Tecniche di programmazione in chimica computazionale

Examples

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Dipole moment and center of charge in molecules

For any molecule/cluster the dipole moment $\vec{\mu}$:

$$\vec{\mu} = \sum_{\alpha} q_{\alpha} \vec{r}_{\alpha}$$

with α running on the atoms, q_{α} are the charges on atoms (Mulliken, Lowdin etc.) and $\vec{r}$ are the atomic coordinates

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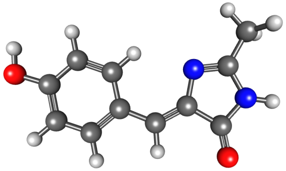
For charged systems, the center of charge $\vec{cc}$ is:

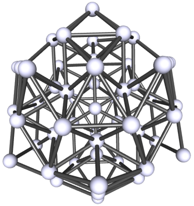
$$\vec{cc} = \frac{\sum_\alpha q_\alpha \vec{r}}{\sum_\alpha q_\alpha}$$

Dipole moment and center of charge in molecules

- Copy files from /home/tpcc/2023/CC to your work space
- HBDI (chromophore of GFP)



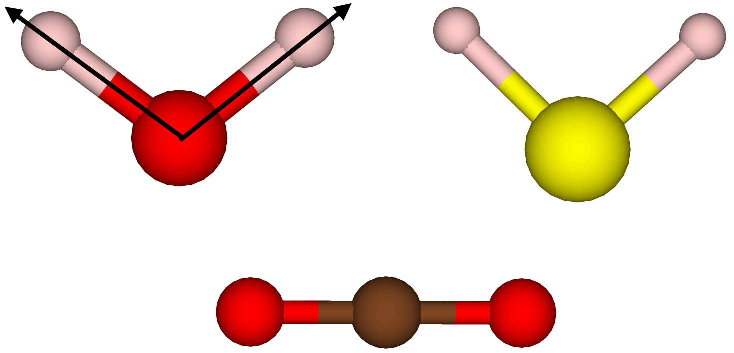
- Ag_{55}^{5+}



Exercises

- Compute center of charge and dipole of the two systems (cc_dip.f90)
- Compute center of mass of the two systems (com.f90)

Bond angle



Copy files from /home/tpcc/2023/bond to your work space
Compute bond angles (bondangle.f90)

Matrix diagonalization

- Square matrix **A** (*NxN*)

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- Matrix diagonalization: $\mathbf{A} = \mathbf{U}\ \mathbf{D}\ \mathbf{U}^{-1}$
- **D** =diag(a_1, a$_2$...a$_N$), a_i eigenvalues of **A**
- **U**: composed of eigenvectors of **A**

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- Example diag.f90

Matrix transpose

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- Example transpose.f90
- Transpose conjugated of a matrix: example tconjug.f90

Franck-Condon factors

Born-Oppenheimer approximation

$$\Psi_{e\nu}(q_e, q_N) = \psi_e(q_e; q_N)\chi_\nu^e(q_N)$$

Total dipole moment

$$\vec{\mu} = -e\sum_i \vec{r}_i + e\sum_N Z_N\vec{R}_N$$

Franck-Condon factors

$$\begin{aligned}\vec{\mu}^{e,e'}_{\nu,\nu'} &= \int \psi_{e'}(q_e;q_N)^* \chi^{e'}_{\nu'}(q_N)^* \left(-e\sum_i \vec{r}_i + e\sum_N Z_N \vec{R}_N\right) \times \\ &\times \psi_e(q_e;q_N)\chi^e_\nu(q_N) dq_e dq_N\end{aligned}$$

