Switching the current through molecular wires with ultra-short laser pulses

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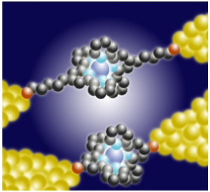
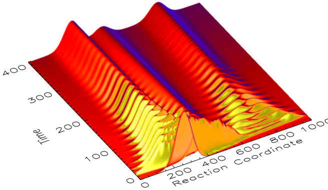


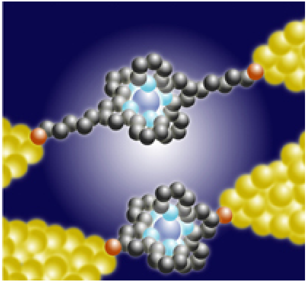
Leipzig

01. December 2006



Outline

Molecular wires



- first reproducible experiments on molecular wires
  - break junctions, STM setups, quantum dot geometries, . . .
- influence of laser light on molecular wires gives an opto-electronic coupling
- with femtosecond laser pulses: high spatial as well as temporal resolution

Density matrices

- time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt}|\Psi(x,t)\rangle = H(x,t)|\Psi(x,t)\rangle$$

- pure state: $\sigma = |\Psi\rangle\langle\Psi|$
- mixed state: $\sigma = \sum_n W_n |\Psi_n\rangle\langle\Psi_n|$
- time propagation

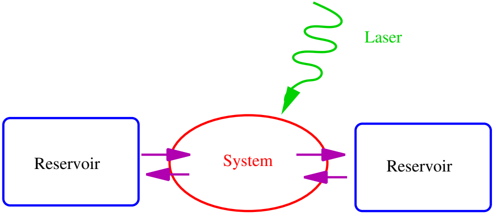
$$\begin{aligned} i\hbar \frac{d\sigma(t)}{dt} &= i\hbar \frac{d|\Psi\rangle\langle\Psi|}{dt} = i\hbar \left(\frac{|d\Psi\rangle}{dt}\langle\Psi| + |\Psi\rangle \frac{\langle d\Psi|}{dt} \right) \\ &= H(t)\sigma(t) - \sigma(t)H(t) = [H(t), \sigma(t)] \end{aligned}$$

- Observables:

$$\begin{aligned} \langle Q \rangle = \langle\Psi|Q|\Psi\rangle &= \sum_n \langle\Psi|n\rangle\langle n|Q|\Psi\rangle \\ &= \sum_n \langle n|Q|\Psi\rangle\langle\Psi|n\rangle = tr(Q\sigma) \end{aligned}$$

Reduced density matrix formalism

- Goal: Description of ultra-fast (fs) processes in the molecular wire
- full quantum dynamics including dephasing, energy dissipation but also coherences, not only steady state, temperature dependence
- splitting in relevant system and electronic reservoirs



- σ - density matrix of the full system
  (relevant system + bath)

$$i\hbar \frac{d\sigma(t)}{dt} = [H(t), \sigma(t)]$$

Reduced density matrix formalism

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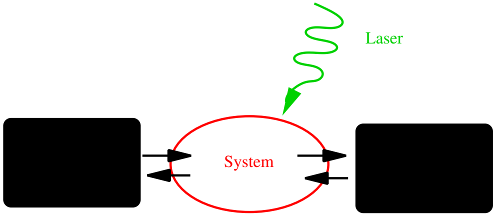


- reduced density-matrix:
  $\rho = tr_R(\sigma)$ - density matrix of the relevant system

$$i\hbar\frac{d\rho(t)}{dt} = [H_S(t), \rho(t)] + \mathcal{D}(t)\rho(t)$$

System-bath coupling

Hamiltonian

$H = H_S + H_R + H_{SR}$

- every reservoir degree of freedom only slightly distorted
  $\Rightarrow$ modeled by harmonic oscillators
- how strongly does the reservoir absorb energy?
  $\Rightarrow$ spectral density $J(\omega)$
- perturbation theory in the system-bath coupling H_{SB}
  (2nd order or higher)

