



Abinit Workshop
code development and results
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Time-dependent DFT, Casida's approach : implementation of spin polarized collinear systems formalism in ABINIT



Implementation by Sangalli Davide,
during his work for the Master's Thesis.

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Plan

- Casida's formalism for TD-DFT
- External potential and spin selection rules for unpolarized and spin polarized systems
- New implementation in ABINIT and test on N₂
- Study of BeH molecule

References :

M.E. Casida, in *Recent Developments and Applications of Modern Density Functional Theory*, edited by J.M. Seminario (Elsevier Science, Amsterdam), p. 391 (1996).

M.E. Casida, *J. Chem. Phys.* 122, 054111 (2005)

M.E. Casida, *J. molec. struct.* 527, 229-244 (2000)

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Casida's approach and approximations..

1 – Project the TDDFT Dyson's equation for the response function

$$\chi^{-1}(\omega) = \chi_0^{-1}(\omega) + K_H + K_{xc}(\omega)$$

in the transition space: $\Phi_{ij\sigma}(\vec{r}) = \varphi_{i\sigma}^{KS}(\vec{r}) \varphi_{j\sigma}^{KS*}(\vec{r})$



$$\chi_{ij\sigma, hk\tau}^{-1}(\omega) = (\chi_{ij\sigma, hk\tau}^0)^{-1}(\omega) + (K_H)_{ij\sigma, hk\tau} + (K_{xc})_{ij\sigma, hk\tau}(\omega)$$

and then reorder the basis set in order to have electron-hole and hole-electron pairs

2 – Finally we get the polarizability from the response function;

$$\alpha_{xz}(\omega) = \sum_{ij\sigma, hk\tau} x_{ij\sigma} \chi_{ij\sigma, hk\tau}(\omega) z_{hk\tau}$$

We know that the poles of polarizability are the spectrum of the system from its many-body representation



$$\alpha = \sum_I \frac{f_I}{\omega_I^2 - \omega^2}$$

So we have to find the poles of our polarizability, i.e. to diagonalise the following matrix

$$\Omega_{ij\sigma, hk\tau}(\omega) = \delta_{\sigma, \tau} \delta_{i, h} \delta_{j, k} (\epsilon_{k\tau} - \epsilon_{h\tau})^2 + 2 \sqrt{(f_{i\sigma} - f_{j\sigma})(\epsilon_{j\sigma} - \epsilon_{i\sigma})} K_{ij\sigma, hk\tau}^{Hxc}(\omega) \sqrt{(f_{h\tau} - f_{k\tau})(\epsilon_{k\tau} - \epsilon_{h\tau})}$$

Spin symmetry

We will work within the adiabatic approximation: $K(\omega) \simeq K(0)$

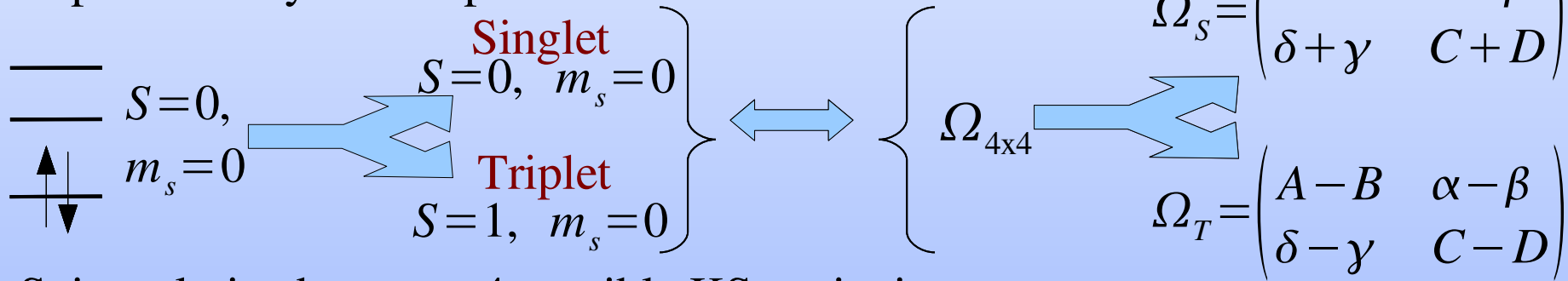
We have the following external potential with selection rules:

$$\delta \hat{V}(t) = \sum_{\sigma} \int d^3 \vec{x} (V_{\uparrow}(\vec{x}, t) \hat{n}_{\uparrow}(\vec{x}) + V_{\downarrow}(\vec{x}, t) \hat{n}_{\downarrow}(\vec{x}))$$