Franck-Condon factors

$$
\begin{aligned}
\vec{\mu}_{\nu,\nu'}^{e,e'} &= \int \psi_{e'}(q_e;q_N)^* \chi_{\nu'}^{e'}(q_N)^* \left(-e\sum_i \vec{r}_i + e\sum_N Z_N \vec{R}_N \right) \times \\
&\times \quad \psi_e(q_e;q_N)\chi_\nu^e(q_N) dq_e dq_N \\
&= -e\sum_i \int \psi_{e'}(q_e;q_N)^* \vec{r}_i \psi_e(q_e;q_N) dq_e \int \chi_{\nu'}^{e'}(q_N)^* \chi_\nu^e(q_N) dq_N \\
&+ \quad e\sum_N Z_N \overbrace{\int \psi_{e'}(q_e;q_N)^* \psi_e(q_e;q_N) dq_e}^{0} \int \chi_{\nu'}^{e'}(q_N)^* \vec{R}_N \chi_\nu^e(q_N) dq_N
\end{aligned}
$$

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$$
\begin{aligned}
\vec{\mu}^{e,e'}_{\nu,\nu'} &= \int \psi_{e'}(q_e;q_N)^* \chi^{e'}_{\nu'}(q_N)^* \left(-e\sum_i \vec{r}_i + e\sum_N Z_N \vec{R}_N\right) \times \\
&\times \quad \psi_e(q_e;q_N)\chi^e_\nu(q_N)dq_e dq_N \\
&= -e\sum_i \int \psi_{e'}(q_e;q_N)^* \vec{r}_i \psi_e(q_e;q_N)dq_e \int \chi^{e'}_{\nu'}(q_N)^* \chi^e_\nu(q_N)dq_N \\
&+ \quad e\sum_N Z_N \underbrace{\int \psi_{e'}(q_e;q_N)^* \psi_e(q_e;q_N)dq_e}_{0} \int \chi^{e'}_{\nu'}(q_N)^* \vec{R}_N \chi^e_\nu(q_N)dq_N \\
&= -e\sum_i \int \psi_{e'}(q_e;q_N)^* \vec{r}_i \psi_e(q_e;q_N)dq_e \int \chi^{e'}_{\nu'}(q_N)^* \chi^e_\nu(q_N)dq_N \\
&= \vec{\mu}^{e,e'} S^{e,e'}_{\nu,\nu'}
\end{aligned}
$$

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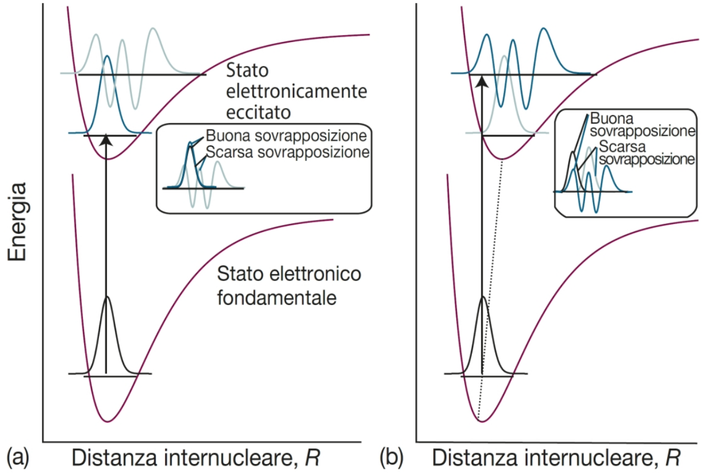
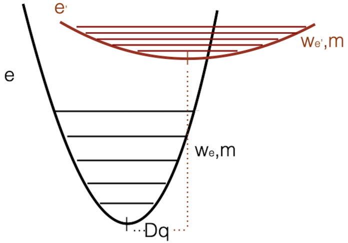
\vec{\mu}^{e,e'}_{\nu,\nu'} &= \int \psi_{e'}(q_e;q_N)^* \chi^{e'}_{\nu'}(q_N)^* \left(-e \sum_i \vec{r}_i + e \sum_N Z_N \vec{R}_N \right) \times \\
&\times \quad \psi_e(q_e;q_N) \chi^e_\nu(q_N) dq_e dq_N \\
&= -e \sum_i \int \psi_{e'}(q_e;q_N)^* \vec{r}_i \psi_e(q_e;q_N) dq_e \int \chi^{e'}_{\nu'}(q_N)^* \chi^e_\nu(q_N) dq_N \\
&+ \quad e \sum_N Z_N \cancelto{0}{\int \psi_{e'}(q_e;q_N)^* \psi_e(q_e;q_N) dq_e} \int \chi^{e'}_{\nu'}(q_N)^* \vec{R}_N \chi^e_\nu(q_N) dq_N \\
&= -e \sum_i \int \psi_{e'}(q_e;q_N)^* \vec{r}_i \psi_e(q_e;q_N) dq_e \int \chi^{e'}_{\nu'}(q_N)^* \chi^e_\nu(q_N) dq_N \\
&= \vec{\mu}^{e,e'} S^{e,e'}_{\nu,\nu'} \\
\mathrm{FC}^{e,e'}_{\nu,\nu'} &= |S^{e,e'}_{\nu,\nu'}|^2
\end{aligned}
$$