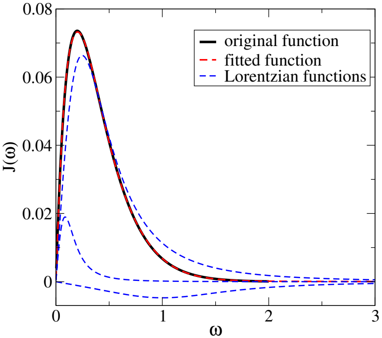
Decomposition of the spectral density

- information on the frequencies of the reservoir modes and their coupling to the system

$$J(\omega) = \frac{\pi}{2} \sum_i \frac{c_i^2}{m_i \omega_i} \delta(\omega - \omega_i)$$

- numerical decomposition into Lorentzians

$$J(\omega) = \sum_{k=1}^{n} \frac{p_k}{4\Omega_k} \frac{1}{(\omega - \Omega_k)^2 + \Gamma_k^2}$$

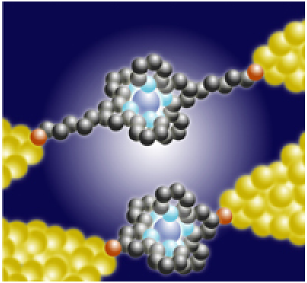


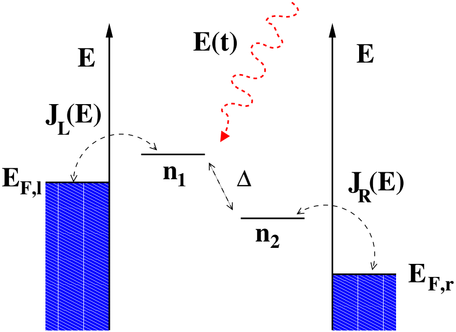
Overview of the theory

- reservoir correlation function $C(t) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} J(\omega) \frac{e^{i\omega t}}{e^{\beta\omega}-1}$
  $\Rightarrow$ sum of exponentials in t
- this allows further analytical treatment
- definition of auxiliary density matrices (time-nonlocal approach) or auxiliary operators $\Lambda_{12}^{k}(t)$ (time-local approach)
- instead of one quantum master equation we get one master equation of the system and several auxiliary master equations
- Matsubara expansion $\Rightarrow$ many master equations for low temperatures
- no further approximation in the light-matter coupling (beyond semi-classical approximation)

U. Kleinekathöfer, J. Chem. Phys. **121**, 2505 (2004).
S. Welack, M. Schreiber, U. Kleinekathöfer, J. Chem. Phys. **124**, 044712(2006).

