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DFT studies of electronic excitation effects: crystal lattice stability, non-adiabatic transitions

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Density Functional Theory

N-electron wave function

$$\Psi(\vec{r}^{\,N})$$

$$\Downarrow$$ Hohenberg-Kohn theorem

One-electron density

$$n(\vec{r})$$

$$\Downarrow$$ Kohn-Sham scheme

N one-electron orbitals

$$\Phi_1(\vec{r}),\ldots,\Phi_N(\vec{r})$$

Connection:

$$N\int d\vec{r}_2\ldots d\vec{r}_N\left|\Psi(\vec{r},\vec{r}_2\ldots\vec{r}_N)\right| = n(\vec{r}) = \sum_{i=1}^{N}\left|\Phi_i(\vec{r})\right|^2$$

Density Functional Theory

$$E[n] = T_s[n] + V_H[n] + E_{xc}[n] + \int d\vec{r}\, n(\vec{r}) v(\vec{r})$$

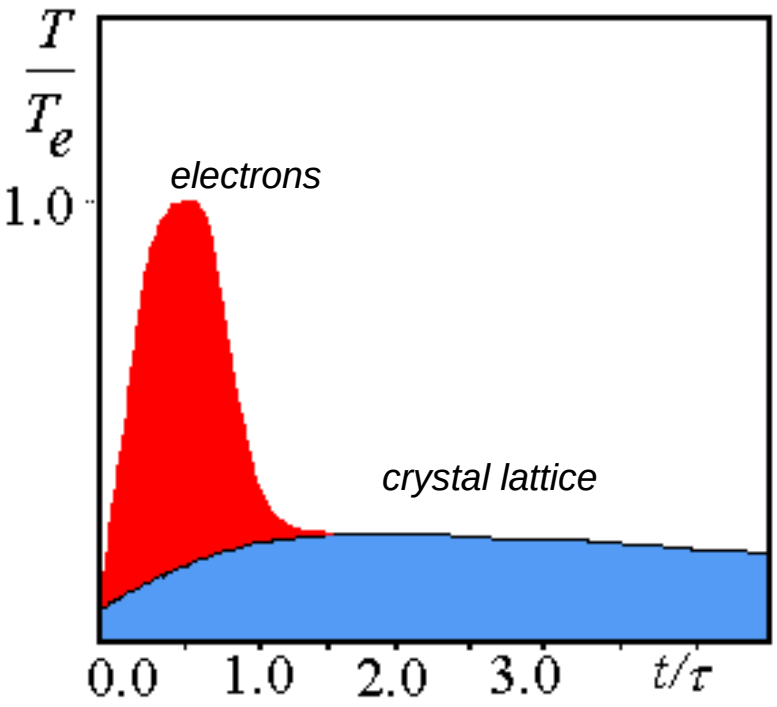
$$T_s[n] = -\frac{1}{2}\sum_{i=1}^{N} \left\langle \Phi_i \left| \nabla^2 \right| \Phi_i \right\rangle$$

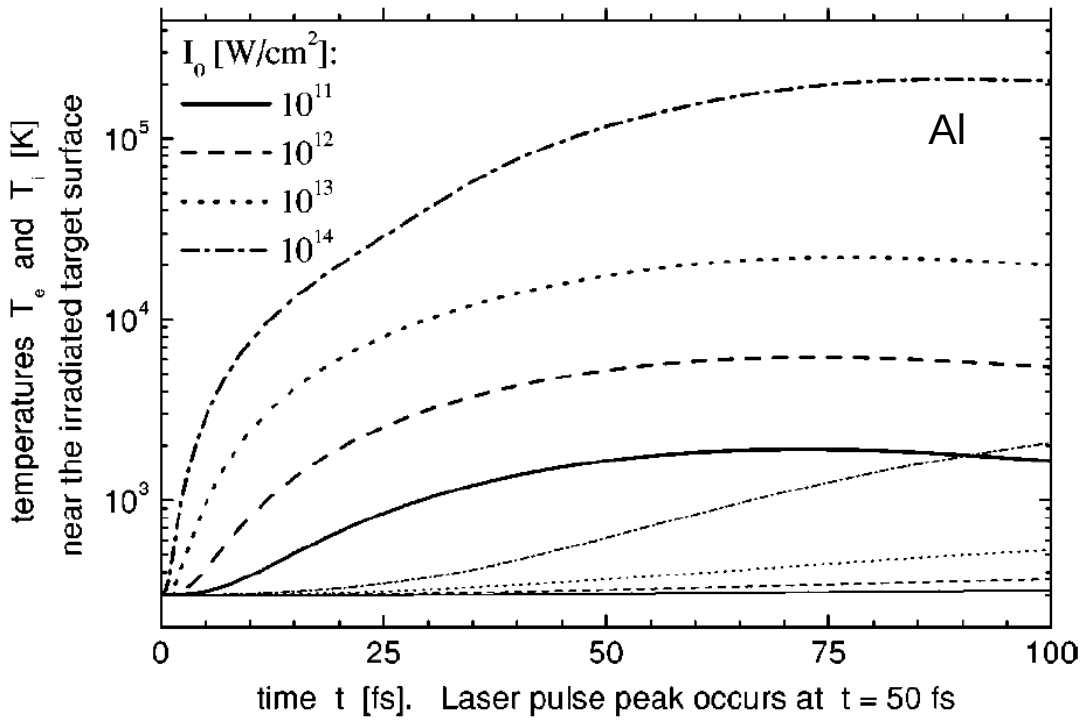
$$\left(-\frac{1}{2}\nabla^2 + \frac{\delta V_H[n]}{\delta n(\vec{r})} + \underbrace{\frac{\delta E_{xc}[n]}{\delta n(\vec{r})}} + v(\vec{r}) \right) \Phi_i = \varepsilon_i \Phi_i$$

