# PROGRAMMING FOR COMPUTATIONAL CHEMISTRY

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

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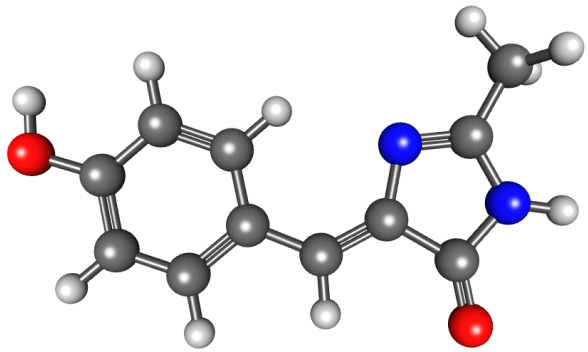
For charged systems, the center of charge $\vec{cc}$ is:

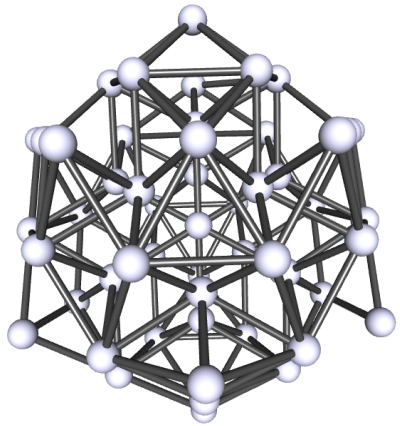
$$\vec{cc} = \frac{\sum_{\alpha} q_{\alpha} \vec{r}}{\sum_{\alpha} q_{\alpha}}$$

# Dipole moment and center of charge in molecules

- Copy files from /home/pcc/2025/CC to your work space
- HBDI (chromophore of GFP)



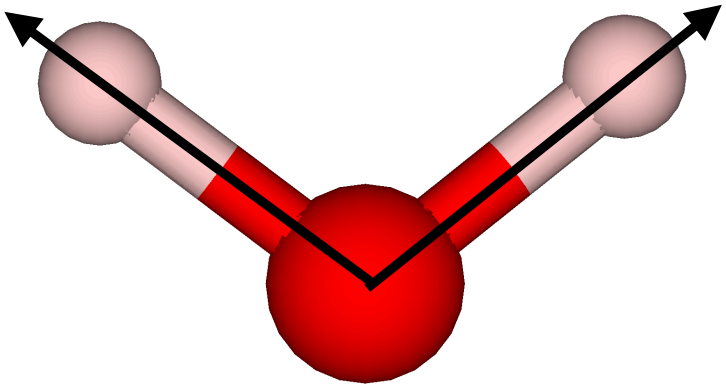
- $Ag_{55}^{5+}$

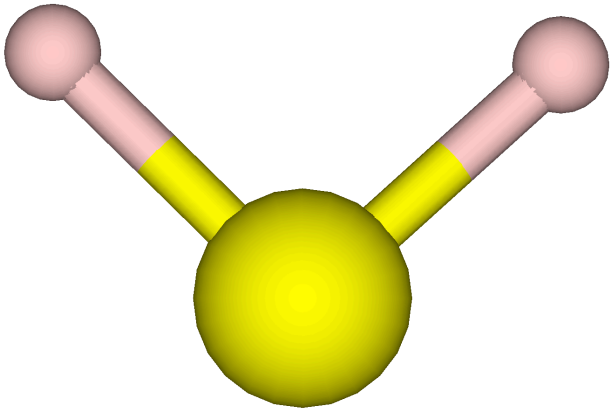


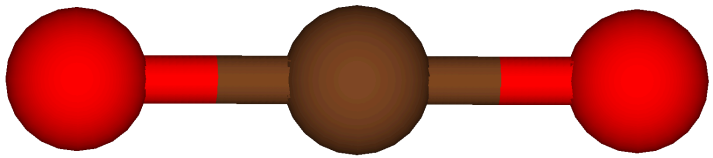
# Exercises

- 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/pcc/2025/CC to your work space
Compute bond angles (bondangle.f90)