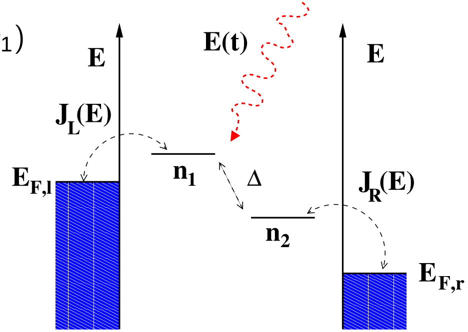
The model



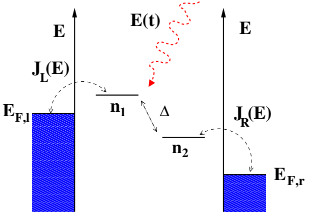


The model

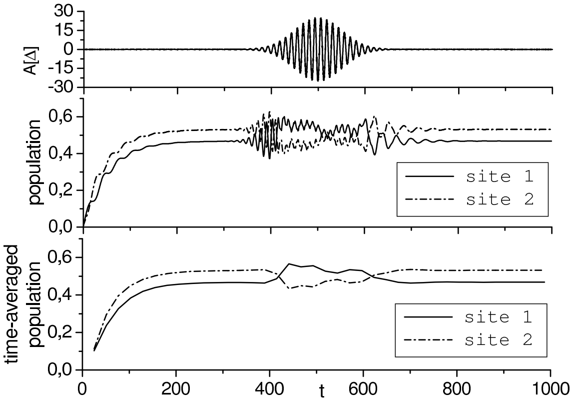
$$
\begin{aligned}
H(t) &= H_S(t) + H_L + H_{SL} \\
H_S(t) &= \sum_n (E_n + U_n(t)) c_n^\dagger c_n - \Delta(c_n^\dagger c_{n-1} + c_{n-1}^\dagger c_n) \\
H_L &= \sum_q \omega_q c_q^\dagger c_q \\
H_{LS} &= \sum_q (V_q c_1^\dagger c_q + V_q^* c_q^\dagger c_1)
\end{aligned}
$$



Population dynamics



$$
\begin{aligned}
U_n(t) &= E(t)\delta_{1n} - E(t)\delta_{2n} \\
E_1 = E_2 &= E_{F,r} + \Delta = E_{F,l} - \Delta
\end{aligned}
$$



Determination of the current

- using electron number operator $N_L = \sum_q c_q^\dagger c_q$

$$I_L(t) = e\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{tr}\,\{N_L\sigma(t)\} = -ie\,\mathrm{tr}\{[N_L, H(t)]\sigma(t)\}$$

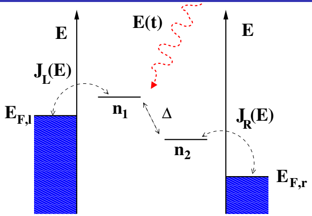
- defining auxiliary operators

$$\begin{aligned}\Lambda_{12}(t) &= \int_{t_0}^{t}\mathrm{d}t'\,C_{12}(t-t')\,U_S(t,t')\,c_1\rho_S(t') = \sum_k^{m+m'}\Lambda_{12}^k(t)\\ \Lambda_{21}(t) &= \int_{t_0}^{t}\mathrm{d}t'\,C_{21}^*(t-t')U_S^\dagger(t,t')\,c_1^\dagger\rho_S(t') = \sum_k^{m+m'}\Lambda_{21}^k(t)\end{aligned}$$

- equations of motion for auxiliary operators $\Lambda_{12}^k(t)$ and $\Lambda_{21}^k(t)$
- final current equation

$$I_l(t) = 2e\,\mathrm{Re}\left(\mathrm{tr}_S\{c_1^\dagger\Lambda_{12}(t)\} - \mathrm{tr}_S\{c_1\Lambda_{21}(t)\}\right)$$

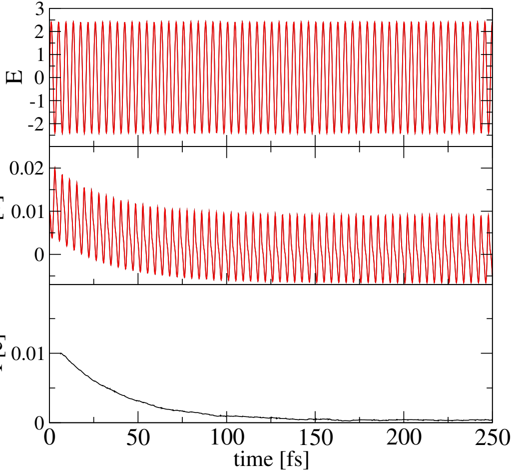
Coherent destruction of tunneling (CDT)



$$U_n(t) = E(t)\delta_{1n} - E(t)\delta_{2n}$$
$$E(t) = E_0 \sin(\omega t)$$

$\Delta = 0.1$ eV

1 [e] $\approx 2.4 \times 10^{-4}$ A



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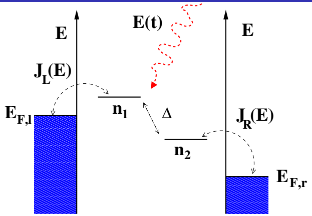