approximations to the exchange-correlation term
LDA, GGA etc.

Dynamics of the crystal lattice after femtosecond pulse irradiation

Two-temperature system
«cold» lattice – hot «electrons»





Fisher et al., 2001

T>0: Mermin functional

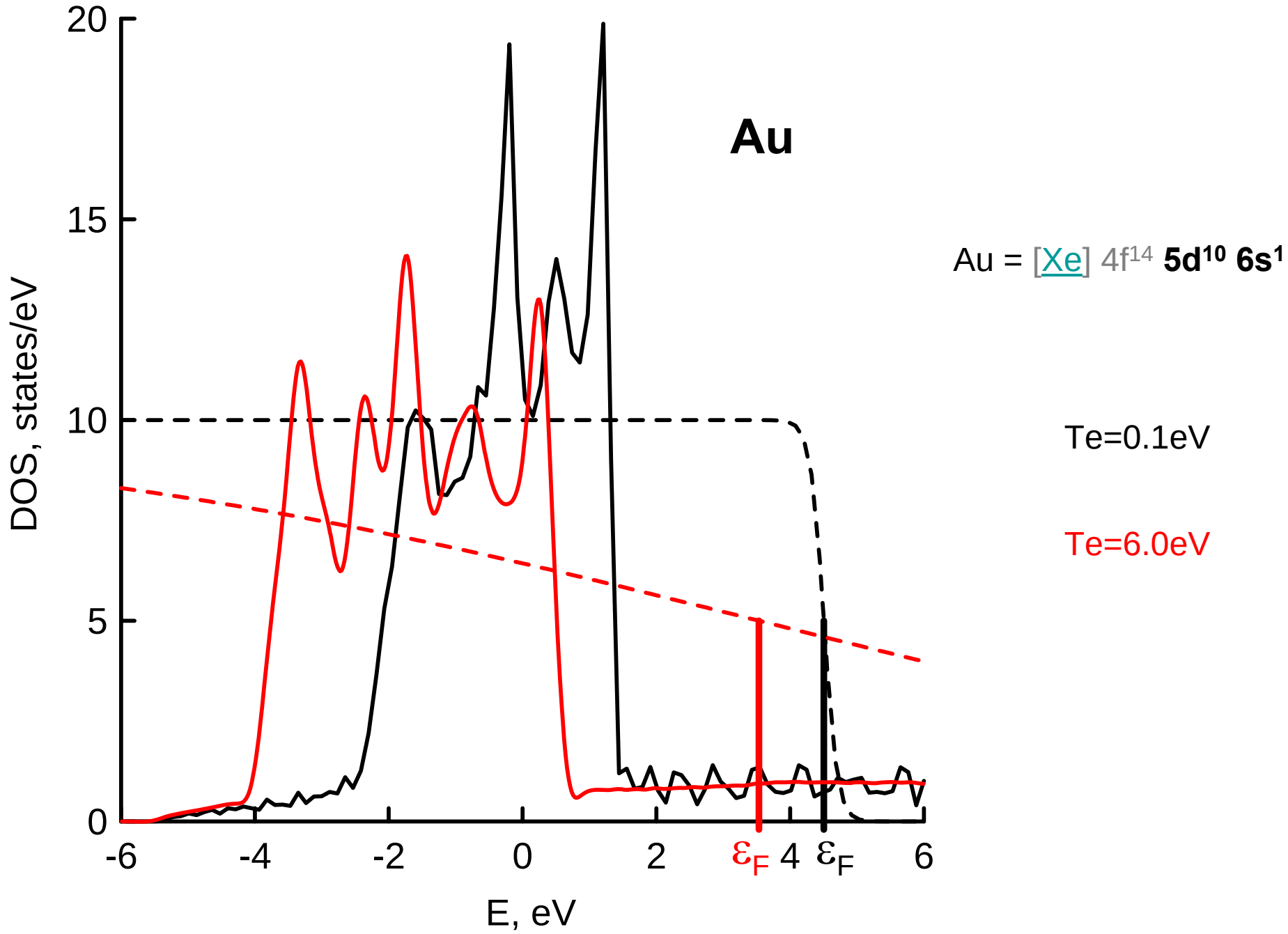
$$f_i(\beta) = \frac{1}{1 + \exp\left[\beta\left(\varepsilon_i - \mu\right)\right]}$$

$$n(\vec{r}) = \sum_{i=1}^{N} f_i(\beta) \left|\Phi_i(\vec{r})\right|^2$$

$$\Omega[n] = T_s[n] + V_H[n] + \Omega_{xc}[n] + \int d\vec{r}\, n(\vec{r}) v(\vec{r})$$