Franck-Condon factors


Energia
Stato elettronicamente eccitato
Buona sovrapposizione
Scarsa sovrapposizione
Stato elettronico fondamentale
(a)
Distanza internucleare, R
(b)
Distanza internucleare, R
Buona sovrapposizione
Scarsa sovrapposizione

Franck-Condon factors

- Harmonic oscillator: $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega\hat{x}^2$ $(\omega = \sqrt{\frac{k}{m}})$



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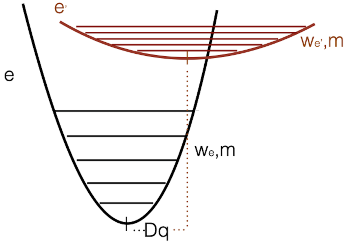

- Harmonic eigenfunctions

$$\chi_0^e(q_N) = \left(\frac{m\omega_e}{\pi}\right)^{1/4} \exp[-(m\omega_e)q_N^2/2]$$

$$\chi_1^e(q_N) = \sqrt{2}\left(\frac{m\omega_e}{\pi}\right)^{1/4} (\sqrt{m\omega_e} q_N) \exp[-(m\omega_e)q_N^2/2]$$

$$\chi_2^e(q_N) = \frac{1}{\sqrt{2}}\left(\frac{m\omega_e}{\pi}\right)^{1/4} \left[2m\omega_e q_N^2 - 1\right] \exp[-(m\omega_e)q_N^2/2]$$

Franck-Condon factors

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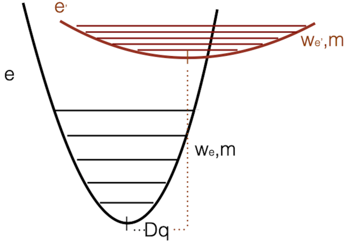

- Harmonic eigenfunctions

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\chi_1^e(q_N) &= \sqrt{2}\left(\frac{m\omega_e}{\pi}\right)^{1/4} (\sqrt{m\omega_e}q_N) \exp[-(m\omega_e)q_N^2/2] \\
\chi_2^e(q_N) &= \frac{1}{\sqrt{2}}\left(\frac{m\omega_e}{\pi}\right)^{1/4} \left[2m\omega_e q_N^2 - 1\right] \exp[-(m\omega_e)q_N^2/2]
\end{aligned}$$

- Example fc.f90

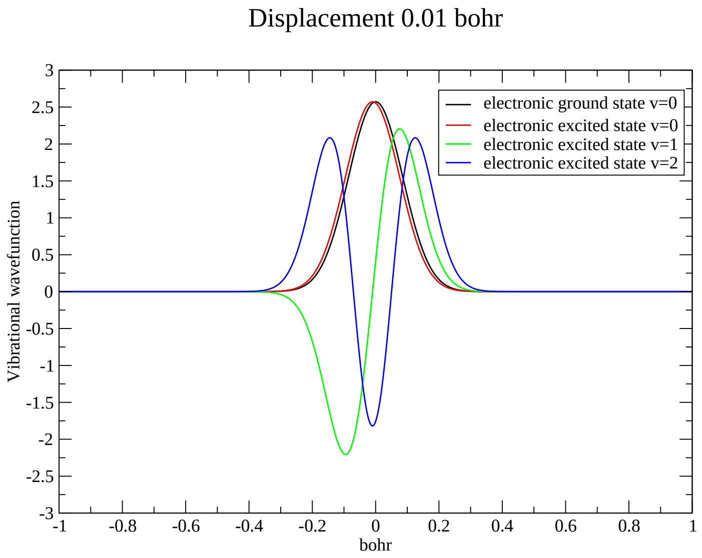
Franck-Condon factors

- Given the same frequencies and displacement, how the FC factor changes with the vibrational quantum number ν (0, 1 or 2) of the electronic excited state?