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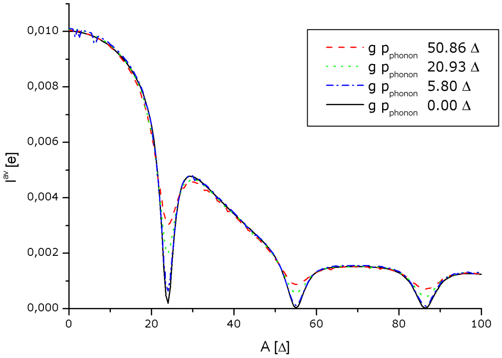
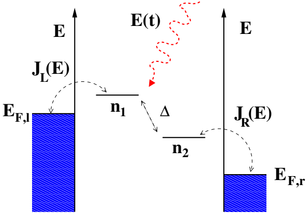


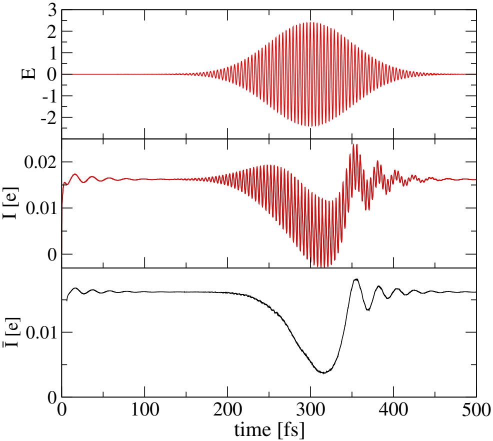
J. Lehmann, S. Kohler, V. May, P. Hänggi, J. Chem. Phys. **121**, 2278 (2003)

CDT: Short laser pulse



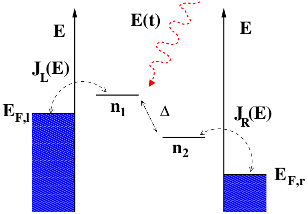
$$U_n(t) = E(t)\delta_{1n} - E(t)\delta_{2n}$$

$$E(t) = E_0 \exp\left(\frac{-(t-T)^2}{\sigma^2}\right)$$



U. Kleinekathöfer, G.-Q. Li, S. Welack, M. Schreiber, Europhys. Lett. **175**, 139 (06)

CDT: Pulse length σ



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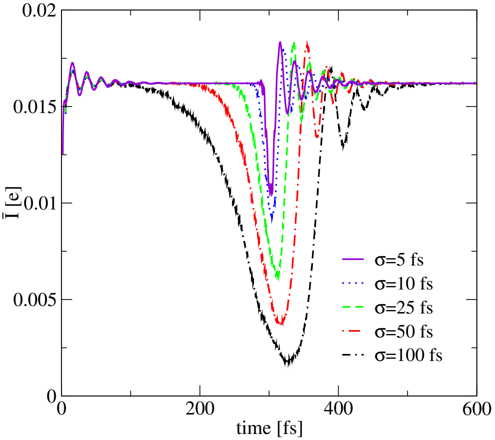
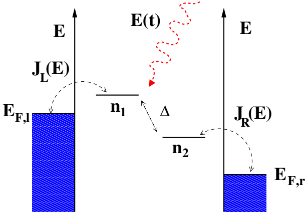
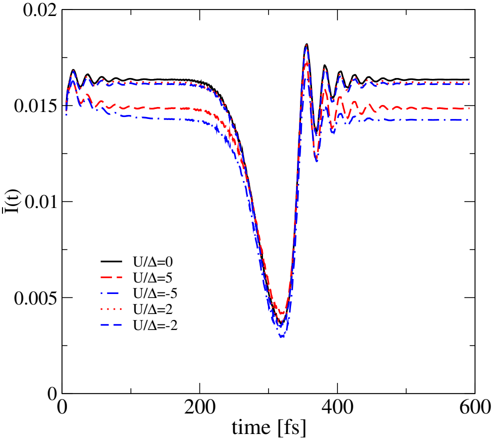