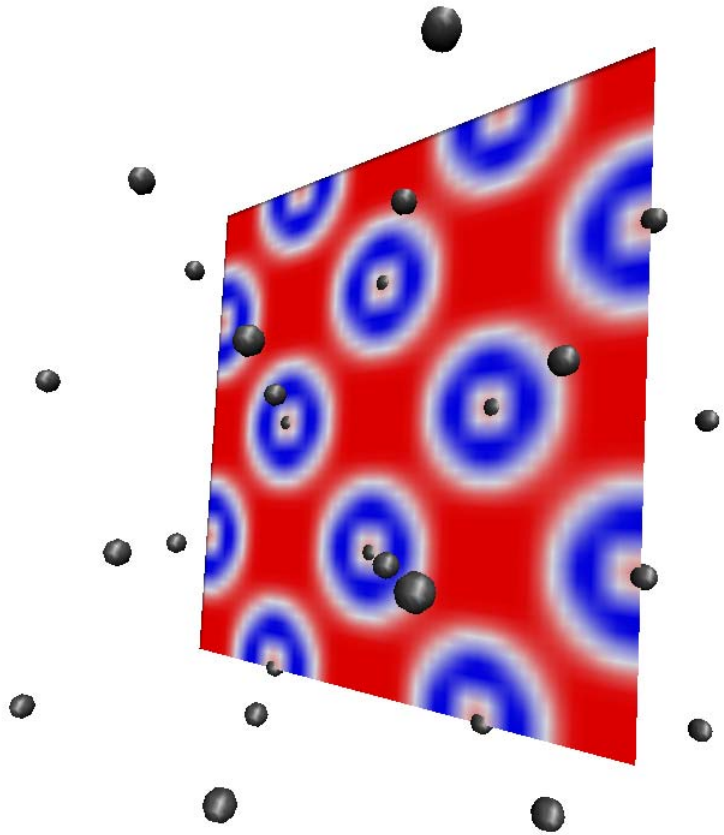
Mermin, 1965

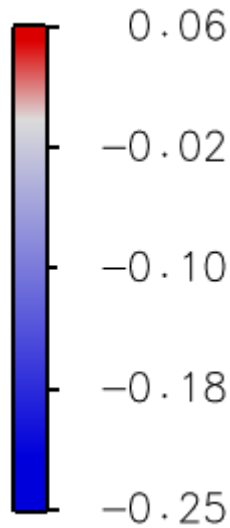
Gold: electron DOS (d- and s-electrons)