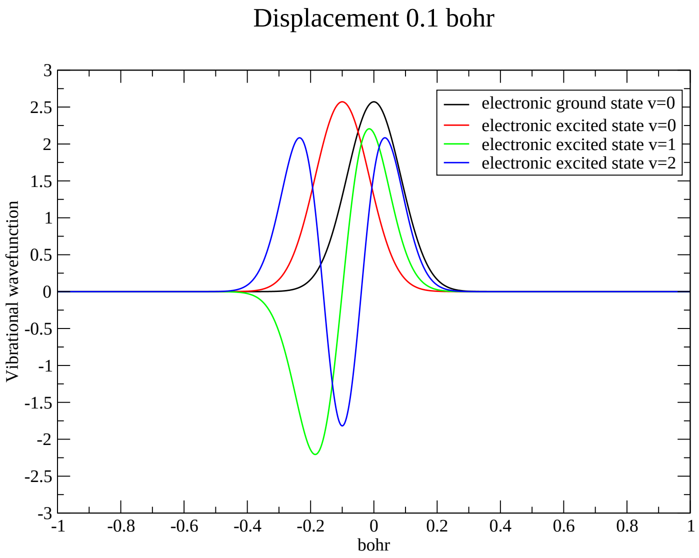
Franck-Condon factors

- Given the same frequencies and displacement, how the FC factor changes with the vibrational quantum number ν (0, 1 or 2) of the electronic excited state?
- Given the same frequencies, how the FC factor changes with the displacement Δq (for a chosen ν)?

"Pseudo" Br_2 results



“Pseudo” Br_2 results



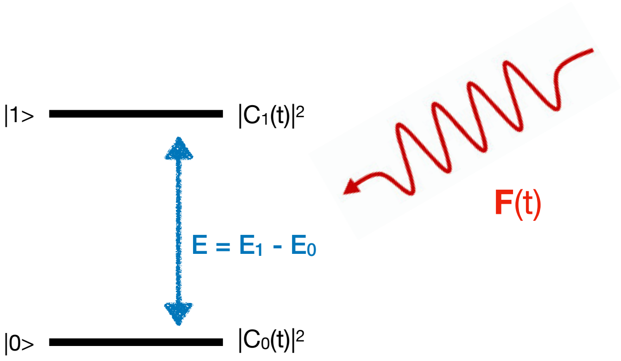
Simulating real-time dynamics

- Light-matter interaction, simulating time-resolved spectroscopies

Simulating real-time dynamics

- Light-matter interaction, simulating time-resolved spectroscopies
- Two-level system

$$|\Psi(t)\rangle = C_0(t)|0\rangle + C_1(t)|1\rangle$$



Simulating real-time dynamics

Time-dependent Schrödinger equation (TDSE)

$$\begin{aligned}
i\frac{\partial|\Psi(t)\rangle}{\partial t} &= \hat{H}(t)|\Psi(t)\rangle \\
\hat{H}(t) &= \hat{H}_0 - \hat{\mu}\cdot\mathbf{F}(t) \\
i\frac{\partial C_0(t)}{\partial t} &= C_0(t)E_0 - \mathbf{F}(t)\left(\langle 0|\hat{\mu}|0\rangle + \langle 0|\hat{\mu}|1\rangle\right) \\
i\frac{\partial C_1(t)}{\partial t} &= C_1(t)E_1 - \mathbf{F}(t)\left(\langle 1|\hat{\mu}|1\rangle + \langle 1|\hat{\mu}|0\rangle\right) \\
\mathbf{F}(t) &= \mathbf{F}_{\max}\exp\left(-\frac{(t-t_{mid})^2}{2\sigma^2}\right)\sin(\omega t)
\end{aligned}$$