CDT: Electron correlation for spinless fermions

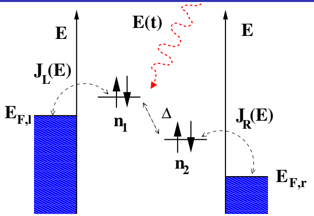


$$H_{corr} = U \sum_n n_n n_{n+1}$$

$$n_n = c_n^\dagger c_n$$

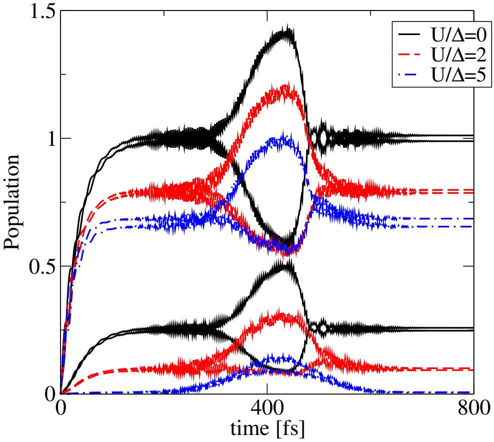


CDT: Electron correlation for fermions with spin



$$H_{corr} = U \sum_n n_{n\uparrow} n_{n\downarrow}$$

$$n_{n\sigma} = c^\dagger_{n\sigma} c_{n\sigma}$$



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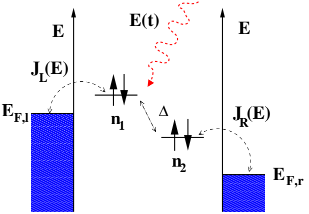

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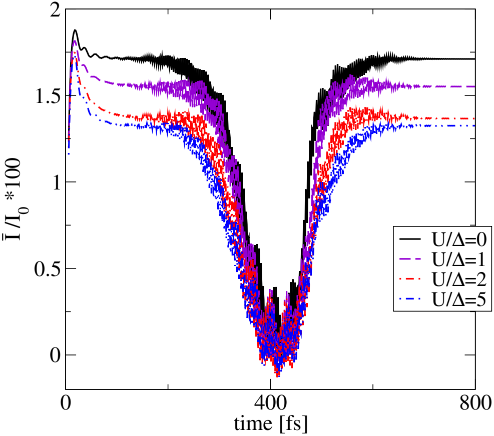
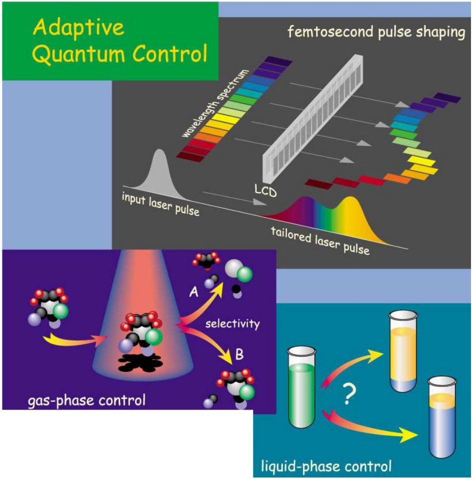
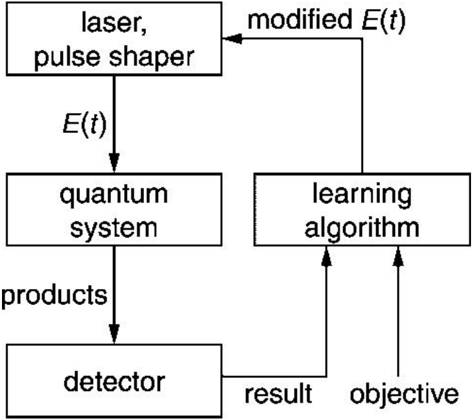


