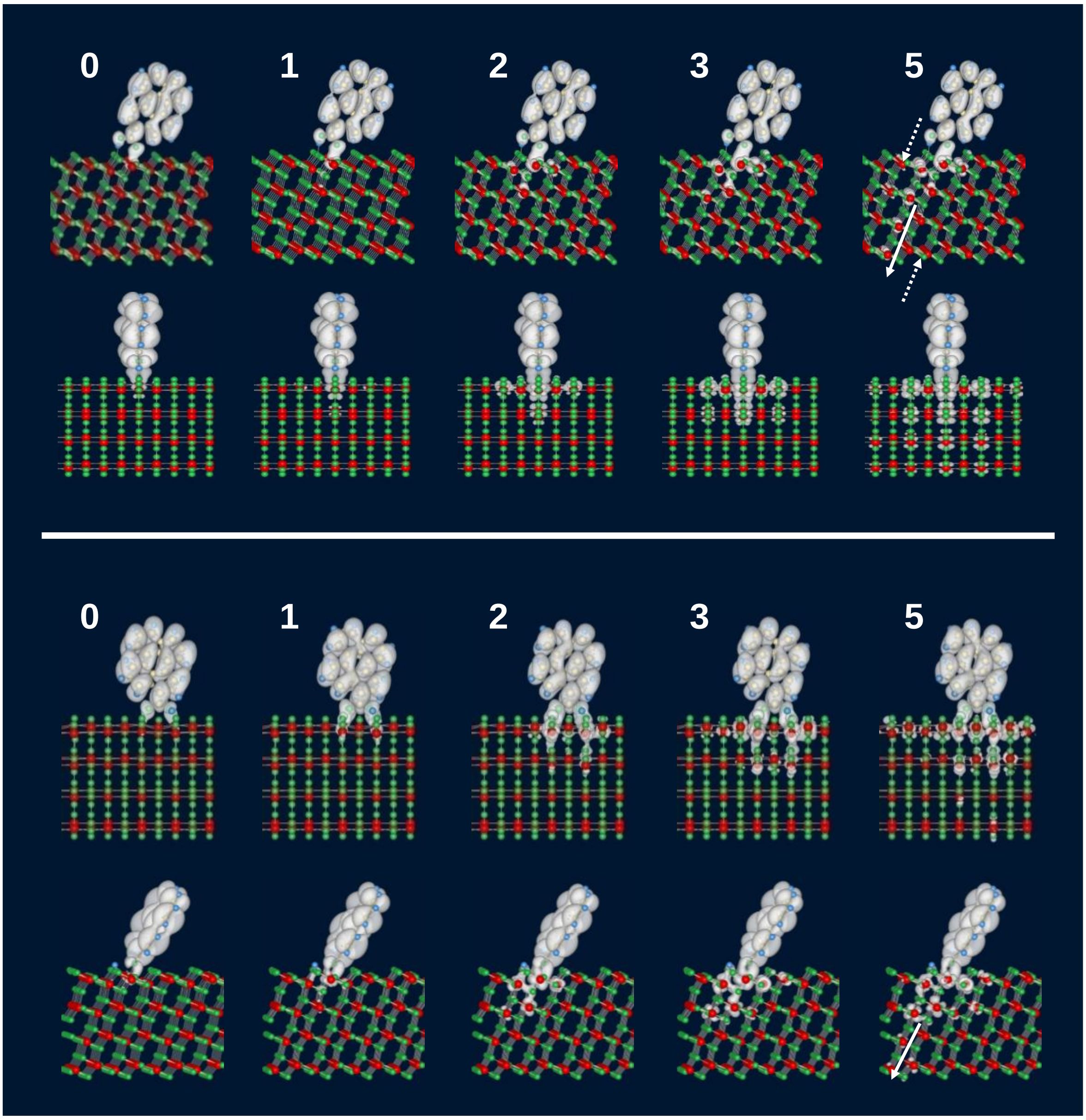
Example. Computed (line) and measured (x) Xenon adsorption spectra.