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- input file, ci_ini.inp ci_energy.inp and ci_mut.inp in /home/tpcc/2023/WaveT
  - input: parameters for propagating TDSE
  - ci_ini.inp: initial populations
  - ci_energy.inp contains excitation energy *E*
  - ci_mut.inp contains dipoles and transition dipoles

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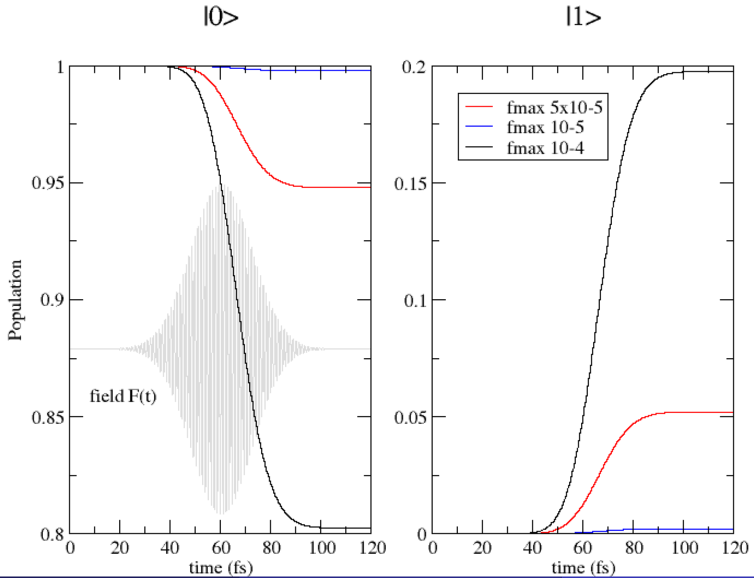
    - ci_energy.inp contains excitation energy *E*
    - ci_mut.inp contains dipoles and transition dipoles
- To run the simulation, copy the files in your working directory, and type ./wavet.x < input > output
- Many files are produced, focus on c_t_1.dat
    - c_t_1.dat: time evolution of $|C_0(t)|^2$ and $|C_1(t)|^2$
      step time Population $|0\rangle, |1\rangle$

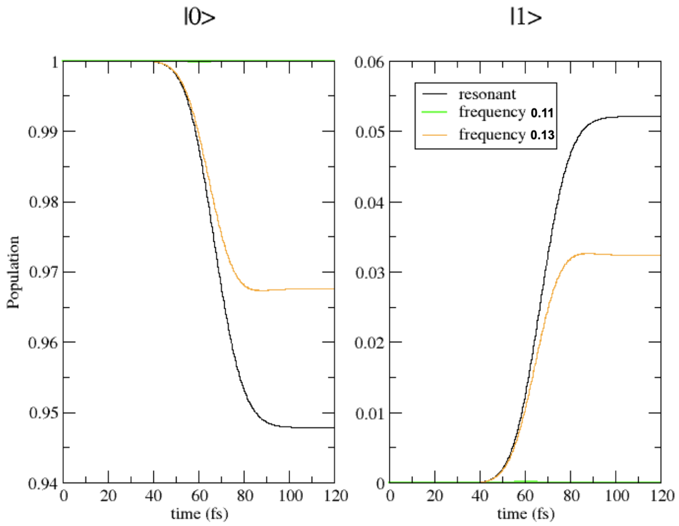
Simulating real-time dynamics

1. Check the last value of $|0\rangle$ and $|1\rangle$ populations by changing the amplitude of the pulse (fmax = 10^{-4}, 5x10^{-5}, 10^{-5}, resonant frequency)
2. Check the last value of $|0\rangle$ and $|1\rangle$ populations by changing the frequency of the pulse (fmax= 5x10^{-5}, omega=0.11, 0.13 and resonant)

Simulating real-time dynamics



Simulating real-time dynamics


|0>
|1>
Population
time (fs)
resonant
frequency 0.11
frequency 0.13