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https://www.ur.de/physics/wilhelm/teaching/sose24-computational-nanoscience

Computational Nanoscience: Exercise Sheet No. 7

In this exercise sheet, we discuss basic light-matter interaction within the framework of real-time TDDFT. The light will be modelled by a time-dependent electric field $\mathbf{E}(t)$. The light polarizes the sample, and the time-dependent dipole moment is often described approximately by

$$\mathbf{p}(t) = \int \mathrm{d}t' \alpha(t - t') \, \mathbf{E}(t') \,, \tag{1}$$

with the polarizability tensor α_{ij}, $i, j \in \{x, y, z\}$.

In order to explore the applicability of Eq. (1), we will compare Eq. (1) to the (formally) exact expression of the dipole moment obtained within TDDFT

$$\mathbf{p}(t) = \int \mathrm{d}^3 r' \, \mathbf{r}' \, n(\mathbf{r}', t) \,. \tag{2}$$

Exercise 7.1: Formulæ for the dipole moment

(a) Interpret Eq. (1): Which quantities are known? Why is there a time integral? Eq. (1) is not valid in general. Give an example, when it does not hold. **[2]**

(b) Why is Eq. (2) formally exact? Why is that not the case most of the time for a standard TDDFT calculation? When is the dipole formula Eq. (2) not sufficient to describe emitted radiation of a generic charge distribution? **[2]**

In order to investigate the applicability of Eq. (1), we first set up our TDDFT calculations in the following:

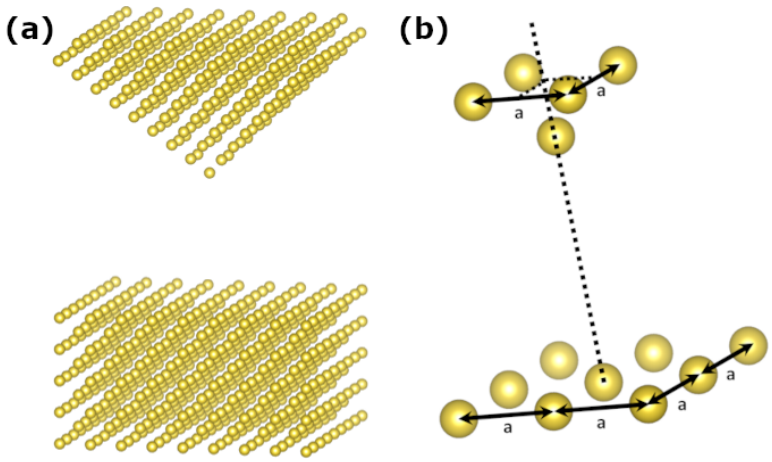

Figure 1: Illustration of tip-substrate geometries (a) Realistic modelling of a tip-substrate geometry with a pyramidal tip and a block-like substrate (b) Minimal model of a tip-substrate geometry, which we use in our calculations

Exercise 7.2: Geometry

Inspired by typical nanoscopy experiments, we want to model a setup with a tip and a substrate. Since a realistic modelling of the full tip-substrate system (as depicted in Fig. 1(a)) is computationally quite expensive, we use a minimal model of tip and substrate to catch the qualitative physics in these setup (cf. Fig. 1(b)):
We use metallic Mg atoms instead of the typical W, Au (etc.) atoms and truncate the setup considerably. The geometry should consist of a 3x3 plane emulating the substrate and a pyramid of 5 atoms (with one atom at the tip apex and 4 in the base plane). The tip-apex atom should be directly above the center atom of the substrate with a distance in z-direction of 3Å (cf. Fig. 1(b)).
Create a xyz-file of the geometry depicted in Fig. 1(b). You can either place the atoms by hand or use e.g. a python script to create the crystal. Place the atoms in a body-centered cubic (bcc) configuration with lattice constant a=4.282Å. **[5]**

Exercise 7.3: CP2K Input file

cp2k input files consist of several sections, of which you have already encountered some for the DFT. In this exercise, we start from an empty input file and build it step by step by going through all the parts necessary for a real-time simulation of electronic motion under a laser pulse.[1]

(a) The very first section is the `GLOBAL` section: There we declare a meaningful `PROJECT` name and `RT_PROPAGATION` as `RUN_TYPE`. **[2]**

