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Institute of Theoretical Physics
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https://www.ur.de/physics/wilhelm/teaching/sose24-computational-nanoscience

Computational Nanoscience: Solution to Exercise Sheet No. 8

Exercise 8.1: Geometry

Geometry for 3Å distance:

```
14

Mg          0.00000000          0.00000000          0.00000000
Mg         -2.14100000         -2.14100000          2.14100000
Mg         -2.14100000          2.14100000          2.14100000
Mg          2.14100000         -2.14100000          2.14100000
Mg          2.14100000          2.14100000          2.14100000
Mg         -4.28200000         -4.28200000         -3.00000000
Mg         -4.28200000         -0.00000000         -3.00000000
Mg         -4.28200000          4.28200000         -3.00000000
Mg         -0.00000000         -4.28200000         -3.00000000
Mg         -0.00000000         -0.00000000         -3.00000000
Mg         -0.00000000          4.28200000         -3.00000000
Mg          4.28200000         -4.28200000         -3.00000000
Mg          4.28200000         -0.00000000         -3.00000000
Mg          4.28200000          4.28200000         -3.00000000
```

Geometry for 7Å distance:

```
14

Mg          0.00000000          0.00000000          0.00000000
Mg         -2.14100000         -2.14100000          2.14100000
Mg         -2.14100000          2.14100000          2.14100000
Mg          2.14100000         -2.14100000          2.14100000
Mg          2.14100000          2.14100000          2.14100000
Mg         -4.28200000         -4.28200000         -7.00000000
Mg         -4.28200000         -0.00000000         -7.00000000
Mg         -4.28200000          4.28200000         -7.00000000
Mg         -0.00000000         -4.28200000         -7.00000000
Mg         -0.00000000         -0.00000000         -7.00000000
Mg         -0.00000000          4.28200000         -7.00000000
Mg          4.28200000         -4.28200000         -7.00000000
Mg          4.28200000         -0.00000000         -7.00000000
Mg          4.28200000          4.28200000         -7.00000000
```

Exercise 8.2: CP2K Input file

```
&GLOBAL
    PROJECT Exc_7
    RUN_TYPE RT_PROPAGATION
&END GLOBAL
&MOTION
    &MD
        ENSEMBLE NVE
        TEMPERATURE 300
        STEPS 1000
        TIMESTEP 0.1
    &END MD
&END MOTION
&FORCE_EVAL
    METHOD QUICKSTEP
    &SUBSYS
        &TOPOLOGY
            &CENTER_COORDINATES
            &END CENTER_COORDINATES
            COORD_FILE_NAME   struc.xyz
            COORD_FILE_FORMAT XYZ
        &END TOPOLOGY
        &CELL
            ABC 10 10 20
            PERIODIC NONE
        &END CELL
        &KIND Mg
            BASIS_SET ORB DZVP-MOLOPT-SR-GTH-q2
            POTENTIAL GTH-LDA-q2
        &END KIND
    &END SUBSYS
    &DFT
        &EFIELD
            INTENSITY 1000000000000.0
            POLARISATION 0 0 1
            WAVELENGTH 5000.0
            ENVELOP GAUSSIAN
            &GAUSSIAN_ENV
                SIGMA 10.0
                T0 45.0
            &END GAUSSIAN_ENV
        &END
        &REAL_TIME_PROPAGATION
            MAX_ITER 25
            EPS_ITER 1.0E-9
            MAT_EXP TAYLOR
```

```
        &END
        &PRINT
            &MOMENTS
                PERIODIC .FALSE.
            &END
        &END
        BASIS_SET_FILE_NAME BASIS_MOLOPT_UCL
        POTENTIAL_FILE_NAME GTH_POTENTIALS
        &MGRID
            CUTOFF 100
        &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
    &END DFT
&END FORCE_EVAL
```

Exercise 8.3: Evaluation of the electric field and the dipole moment

(a) In Fig. 1, we can observe that for 3Å distance, the time-dependent dipole $p_z^{d=3\text{Å}}(t)$ follows the field closely, whereas $p_z^{d=7\text{Å}}(t)$ shows a clear phase-shift of the positive field crest, which we attribute to the tunneling occurring for this geometry.

(b) The physical reason for the oscillations are interband contributions, i.e. the occupation oscillates indefinitely between occupied and unoccupied bands, since there is no damping mechanism, which dissipates the energy. In Fig. 2, we observe the frequency of the electric field at 60 THz for $p_z^{d=3\text{Å}}(\omega)$.

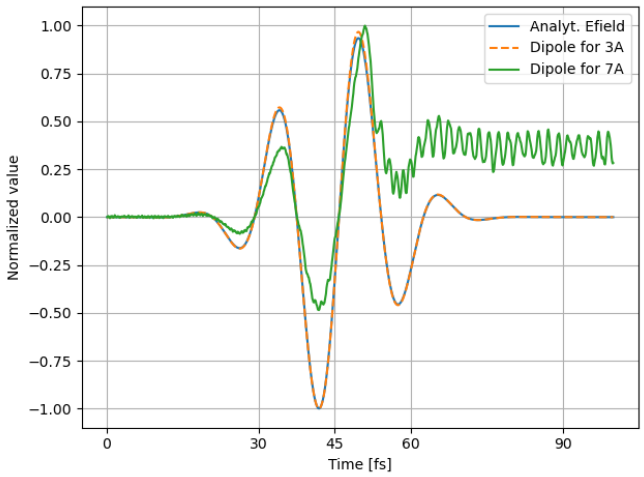

Figure 1: Results of the real-time TDDDFT simulation. The dipole for 3Å distance follows the field closely, whereas the dipole for 7Å distance shows a clear phase shift as well as oscillations in the right tail.

