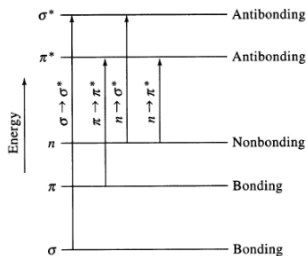


Calculations of electronic excited states

Electronic excited states

- Uses electromagnetic radiation in UV and visible region
- UV light: ~190 to 400 nm
- VIS light: 400 to 700 nm
- Excitations in valence electronic structure
- $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$...
- X-RAYS: High-energy irradiations - excitation of core electrons

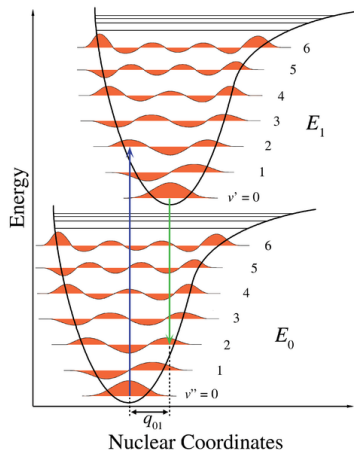


Selection rules

- “Allowed” and “forbidden” transitions
- Nonzero transition dipole moment:

$$\mu_i = \int \Psi_{final} \hat{\mu}_i \Psi_{initial} d\tau \neq 0 \quad (1)$$

- Intensities according to size of TD
- Blue - vertical excitation
- Green - emission



Linear Response Time-dependent DFT

- Vertical excitation energies vs adiabatic excitation energies
- Energy quantum absorbed by molecule
- The time-dependent Schrödinger equation:

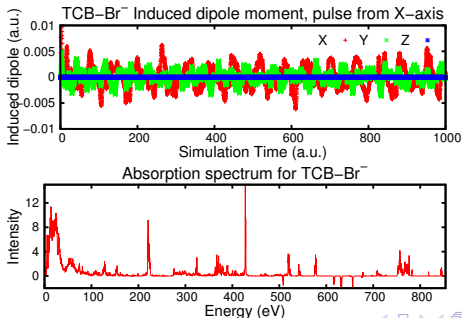
$$i \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H}(\mathbf{r}, t) \Psi(\mathbf{r}, t) \quad (2)$$

$$\hat{H} = \hat{T}(\mathbf{r}) + \hat{W}(\mathbf{r}) + \hat{V}_{ext}(\mathbf{r}, t) \quad (3)$$

- Check for low-lying excited states using TDDFT
- Use DFT with caution for molecules with ES lower than ~ 1.5 eV
- General problem - Functionals are fitted to GS not ES

Real Time TDDFT

- Alternative approach to investigate excited states
- Free evolution of excited wavefunction irradiated by pulse
- Fourier transformation of induced dipole moments
- (Compare with FT-NMR, FT-IR, FT-Raman)
- All excitations in a single simulation (valence to core)
- Computationally EXTREMELY demanding method



- <http://rel-qchem.sav.sk/>
- **Relativistic Spectroscopy**
- Developed at Slovakian Academy of Science and University of Tromsø
- Up to four-component (fully relativistic) approach
- Calculation of NMR, EPR and electronic excitations
- Under heavy development - Cutting edge methods
- No proper manual.

Simulation setup

- In most general case 3 independent simulations needed
- Irradiation from x-, y-, z- directions
- For symmetric systems can be reduced to
 - 2 - $C_{\infty v}$, $D_{\infty d}$
 - 1 - spherical
- Setup of calculation:
 - EOM_SOLVER: propagation scheme (always use MAGNUS)
 - ITERATIONS: SCF convergence threshold followed by maximum allowed microiterations per step
 - TIME: Time step size (in a.u.) and number of steps
 - FIELD: DELTA (i.e. Dirac delta pulse) and field size
 - FIELD_DIRECTION: x- y- and z- component of the field vector
 - CHECKPOINT: save information to WF every N steps
 - ANALYSIS_ORBITALS: virtual and occupied range of orbitals

Important remarks

- Maximum microiterations between steps: 6 (3-4 is fine)
- 1000 a.u. of time from each independent direction
- Typically time steps around 0.1 a.u.
- Higher energy excitations require lower timestep - higher frequency oscillations
- Fiddle a bit with values to obtain stable simulation
- Induced dipole should have at least 4 significant digits with respect to SCF during propagation
- Orbital analysis must be set in advance (cannot be recovered after simulation)
- Energy must be conserved

ReSpect: K-edge spectrum of Ne

- Start with the template distributed in IS
- This is a minimal input for ReSpect SCF
- TDSCF section is almost ready, just commented out (# initiates a comment line)
- Go to the manual page and fill in the calculation details
- Use NR/B3LYP/aug-ucc-pvtz method
- Run SCF first, then select the orbitals you wish to include for the analysis
- K-edge means excitations from 1st period orbital
- Four numbers define the orbital contributions in output:
 $VIR_1 VIR_N OCC_1 OCC_N$

Running ReSpect & Analysing Results

- Respect is within modules
- Usage:
 - `$ respect --help # perform ReSpect calculation`
 - `$ spectrum.py --help # Fourier Transformation of data`
 - `$./analysis_matrix_block.py --help # Orbital analysis`
- Results:
 - `input.out # general output of calculation`
 - `input_spectrum.out # Spectrum itself (plot 2:6 for energy in eV)`
 - `input_peaks.out # Lists only peaks`
 - `inputENERGY_TMatrix.out # Matrix of orbital excitations`

Gaussian: K-edge spectrum of Ne

- Keyword “TD”
- Calculate 200 singlet excited states
- Use same basis set as in ReSpect
- Basis set directory:
/software/ncbr/softrepo/ncbr/respect/4.0.0-beta.4+Sep15/x86_64/para/BAS/mdks_gaussian_format/

Experimental spectrum of the K-edge of Neon

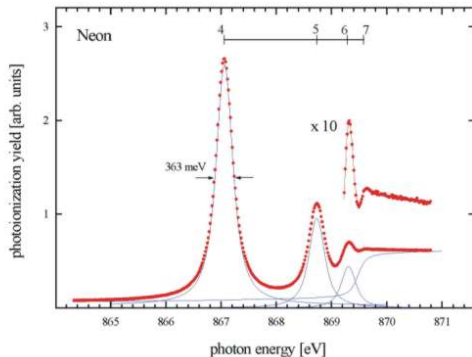


Figure: K-edge spectrum of Neon.¹

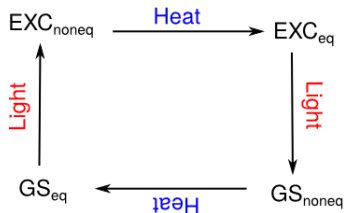
¹<http://www.bessy.de/rglab/beamline3.html#Neon>

Colors of dihalogens

- Calculate the vertical excitation energies of Br_2
- Calculate the emission energy from the “allowed” state
- Use PBE1PBE/6-311+G(2d) method

Thermodynamic cycle

- GS - Ground state WF
- EXC - Excited state WF
- eq - equilibrium geometry
- noneq - nonequilibrium geometry



- Calculate first three excited triplet and singlet states
td=(nstates=3,50-50)
- Select the allowed states and optimize the first excited one:
- opt=readfc td=(nstates=3,{singlets/triplets},root=1,read)
- Excitations/emissions including **solvent effects** are described at Gaussian SCRF manual page

$$\Delta E = \frac{hc}{\lambda} \quad (4)$$