# Matrix diagonalization

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

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- **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

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

# Franck-Condon factors

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

$\to 0$

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&+ \quad e\sum_N Z_N \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 \qquad \to 0 \\
&= -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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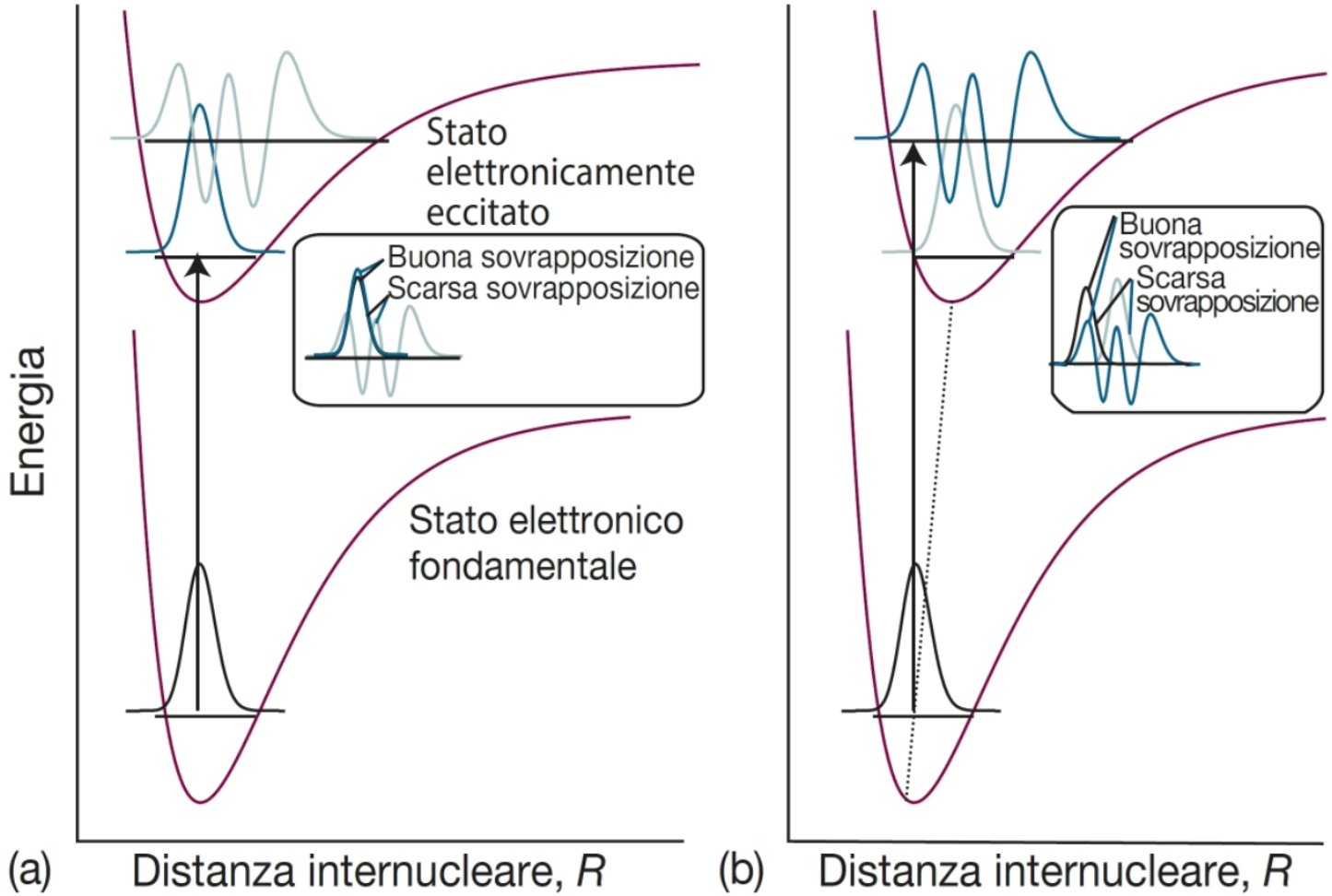
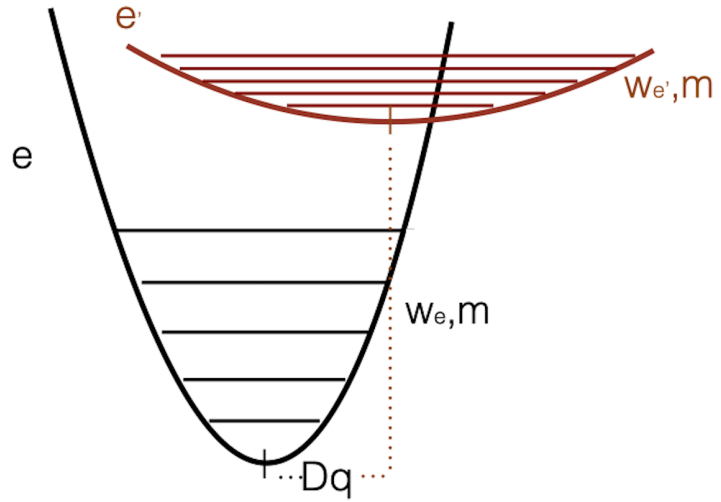
&= \vec{\mu}^{e,e'} S^{e,e'}_{\nu,\nu'} \\
\mathrm{FC}^{e,e'}_{\nu,\nu'} &= |S^{e,e'}_{\nu,\nu'}|^2
\end{aligned}
$$