Redistribution of the electron density after the electron temperature increase

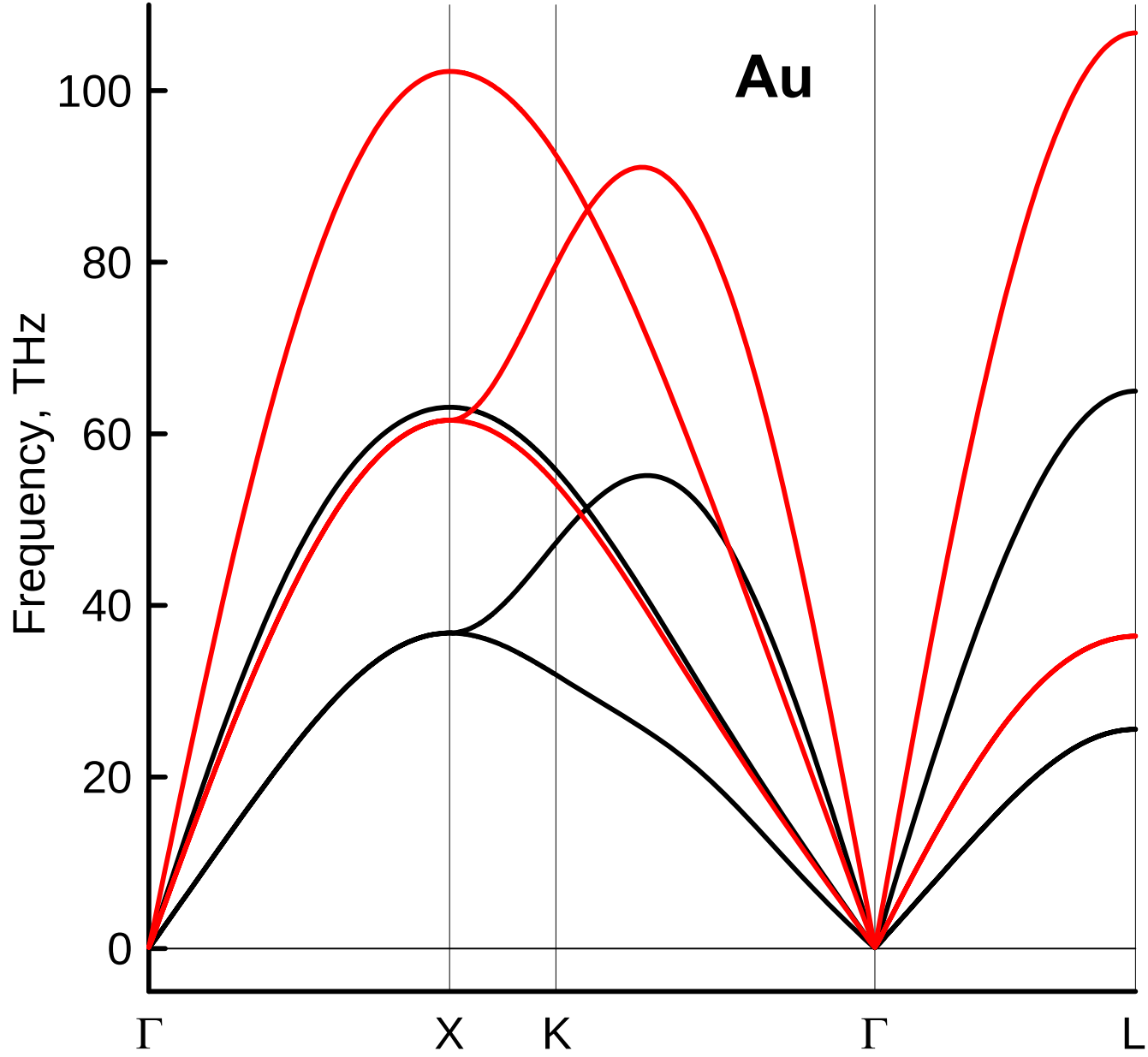
f.c.c. Au

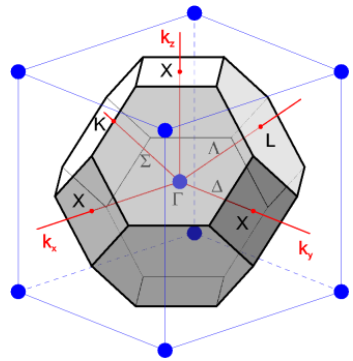




$$\Delta n_e(r) = n_e(r)\big|_{T_e=6eV} - n_e(r)\big|_{T_e=0.1eV}$$

FCC gold phonon spectrum after pulse irradiation