(b) Second, we need the `MOTION` section for doing actual dynamics. There, we invoke the `MD`-subsection with `NVE` as `ENSEMBLE`, room-`TEMPERATURE` (300.0 K) and a total time of 100 fs with step size of 0.1 fs, which is declared by `STEPS`[2] and `TIMESTEP`. **[2]**

(c) We finalize the input with the `FORCE_EVAL` section. There, we introduce, as usual, `METHOD` as `QUICKSTEP` as well as the following subsections: **[4]**

(i) In the `SUBSYS`-subsection, we include the coordinates from the previous exercise 7.2, center it (by the builtin keyword) and declare the `CELL` with `PERIODIC NONE` and `ABC 10 10 15`.[3] Last, we declare the `KIND`-subsection as follows

```
&KIND Mg
  BASIS_SET ORB     DZVP-MOLOPT-SR-GTH-q2
  POTENTIAL         GTH-LDA-q2
&END KIND
```

to use GTH-pseudopotentials with the two outer-shell electrons, which reduces the computational cost compared to all electrons of Mg.

(ii) The `DFT`-subsection is quite lengthy and a large part mainly concerns details on the SCF-convergence. Since that is not our primary topic, we don't discuss that here in detail, but only

[1] For quantitative simulations, one needs to check the convergence of all parameters. In this case, we look for qualitative results.

[2] This is NOT the total time, but $\frac{\text{total time}}{\text{step size}}$

[3] In general, the electronic density $n(\mathbf{r}, t)$ has to *fit* in that box. That means that the electron density should be vanishing at the cell boundary. Usually, a vacuum of 5Å on each side is sufficient for that.

state these parts at the end of this exercise. The physical, and thus interesting parts :), concern the propagation in real time under the influence of the electric field. We parametrize the laser pulse by an electric field

$$E(t) = E_0 \cos(\omega_0 t)\, e^{-(t-t_0)^2/(2\sigma^2)}\,. \tag{3}$$

in z-direction (`POLARIZATION 0 0 1`). We use a frequency $\omega_0 = 2\pi \cdot 60$ THz, i.e. a wavelength of $\lambda = \frac{c}{\omega_0/(2\pi)} = 5000$ nm, and an envelope with width $\sigma = 10$ fs centered at $t_0 = 45$ fs. Why is that frequency/wavelength a reasonable choice and what would happen to the shape of the pulse by increasing/decreasing by a factor of 10?

Eventually, we arrive at the input

```
&EFIELD
   INTENSITY NEEDS_TO_BE_SPECIFIED
   POLARISATION 0 0 1
   WAVELENGTH 5000.0
   ENVELOP GAUSSIAN
   &GAUSSIAN_ENV
      SIGMA 10.0
      T0    45.0
   &END GAUSSIAN_ENV
&END
```

The intensity in $\frac{\mathrm{W}}{\mathrm{cm}^2}$ corresponds to an E_0 in atomic units ($\frac{E_H}{a_B} \approx 82.4 \frac{\mathrm{V}}{\mathrm{nm}}$) given by

$$E_0 = \sqrt{\frac{\texttt{INTENSITY}/(\frac{\mathrm{W}}{\mathrm{cm}^2})}{3.5094410 \cdot 10^{16}}} \cdot \frac{E_H}{a_B}\,, \tag{4}$$

as specified in the manual originating from the atomic units of the energy flux $I_0 = \frac{cE_H^2}{8\pi}$ (cf. this reference) and the relation $I = E_0^2$ in atomic units.
We will discuss the range of parameters for `INTENSITY` in the next exercise.
Moreover, we specify some convergence parameters for the real-time simulation

```
&REAL_TIME_PROPAGATION
   MAX_ITER 25
   EPS_ITER 1.0E-9
   MAT_EXP TAYLOR
&END
```

The main quantity of interest will be the time-dependent dipole moments from Eq. (2), which we print by the `PRINT`-subsection within the `DFT`-subsection:

```
&PRINT
  &MOMENTS
    PERIODIC .FALSE.
  &END
&END
```