# Franck-Condon factors



# 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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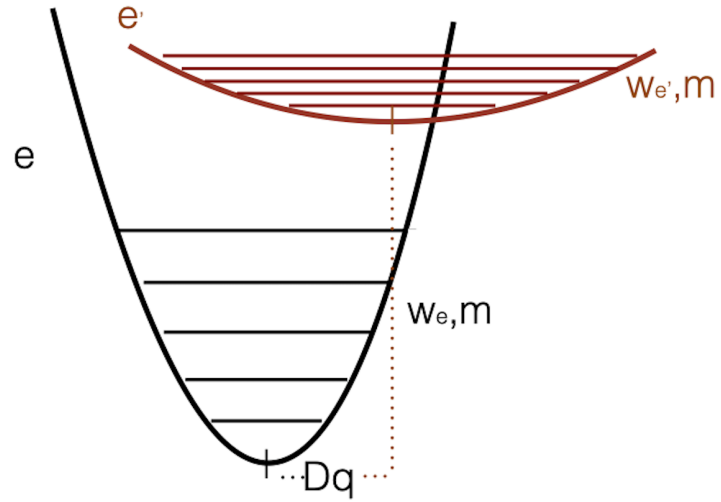


- Harmonic eigenfunctions

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

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

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

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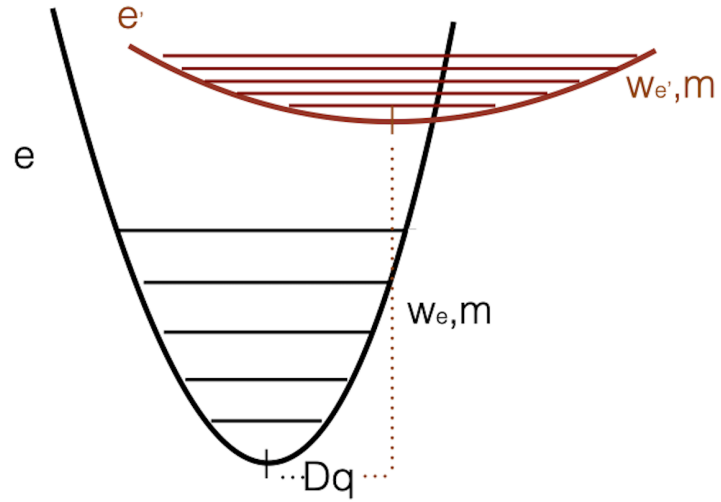