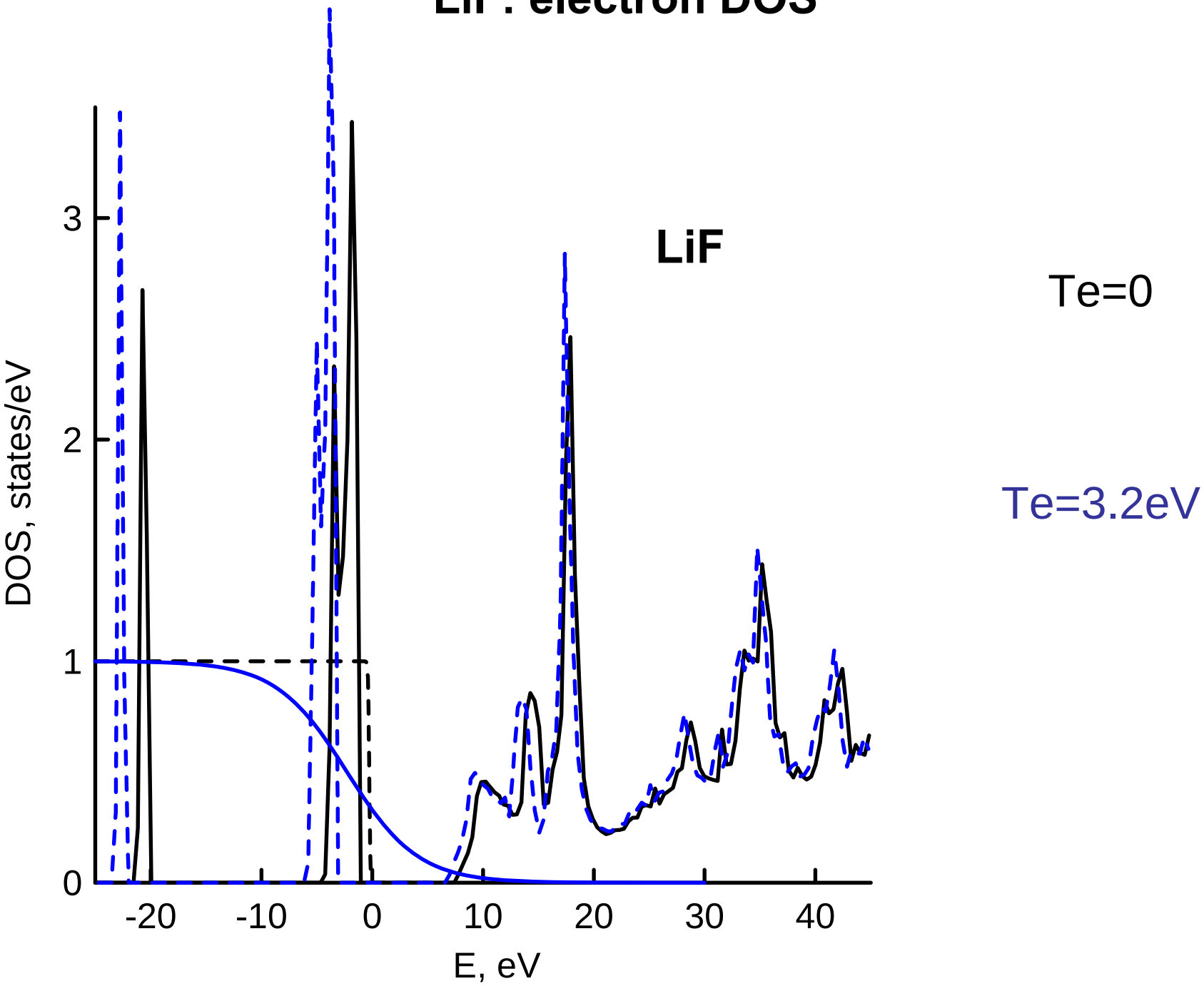




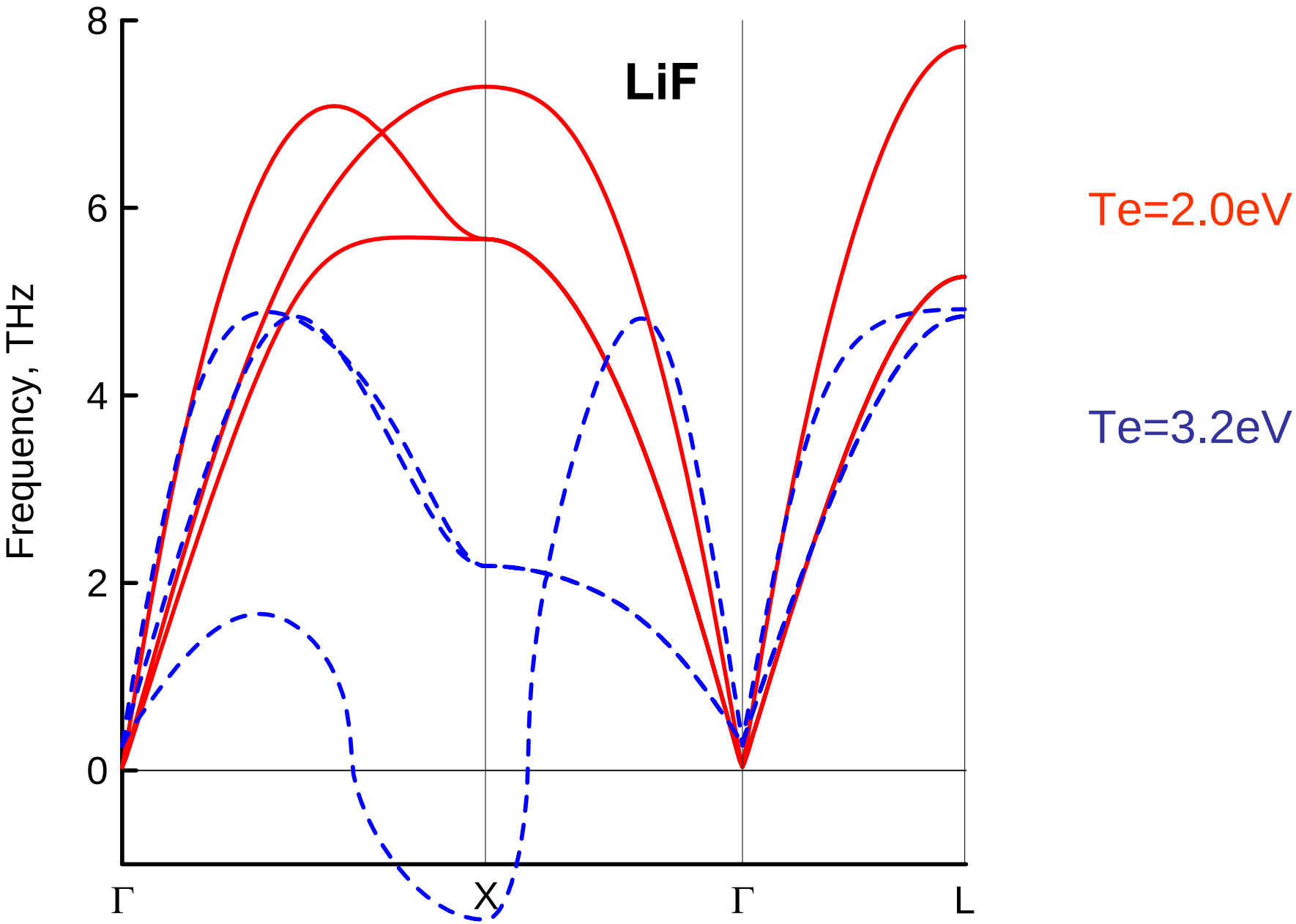
Te=0.1eV

Te=6.0eV

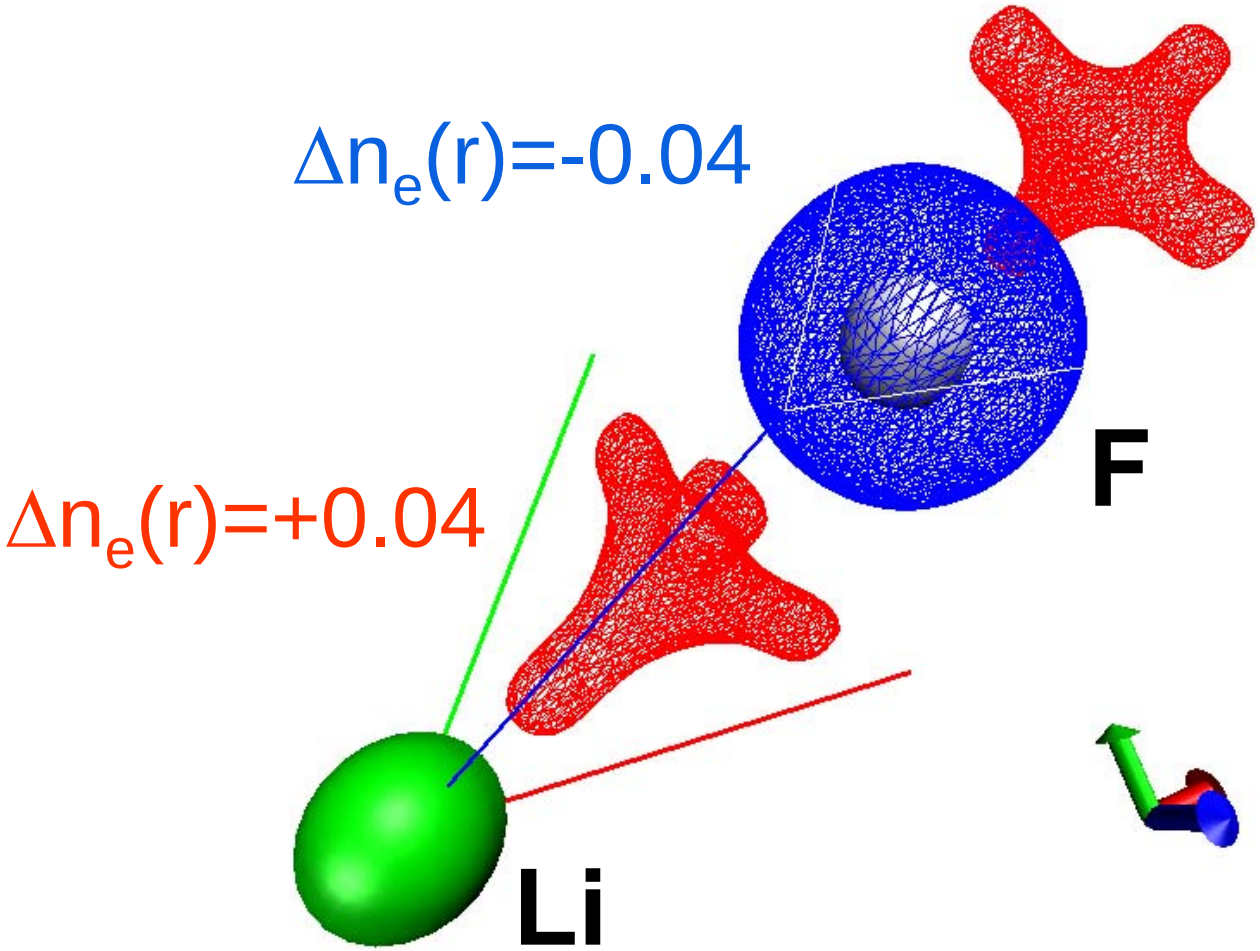
LiF: electron DOS



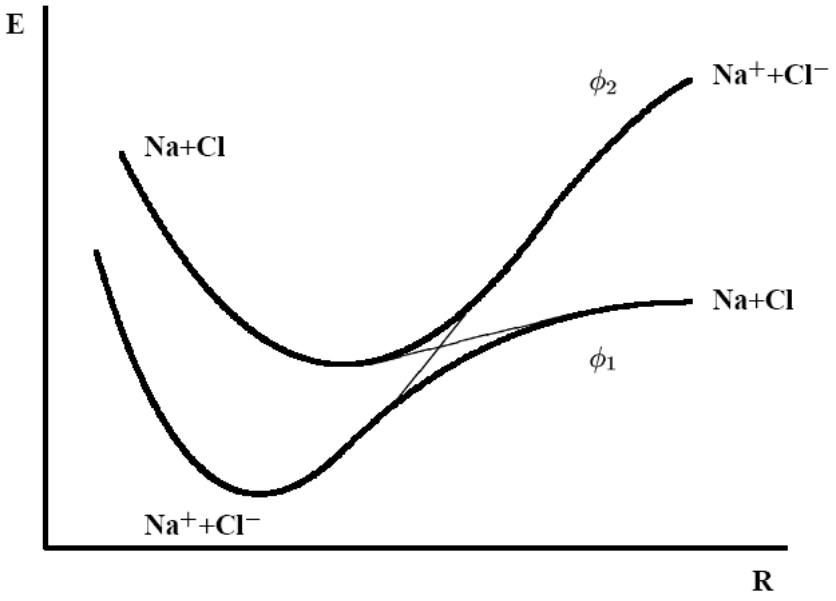
Фононный спектр LiF

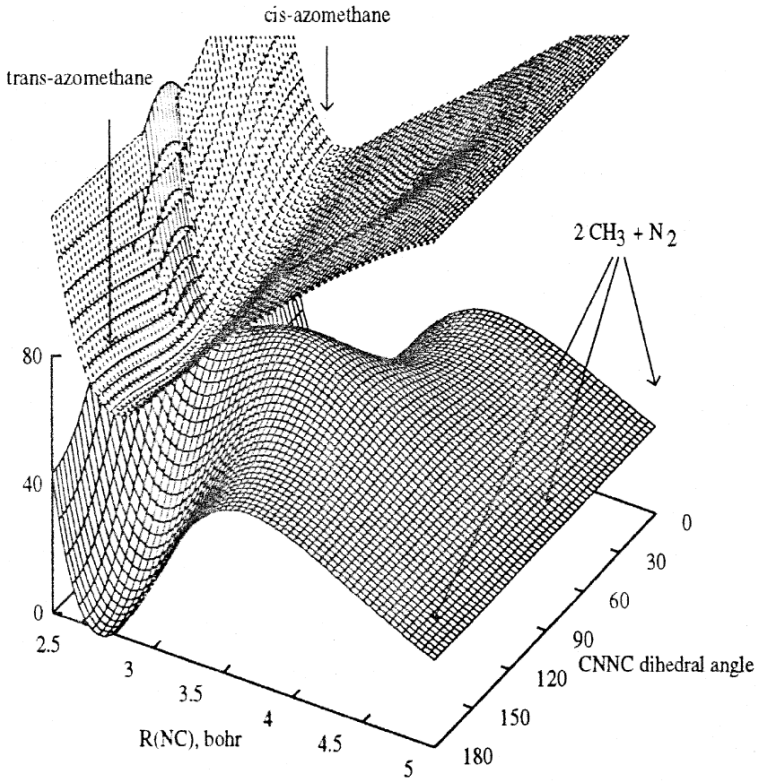