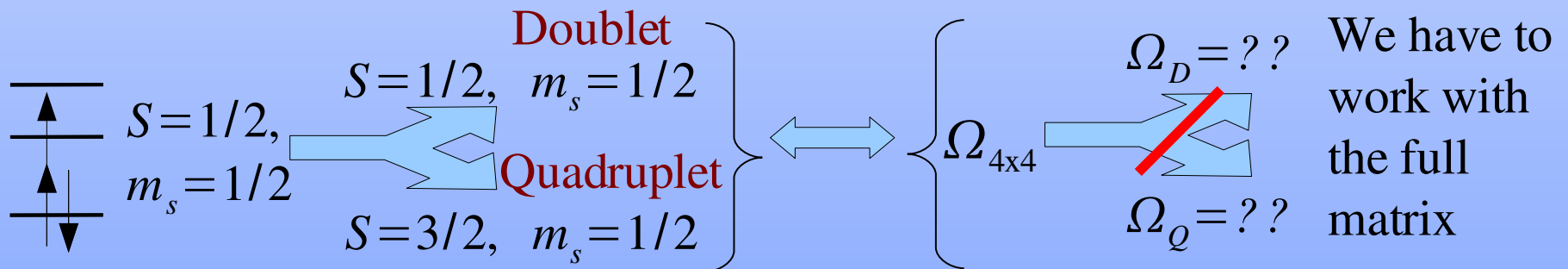
$$= \int d^3 \vec{x} (V(\vec{x}, t) \hat{n}(\vec{x}) + B_z(\vec{x}, t) \hat{m}_z(\vec{x}))$$

\longleftrightarrow $\delta S = 0, 1$
 $\delta m_s = 0$

Unpolarized system. 4 possible KS excitations

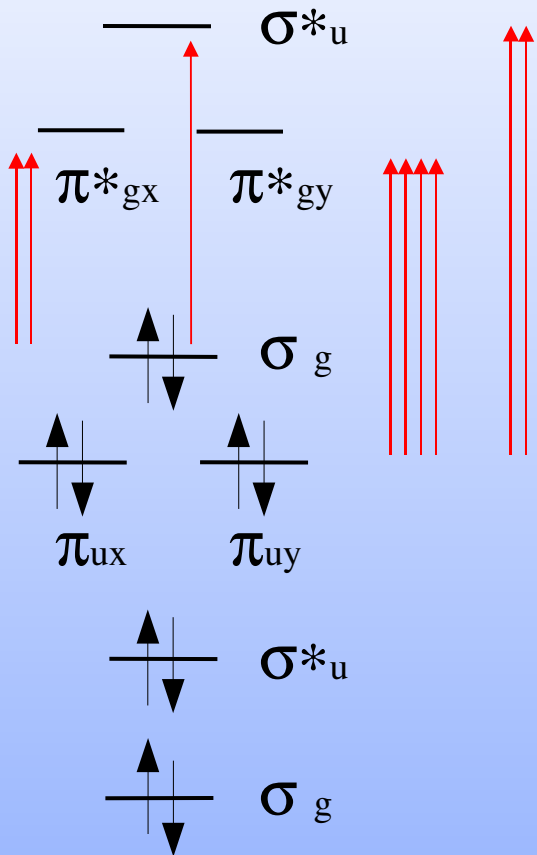


Spin-polarized system. 4 possible KS excitations



Spin-symmetry has been destroyed by the adiabatic approximation

Nitrogen molecule : TDDFT



Values for: ecut 45 Hartree, nband 30, acell 12 11 11 Bohr

	Kohn-Sham	TDDFT, nsppol==1		nsppol==2
		triplet	singlet	
Π_u	10.92 eV	10.46 eV	10.90 eV	10.90 eV
Σ_u	9.78 eV	9.78 eV (ionized)		10.32 eV
Δ_u		8.90 eV	10.32 eV	9.89 eV
Σ_u		7.87 eV	9.78 eV	9.78 eV
Σ_g	9.52 eV	9.32 eV	9.89 eV	9.36 eV
Π_g	8.39 eV	7.75 eV	9.36 eV	9.32 eV
				8.90 eV
				7.87 eV
				7.75 eV

Ok. The results are the same.