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- Example fc.f90

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

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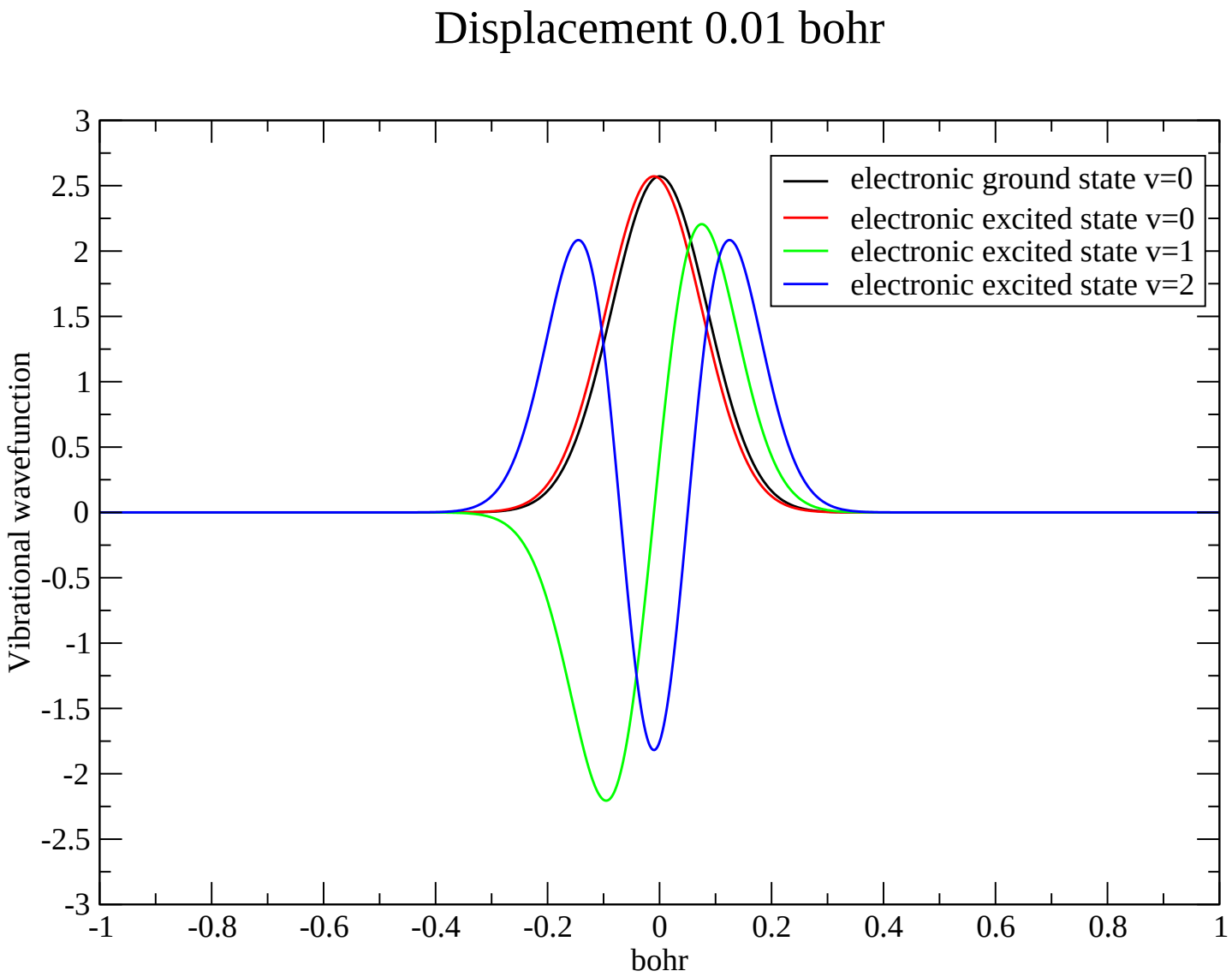
- Given the same frequencies and displacement, how the FC factor changes with the vibrational quantum number $\nu$ (0, 1 or 2) of the electronic excited state?
- Given the same frequencies, how the FC factor changes with the displacement $\Delta q$ (for a chosen $\nu$ )?