Coherent control with femtosecond laser pulses

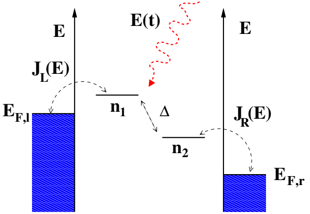


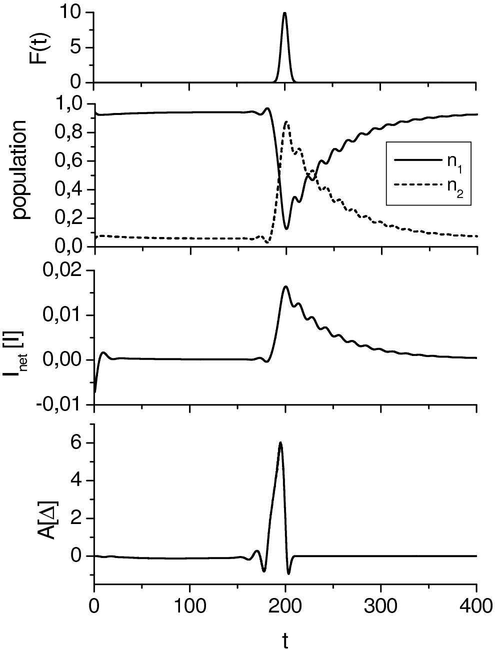


T. Brixner und G. Gerber,
ChemPhysChem **4**, 419 (2003).

R.S. Judson and H. Rabitz
Phys. Rev. Lett. **68**, 1500 (1992).

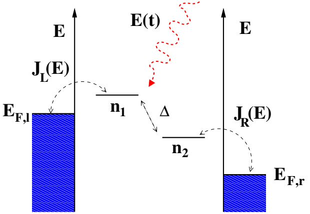
CDT: Optimal control of current with 2 sites



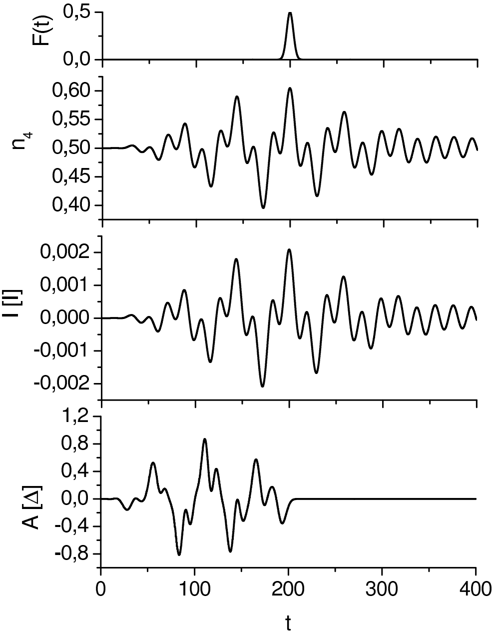


- maximal current at peak of goal function $F(t)$
- $E_1 - E_2 = -4\Delta$
- $E_{F,l} - E_{F,r} = 2\Delta$

CDT: Optimal control of current with 4 sites



- maximal current at peak of goal function $F(t)$
- $E_1 = E_2 = E_3 = E_4$
- $E_{F,l} = E_{F,r}$

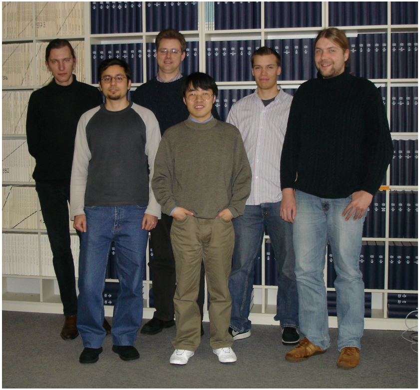


Summary

- density matrix approach to the electron transport through molecular wires
- numerical decomposition of the spectral density
- no approximation in the light-matter coupling beyond the semi-classical approximation
- calculation of population dynamics and current
- coherent destruction of tunneling also for rather short laser pulses
- first tests of optimal control of the current

Acknowledgments: The Group

- Quantum and Molecular Dynamics subgroup



  - A. Novikov (now Rochester), S. Pezeshki, U. Kleinekathöfer (soon Bremen), G.-Q. Li, S. Welack (now Hong Kong), M. Schröder, J. Liebers (not shown)