The frequency-dependent dipole $p_z^{d=7\text{Å}}(\omega)$ shows additional frequencies, especially a peak at 2.1 eV, which lies in the typical range for the energy differences of the system (cf. next exercise).

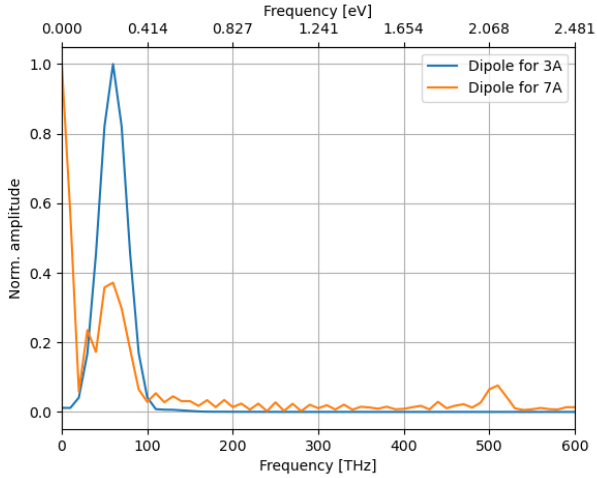

Figure 2: Results of the real-time TDDDFT simulation in frequency space normalized to 1. We observe one main peak for $p_z^{d=3\text{Å}}(\omega)$ at 60 THz, as expected from the time-dependent dipole $p_z^{d=3\text{Å}}(t)$ in Fig. 1 following the electric field with $\omega_0 = 2\pi \cdot 60$ THz. In contrast, the spectrum of $p_z^{d=7\text{Å}}(\omega)$ has features in addition to the peak at 60 THz. In particular, the small peak in $p_z^{d=7\text{Å}}(\omega)$ at 2.1 eV characterizes the oscillations in the right tail of $p_z^{d=7\text{Å}}(t)$ of Fig. 1.

(c) In order to describe the oscillation of the dipole moment

$$\mathbf{p}(t) = \int \mathrm{d}^3 r \, \mathbf{r} \, n(\mathbf{r}, t) \,, \tag{1}$$

we need to expand the density $n(\mathbf{r}, t) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r}, t)|^2$ in terms of the initial orbitals $\psi_i(\mathbf{r}, t_0) = \varphi_i(\mathbf{r})$, as proposed on the exercise sheet.

We start from the TDKS equation (lecture notes, Eq. (15.16)) after the laser pulse, i.e. $v(\mathbf{r}, t) =$

$\mathbf{d}(\mathbf{r},t)\cdot\mathbf{E}(t)=0$:

$$\left[-\frac{1}{2m}\nabla^2+v_{\text{ext}}(\mathbf{r})+v_{\text{H}}[n](\mathbf{r},t)+v_{\text{xc}}[n](\mathbf{r},t)+v(\mathbf{r},t)\right]\psi_j(\mathbf{r},t)=i\frac{\partial}{\partial t}\psi_j(\mathbf{r},t)\,. \tag{2}$$

By using the stationary KS equation

$$\left[-\frac{1}{2m}\nabla^2+v_{\text{ext}}(\mathbf{r})+v_{\text{H}}[n](\mathbf{r},t)+v_{\text{xc}}[n](\mathbf{r},t)\right]\varphi_n=\varepsilon_n\varphi_n\,, \tag{3}$$

$$h^{\text{KS}}\varphi_n=\varepsilon_n\varphi_n\,, \tag{4}$$

we can rewrite Eq. (2) (with $v(\mathbf{r},t)=\mathbf{d}(\mathbf{r},t)\cdot\mathbf{E}(t)=0$ for $t\to\infty$) as

$$\sum_n \varepsilon_n c_{jn}(t)\varphi_j(\mathbf{r})=i\frac{\partial}{\partial t}\sum_m c_{jm}(t)\varphi_m(\mathbf{r})\,, \tag{5}$$

where we expanded

$$\psi_j(\mathbf{r},t)=\sum_n c_{jn}(t)\varphi_j(\mathbf{r})\,, \tag{6}$$

since the non-zero electric field in the intermediate time can introduce a mixing of the Ground State KS orbitals.

Using the completeness and orthonormality of the KS orbitals as well as an exponential ansatz, we obtain from Eq. (5):

$$c_{jn}(t)=c_{jn}(t=t_0)e^{-i\varepsilon_m(t-t_0)}\,, \tag{7}$$

i.e. each coefficient oscillates with a phase given by the respective KS orbital energy.

Reinserting that, we find an interference effect, which leads to the observed oscillations

$$n(\mathbf{r},t)=\sum_i^{\text{occ}}\left|\sum_{n,m}c^*_{jn}(t-t_0)c_{jm}(t-t_0)e^{i(\varepsilon_n-\varepsilon_m)(t-t_0)}\varphi^*_n(\mathbf{r})\varphi_m(\mathbf{r})\right|^2\,, \tag{8}$$

with the previously discussed characteristic energy scale of the band gap $\varepsilon_n-\varepsilon_m$.

(d) In case, $\mathbf{E}(t)=0$, $\forall t$, the stationary KS equation holds at all times and therefore the expansion in Eq. (6) reduces to one coefficient $c_{jn}=\delta_{jn}$. Hence, the density takes the usual form

$$n(\mathbf{r},t)=\sum_i^{\text{occ}}\left|\varphi^*_i(\mathbf{r})\varphi_i(\mathbf{r})\right|^2\,, \tag{9}$$

without time dependence, in particular without oscillations.