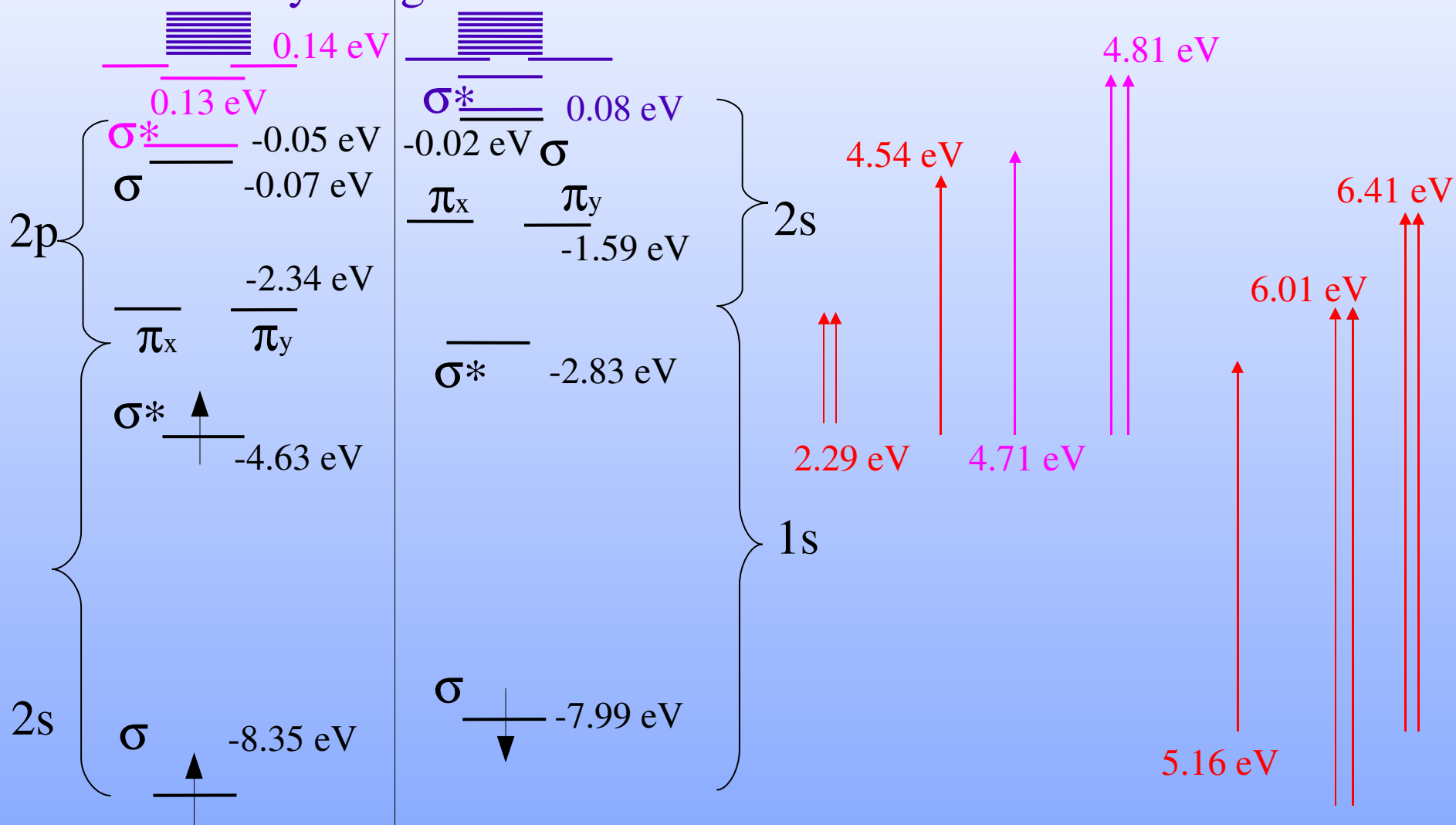
BeH molecule: easiest polarized molecule