Перераспределение электронной плотности при нагреве электронной подсистемы в элементарной ячейка кристалла LiF



Non-adiabatic molecular dynamics





Calculations of the potential energy surfaces of excited states:

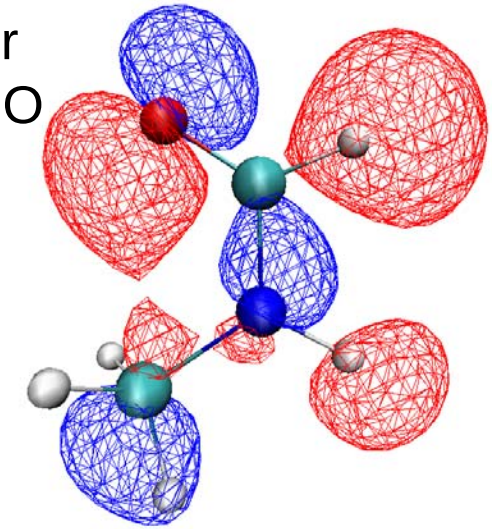
- First singlet excited state
  Restricted Open-shell Kohn-Sham (ROKS)
- Higher excited states in perspective
  Linear Response Time-Dependent Density Functional Theory (LR TDDFT)

Non-adiabatic transitions:

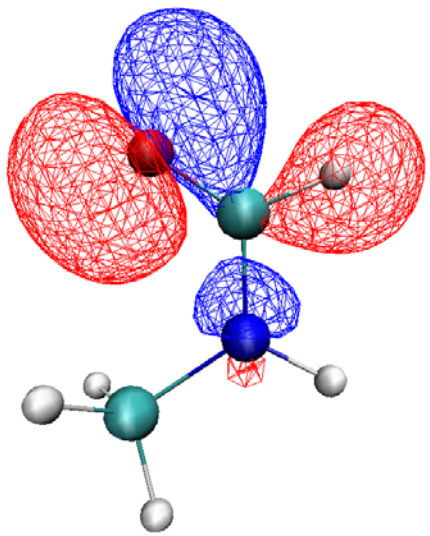
- Semi-classical Tully approach for surface hopping