# "Pseudo" $Br_2$ results



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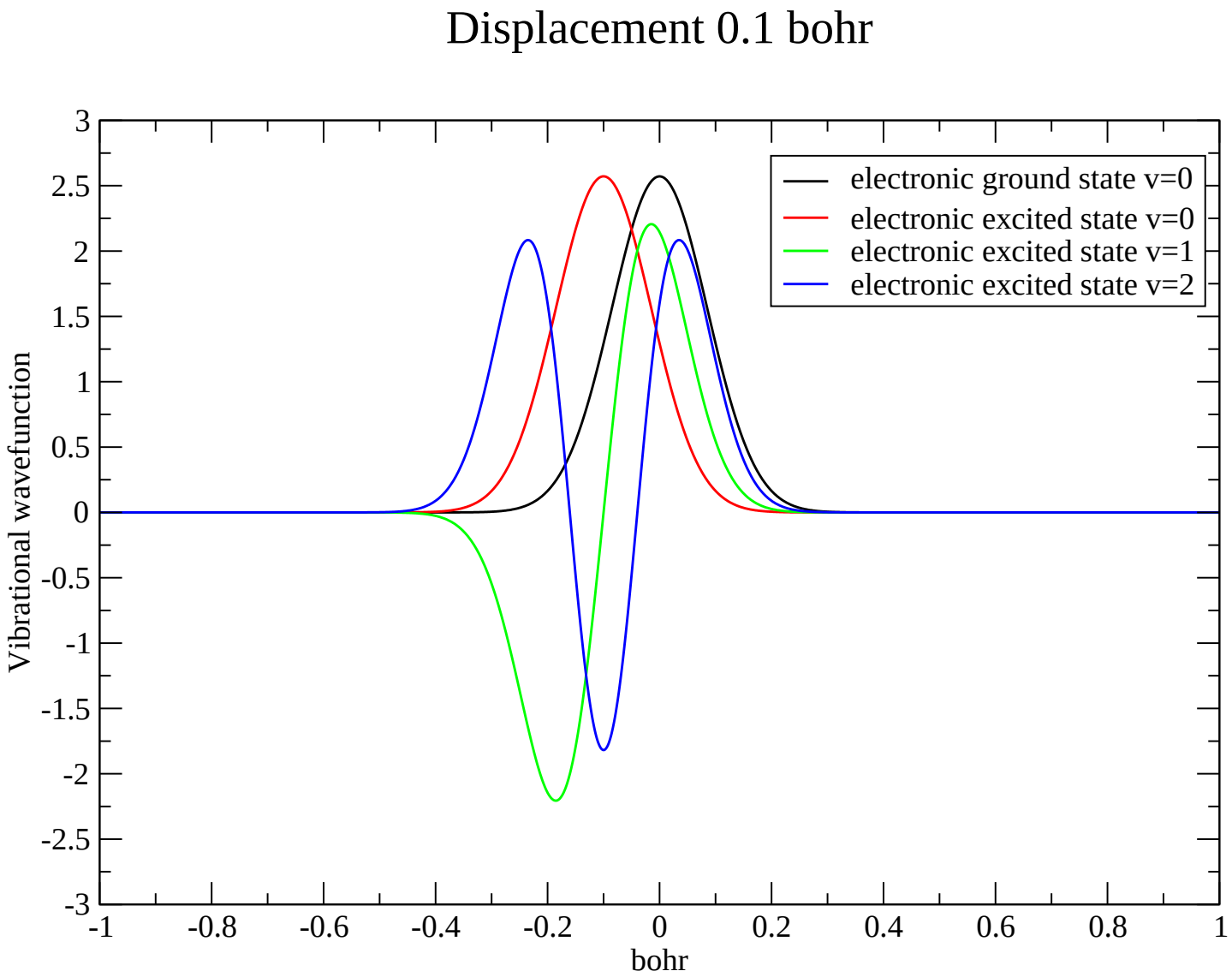