spin up

spin down

lowest KS transitions

Rydberg states



BeH molecule : TDDFT

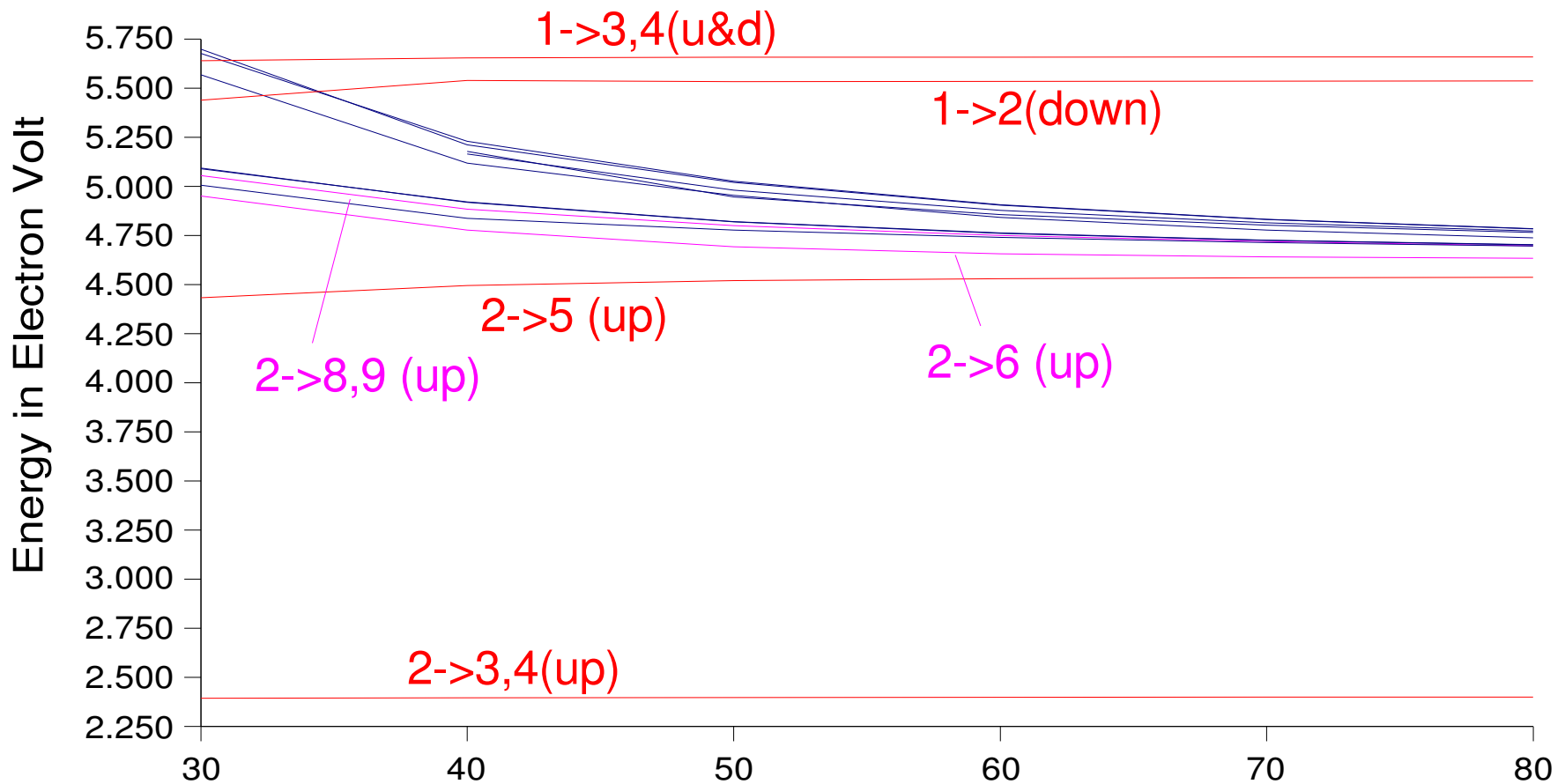
	Kohn-Sham	TDDFT	Main excitations	Casida's paper	Exp.	
4 Π	6.41 eV	~5.65 eV	1->3,4 (u&d) + ..??...	5.73 eV	7.27 eV	
3 Π	6.01 eV		Vacuum+ 1->3,4(u&d)	5.67 eV	6.74 eV	
5 Σ	5.16 eV		5.44 eV	1->2 (down) + vacuum	5.42 eV	6.71 eV
4 Σ			5.19 eV	Vacuum+ 1->2 (down)	5.13 eV	6.12 eV
2 Π	4.81 eV	4.80 eV	2->8,9 (up)	4.86 eV	6.31 eV	
3 Σ	4.71 eV	4.70 eV	2->6 (up)	4.77 eV	5.61 eV	
2 Σ	4.54 eV	4.52 eV	2->5 (up)	4.59 eV	5.51 eV	
1 Π	2.29 eV	2.40 eV	2->3,4 (up)	2.39 eV	2.56 eV	

- 1 – We obtain good results compared to the ones of Casida. (within 0,05 eV of error)
- 2 – Not really good compared with experiments, probably due to the problem already outlined before of broken spin symmetry and for the asymptotic behaviour of the kernel.
- 3 – Mixing with vacuum is really difficult to analyse...

Convergence of excitations energies

Data are well converged for energy cut-off and number of states taken into account. Things are a little more difficult for cell size...

Cubic cell; dimensions in Bohr



Some notes on running the code

First dataset

Ground State SCF
(with occupied bands)



Second dataset

Non-SCF calculation
(with many bands)
+TDDFT

The most difficult parameter to converge remains the cell size. Mainly because our excitations are mixing with vacuum that (we are in a box) is continuously changing.

The programs remains really memory demanding, our calculations need up to 9GB of RAM. We were lucky that BeH only needs ecut 10 Hartree.

The data presented here have been calculated with:
acell 3*50, nband 50, ecut 10 and are not yet fully converged.
(The first energy differences are converged within 0.01 eV. For states far above the HOMO may be difficult to reach convergence. Anyway we kept them as they are mixing with the first excitations...)