- DFG for financial support (GK, SPP, individual grants)

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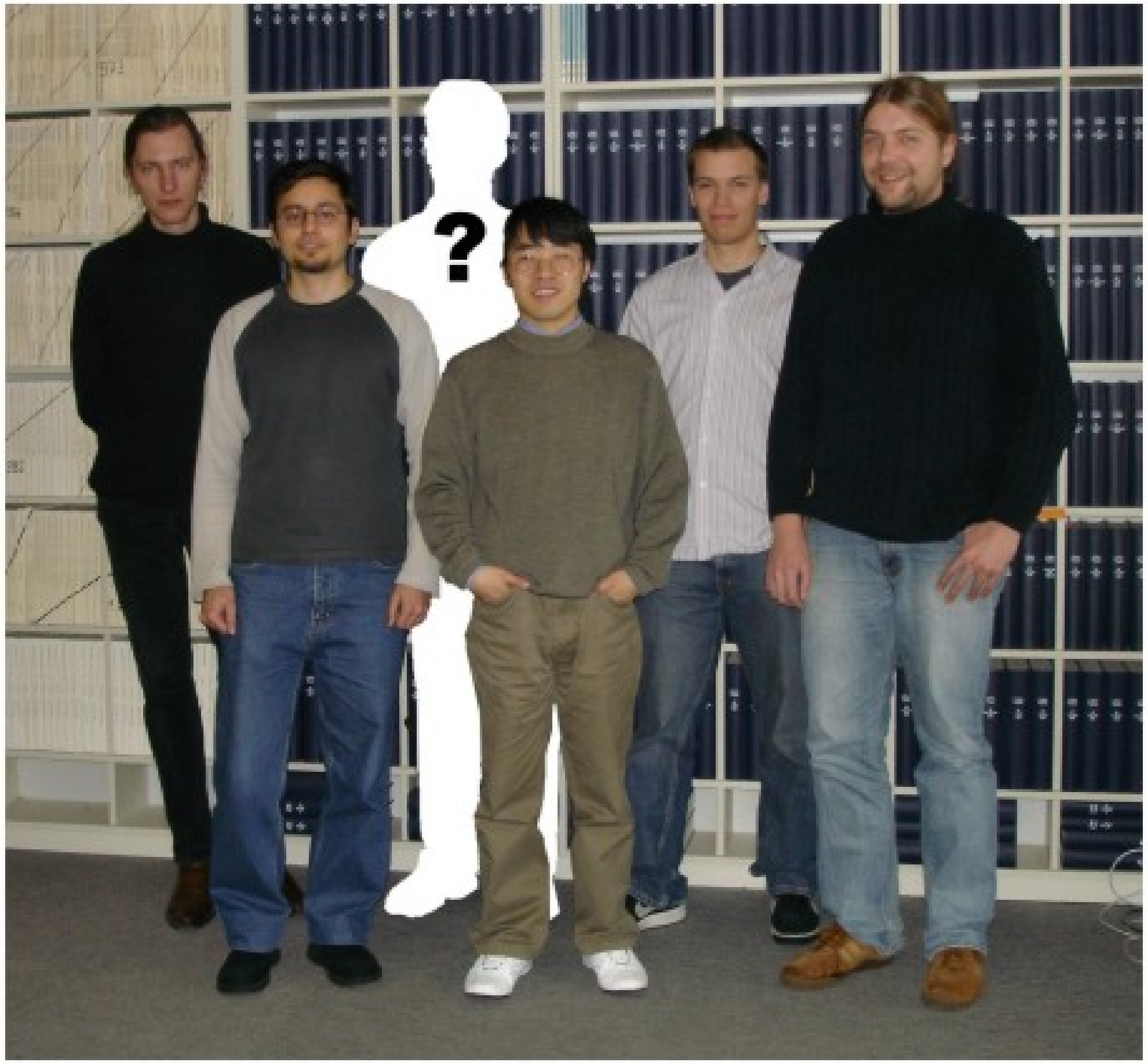

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