# Simulating real-time dynamics

- Light-matter interaction, simulating time-resolved spectroscopies

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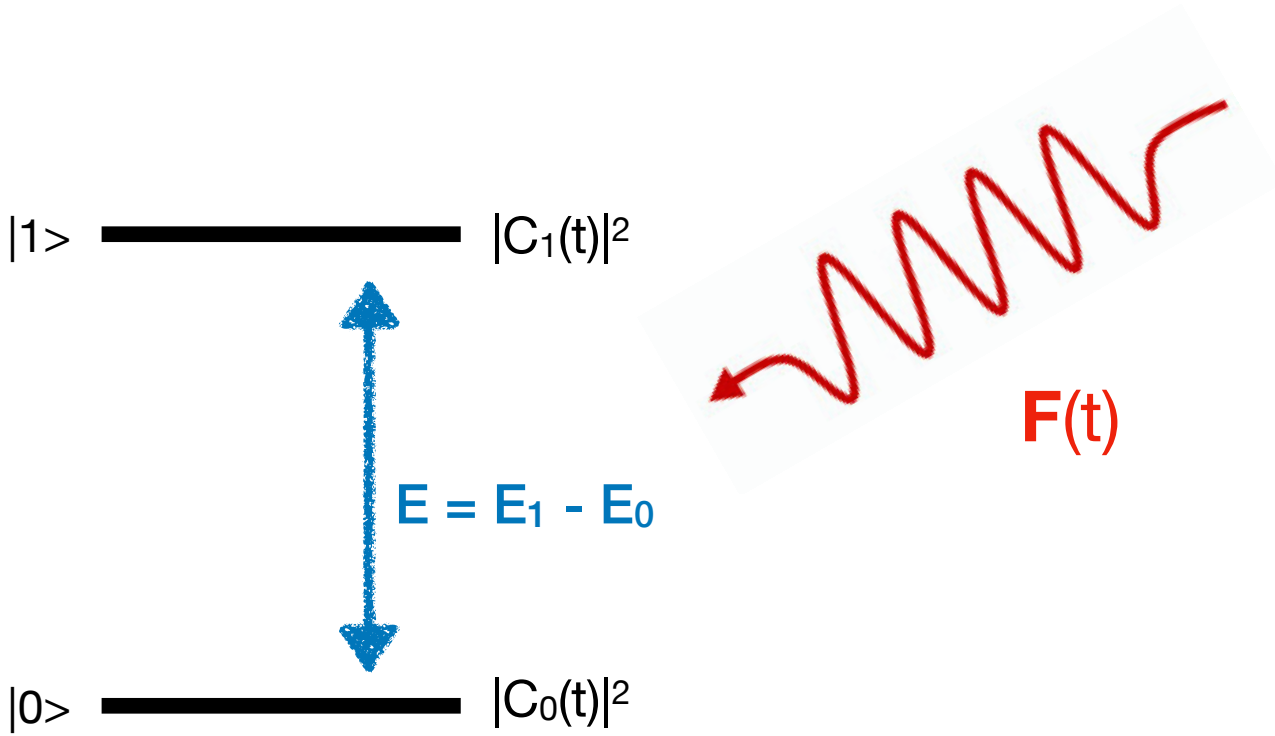
- Light-matter interaction, simulating time-resolved spectroscopies
- Two-level system

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



# 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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- Executable wavet.x in /home/pcc/2025/WaveT