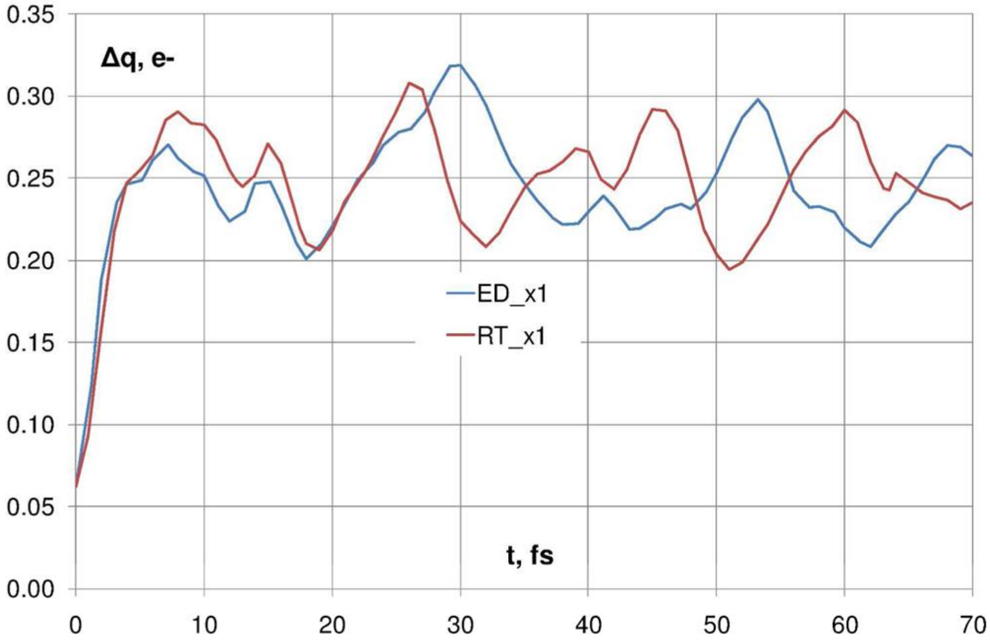
Mostly the usage of TD-DFT is simple and it is implemented to most of the quantum chemical programs

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 were 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. It the excitation is non-dissociative the Ehrenfest dynamics usually is not relevant for heavy atoms.

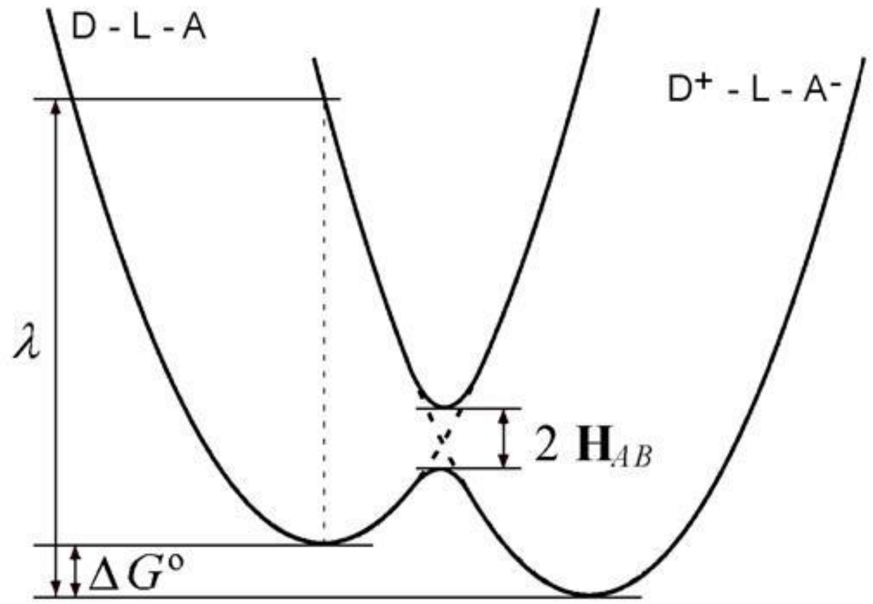


Constraint DFT (CDFT)

The DFT is a ground model and often not very suitable form charge transfer reactions. Sometimes the charge is localize somewhere in the system and is then transferred to somewhere else. In case of symmetric charge transfer the DFT ground state contain both of the states whereas the real ground state is usually unsymmetric.

The standard model for charge transfer is the Marcus theory. The two minimum 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 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.

The mathematical solution is not so simple but with this approach the Marcus parameters can be computed by doing two MD 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:

$$\Delta E(R_N) = E_A(R_N) - E_B(R_N)$$

Now

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

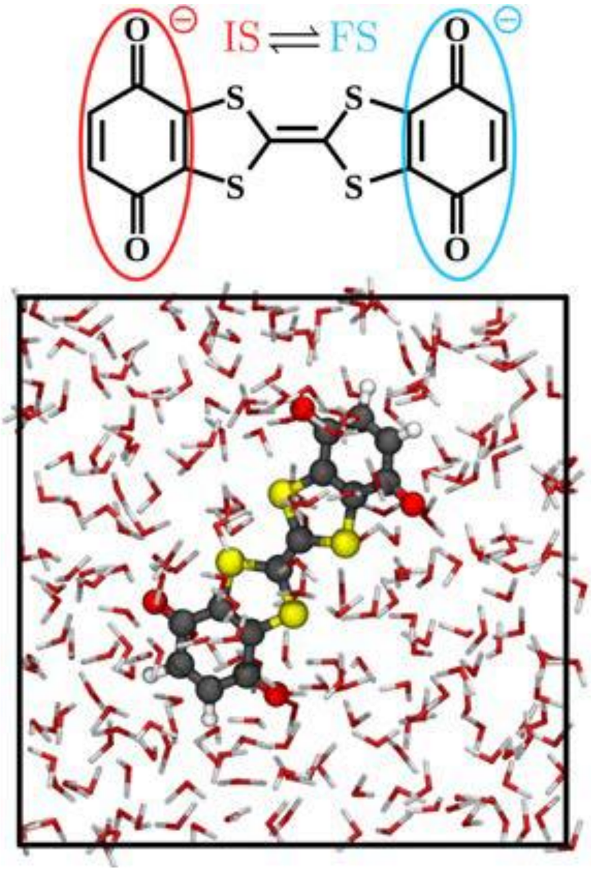
Here the $\langle\rangle_T$ means the MD time average of the simulations.

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

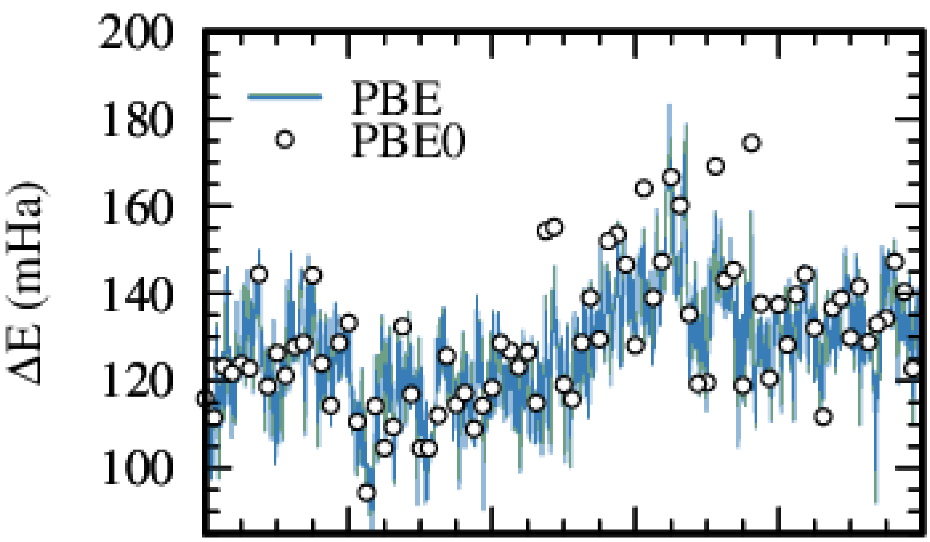
More details

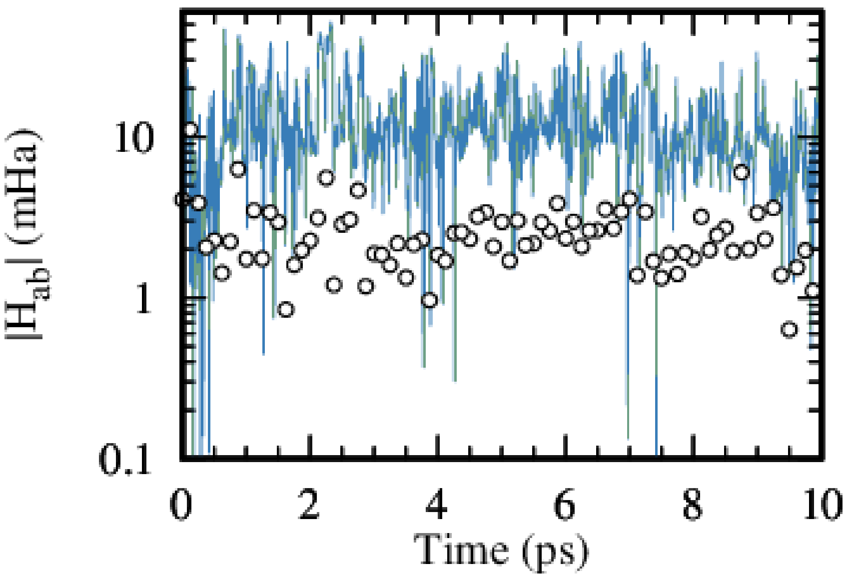
Holmberg, N.; Laasonen, K.; *J. Chem. Theory Comput.*, 13 (2017), 587-601, DOI: 10.1021/acs.jctc.6b01085

The test system



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




$|H_{ab}|$ (mHa)
10
1
0.1
0
2
4
6
8
10
Time (ps)