As announced, the rest of the DFT-subsection reads as:

```
BASIS_SET_FILE_NAME  BASIS_MOLOPT_UCL
POTENTIAL_FILE_NAME  GTH_POTENTIALS
&MGRID
  CUTOFF 50
&END MGRID
&SCF
  EPS_SCF 1.0E-7
  MAX_SCF 500
  ADDED_MOS -1
  CHOLESKY INVERSE
  &SMEAR ON
     METHOD FERMI_DIRAC
     ELECTRONIC_TEMPERATURE [K] 300
  &END SMEAR
  &MIXING
     METHOD BROYDEN_MIXING
     ALPHA 0.1
     BETA 1.5
     NBROYDEN 8
  &END
&END SCF
&POISSON
  PERIODIC NONE
  POISSON_SOLVER MT
&END POISSON
&XC
  &XC_FUNCTIONAL LDA
  &END XC_FUNCTIONAL
&END XC
```

Exercise 7.4: Real-time dynamics from TDDFT and comparison to Eq. (1)

Now, we use the geometry from Exc. 7.2 and the input from Exc. 7.3 to test the applicability of Eq. (1). To that end, we *screen* a range of electric field strengths to find the regime, where Eq. (1) is valid. Start several cp2k calculations (in different directories) with the above input, where you specify the `INTENSITY` as given by Eq. (4), such that you screen for E_0, which correspond to `INTENSITY` between `1e7` and `1e14` (spaced by factors of 10 (logarithmically) for each run; cf. Table in Exc. 4(c),(i)).
Make use of all 6 cores for the calculations

```
export OMP_NUM_THREADS=1
nohup mpirun -np 6 cp2k.psmp INPUT.inp &> cp2k.out &
```

and make sure that you only start one calculation at once. Check that there is no calculation running before you start a new one by using `top` or `htop`. Otherwise, the calculations will slow each other down considerably. **[4]**

(a) In the output file, dipole moments are printed, which look like

```
 ELECTRIC/MAGNETIC MOMENTS
  Reference Point [Bohr]                0.00000000      0.00000000      0.00000000
  Charges
    Electronic=     -28.00000000     Core=     28.00000000     Total=      0.00000000
  Dipoles are based on the traditional operator.
  Dipole moment [Debye]
    X=  0.1444815E-11 Y=  0.1444815E-11 Z=  0.7116430E+01  Total=       7.1164305
```

Extract the values for the z-coordinate,[4] i.e. `0.7116430E+01` in the example, by using either[5]

```
grep "Z=  " cp2k.out | awk '{print $6}'
```

or a (python) script.[6]

The moments are printed (`STEPS`+1) times (You can count the number of printed lines by `grep "Z= " cp2k.out | wc -l`, where the first one is for the preliminary DFT calculation, i.e. $p_z(t_0)$. Ignore that first line with $p_z(t_0)$ and evaluate the dipole moments starting from the second line, i.e. $p_z(t_1)$. **[4]**

(b) Before we interpret this raw data of the dipole $p_z(t)$, we want to clean it a bit: Subtract the first moment $p_z(t_1)$ from the overall $p_z(t)$, to get rid of the constant offset in the dipole introduced by the asymmetry of the geometry. **[1]**

(c) Plot the dipoles $p_z(t) - p_z(t_1)$ such that you can see deviations from the regime of applicability of Eq. (1) in two ways:

(i) Extract the maximum value of the dipoles $p_z(t)-p_z(t_1)$ as well as the electric field peak strength E_0 and fill the following table:

Intensity (at.u.)	Electric field peak strength	Maximum dipole strength
10^7		
10^9		
10^{11}		
10^{13}		
$5 \cdot 10^{13}$		
10^{14}		

Now, plot this data in a double-logarithmic way. Which arrangement of the data points do you expect in the regime of applicability, you have deduced in Exc. 1(a)? Include that in the plot as a qualitative guide to the eye. How does the deviation from that look like? **[5]**

[4] As you can see in the printed example, we have an isotropic system, i.e. we irradiate the sample with $\mathbf{E}(t) \| \hat{z}$ and obtain also (predominantly) a dipole moment in z-direction $\mathbf{p}(t) \| \hat{z}$.

[5] This command is for the bash-shell. You might have to activate this shell by executing `bash` in advance in the terminal.

[6] You can also use python instead of `grep` by employing `readlines` to extract the lines of the file, search for `Dipole moment [Debye]` and write the z-entry by splitting the line after.

(ii) Plot $\frac{p_z(t)-p_z(t_1)}{E_0}$. How does the deviation from the regime of applicability express itself in this plot? Potentially, you can observe oscillations in the right tail of the dipole for large t. We will discuss these on the next exercise sheet. **[4]**