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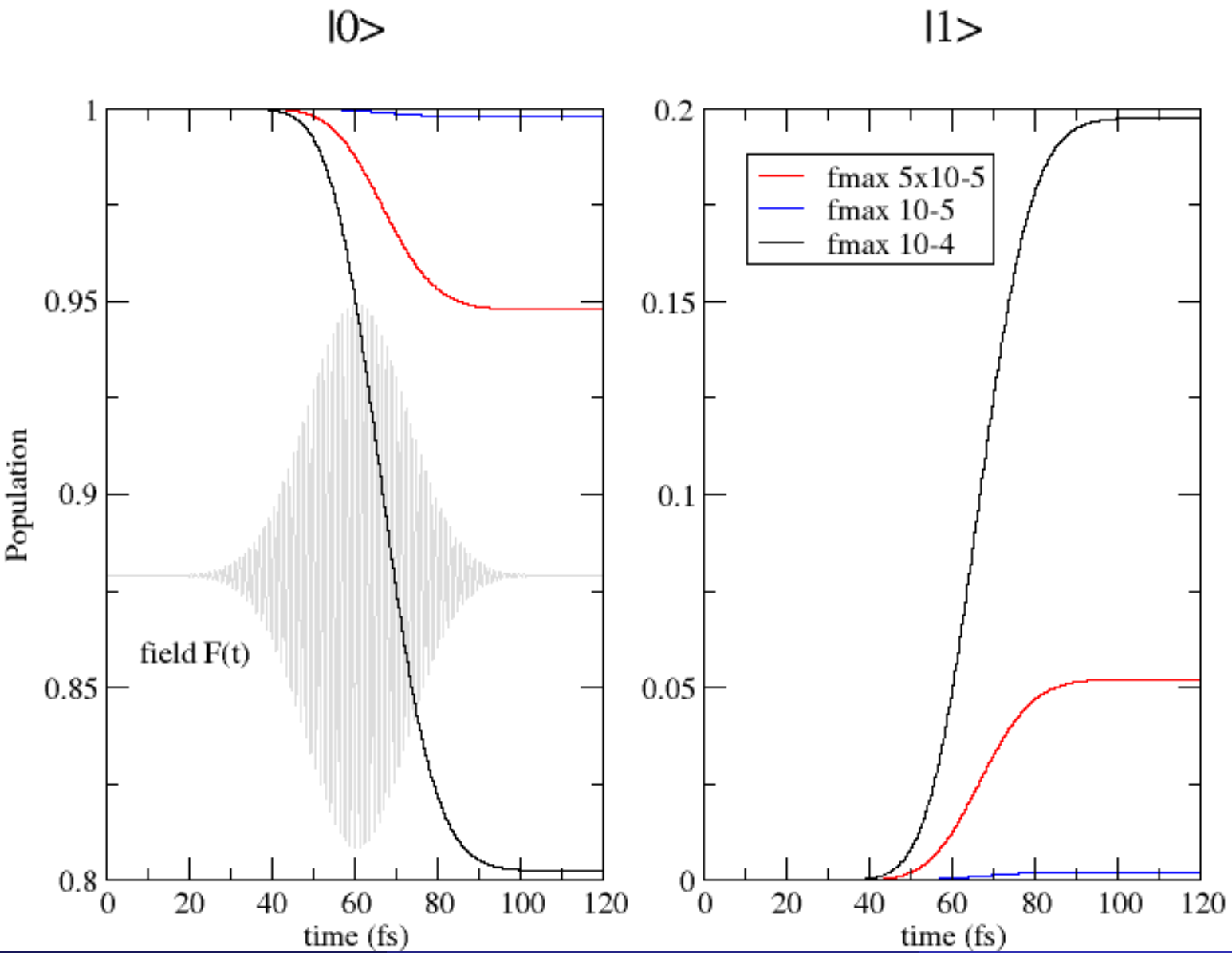
- To run the simulation, copy the files in your working directory, and type ./wavet.x < input > output
- Many files are produced, focus on c_t_1.dat
  - c_t_1.dat: time evolution of $|C_0(t)|^2$ and $|C_1(t)|^2$ *step time Population* $|0\rangle$, $|1\rangle$

# Simulating real-time dynamics

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

# Simulating real-time dynamics



# Simulating real-time dynamics