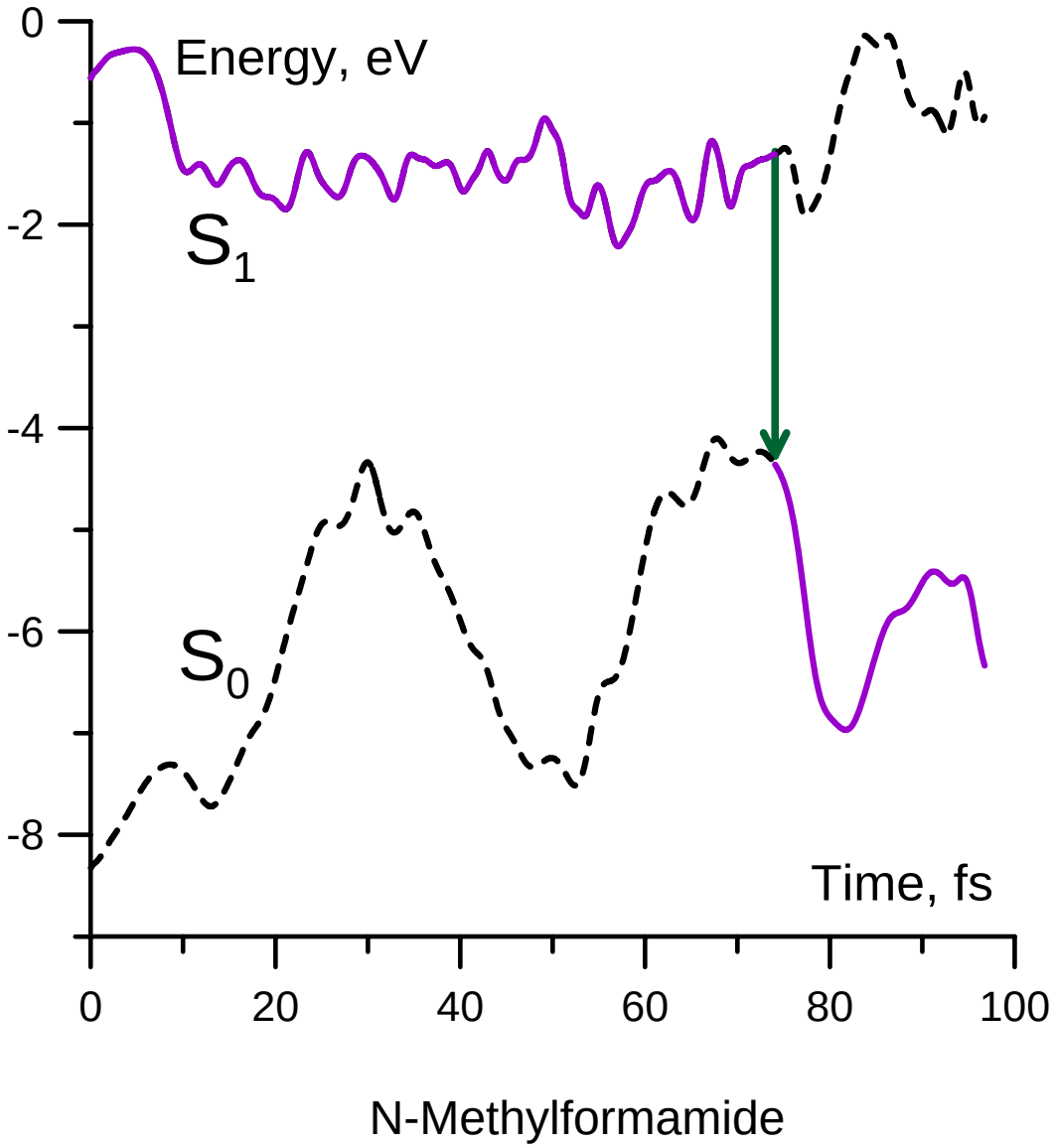
Single molecular-dynamics trajectory of the radiationless decay process of the N-methylformamide molecule

S_1:
lower
SOMO



S_0:
HOMO





Conclusions

The excitation of the electronic subsystem results in the loss of mechanical stability of the fcc LiF lattice that is manifested as an appearance of the soft acoustic phonon mode. The corresponding redistribution of the electronic density implies that the originally strongly ionic interatomic interaction becomes more of covalent character with the rise of electronic temperature.

DFT based approaches allows the description of the first excited singlet state. The S1 excitation energy for the N-methylformamide molecule is in good agreement with experimental data. The corresponding model of the radiationless decay is built using the semiclassical surface-hopping approach.