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Computational Nanoscience: Exercise Sheet No. 8

On this exercise sheet, we want to examine the motion of electrons in a real material under the influence of a laser pulse. Specifically, we will discuss the mechanisms found in one of the most recent publications in Regensburg[1], leading to the concept of *NOTE* (near-field optical tunnelling emission) microscopy.

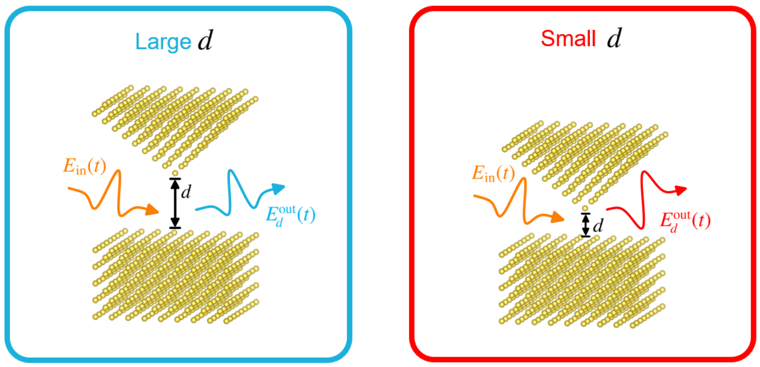

Figure 1: Schematical depiction of near-field effects in a tip-sample junction. A THz laser pulse ($E_{\text{in}}(t)$) is coupled to a sharp tip above a surface, which causes a dipole and therefore an outgoing field (E_d^{out}). It has been found that the distance d has a profound influence on the time profile of the outgoing field, i.e. a phase is introduced, which is depicted by the distinct shapes of E_d^{out}.

In Fig. 1, we depict schematically the experimental setup: A laser pulse ($E_{\text{in}}(t)$) is shined on a metallic tip-substrate interface, which causes a time-dependent dipole, which depends on the specific geometry in the experiment. It has been found that the time-dependent dipole $\mathbf{p}^d(t)$ depends on the distance between tip and substrate d, i.e. the time-dependent density of the system also depends on d:

$$\mathbf{p}^d(t) = \int \mathrm{d}^3r'\, \mathbf{r}'\, n^d(\mathbf{r}', t)\,. \tag{1}$$

Explicitly, that can be seen by examining the time-profile of $\mathbf{p}^d(t)$ for varying d, which exhibits a phase shift depending on the distance d. Since the acceleration of charges causes electromagnetic radiation, i.e. $E_d^{\text{out}} \propto \partial_t^2 \mathbf{p}^d(t)$, also the outgoing electric field E_d^{out} shows a phase shift (as schematically depicted by the pulse shapes of E_d^{out} in Fig. 1).
In the following, we will set up a real-time TDDFT calculation, where we can observe that behavior in a (very) simplified model system.

Exercise 8.1: Geometry

From the last exercise sheet, we already have a geometry with the distance of 3Å. Additionally, create a geometry with a tip-substrate separation of 7Å to simulate the different distances of the oscillating tip. Please start from the proposed geometry of the last solution as the results are very sensitive to the chosen geometry. **[2]**

[1] Siday, T., Hayes, J., Schiegl, F. et al. All-optical subcycle microscopy on atomic length scales. Nature 629, 329–334 (2024). https://doi.org/10.1038/s41586-024-07355-7

Exercise 8.2: CP2K Input file

We adapt the Input of the last sheet as follows: We increase the `CUTOFF` in the `MGRID`-section from `50` to `100`, adapt the cell size to `10 10 20` and give it a new `PROJECT` name. Moreover, we employ an electric field of $E_0 \approx 0.44 \frac{\mathrm{V}}{\mathrm{nm}}$, corresponding to `INTENSITY 1e12`, which is chosen to yield the most significant phase shift of $\mathbf{p}^d(t)$ for the employed geometry[2]. **[2]**

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

Now, we are ready to execute cp2k. Since these are two lengthy calculations, you want to use as much as possible of the computers resources (i.e. 6 cores for the PHY CIP) and start each of the two geometries (with the same input file, in different directories) by executing the nohup-command two times (Wait for the successful termination of the first job before you start the second one!):

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

This will take approximately 20-30 min.
As soon as both jobs are successfully finished (i.e. the usual cp2k output time table is printed without spurious error codes), we are good to go.

(a) We reuse the procedure of the last exercise sheet to extract the time-dependent dipole data, but each procedure independently for the two different calculations with different tip-substrate distance d: We extract the (`STEPS+1`) values for $p_z^d(t)$, ignore $p_z^d(t_0)$ and subtract the first value $p_z^d(t_1)$ from the following $p_z^d(t)$. For each calculation, we further normalize the obtained value $p_z^d(t) - p_z^d(t_1)$ by its maximum value, i.e. we arrive at

$$\frac{p_z^d(t) - p_z^d(t_1)}{\max\limits_{t'}(p_z^d(t') - p_z^d(t_1))} \quad . \tag{2}$$

Finally, we plot the time-dependent dipoles for the two distances as well as the electric field ($E(t) = E_0 \cos(\omega_0 t)\, e^{-(t-t_0)^2/(2\sigma^2)}$), where you should observe the following main features: **[8]**

(i) The electric field is centered at 45 fs and decays with a Gaussian envelope towards small and large times (approx. 50 fs away from t_0 it should be close to 0).

(ii) The time-dependent dipole for 3Å should follow the electric field closely.

(iii) The time-dependent dipole for 7Å will show a phase shift of the maxima, especially the positive maximum at $t \approx 50$ fs.

(iv) Additionally, you will observe some oscillations after this phase-shifted peak in the time-dependent dipole for 7Å. We will discuss these in the next part.

(b) At the right tail of the dipole for 7Å, you can observe some oscillations. What could be the physical reason for them?

Hint 1: Examine the frequency of these oscillations; either by hand or by fourier-transforming it in your script. Which order of magnitude in the physical system fits to the frequency?

Hint 2: Reduce the energy structure of the geometry to a two-band model and think of your time-dependent quantum mechanics lecture/exercises. **[4]**

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[2] The optimal electric field for a pronounced phase shift strongly depends on the geometry and material. Both in simulations and experiment, one needs to find that value in advance.

(c) How can we analytically derive the oscillations in the time-dependent dipole moment $\mathbf{p}(t)$ [Eq. (1) without superscript d]?

To do that, use the TDDFT equations (lecture notes, Theorem 15.2) to expand the density $n(\mathbf{r}, t) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r}, t)|^2$. Further, employ the time-evolution of the single-particle orbitals $\psi_i(\mathbf{r}, t)$ (lecture notes, Eq. (15.16)) **after** the laser pulse (i.e. $t \to \infty$, where $\mathbf{E}(t) \to 0$) together with an expansion of the time-dependent single-particle orbitals $\psi_i(\mathbf{r}, t)$ in terms of the initial orbitals $\psi_i(\mathbf{r}, t_0) = \varphi_i(\mathbf{r})$.**[3]**

(d) What happens to the expression you found for the dipole oscillations if there was no laser pulse at all, i.e. $\mathbf{E}(t) = 0 \, \forall t$? **[2]**