

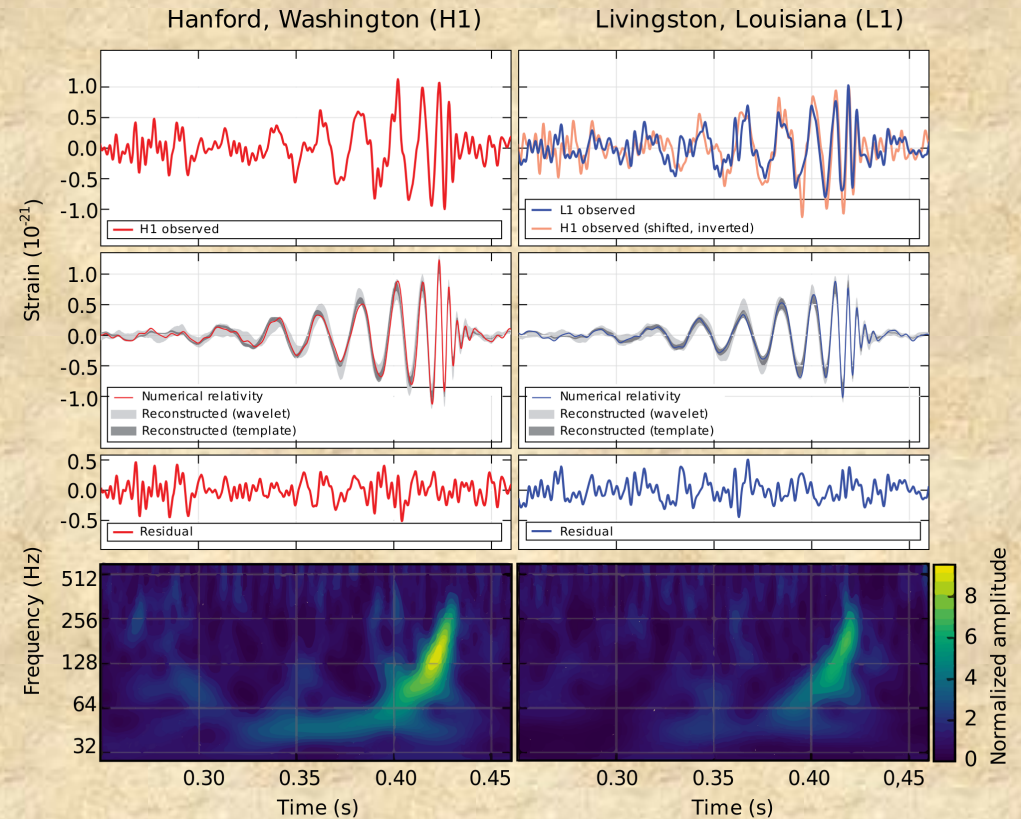
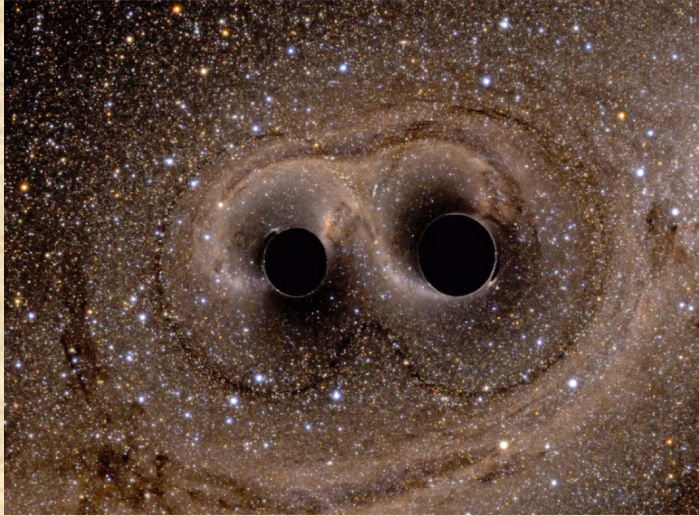
The calculation of optical spectra

*Tout de même, avant de mourir,
je voudrais deviner ce que c'est,
la couleur.*

Pablo Picasso

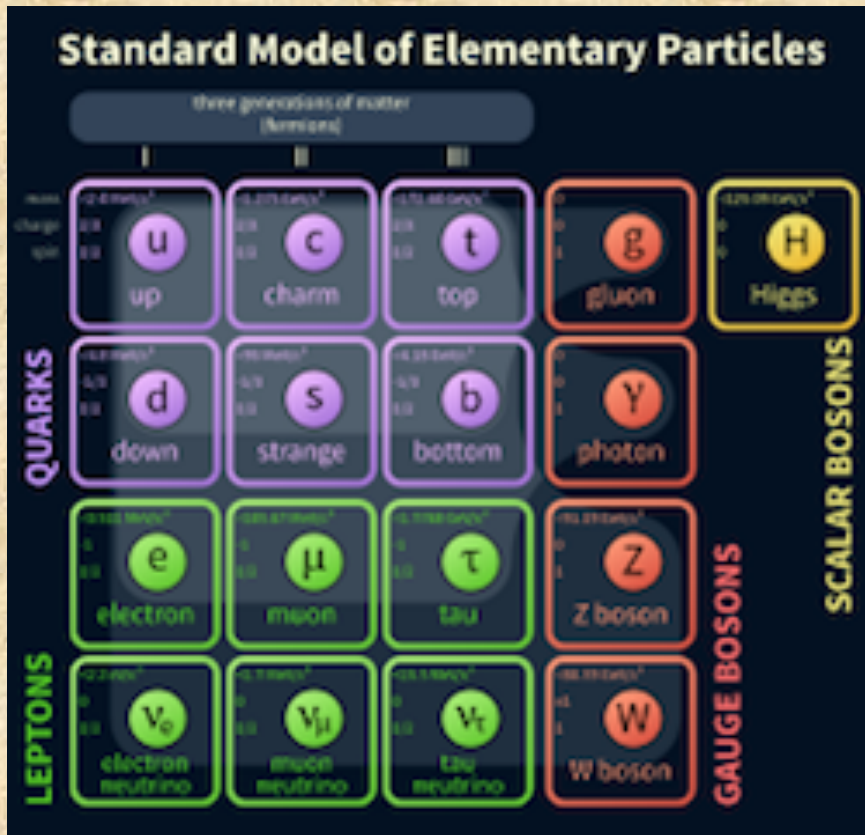
- ◆ Colours
- ◆ State of the art
- ◆ Why is it difficult?
- ◆ Do you need to be a superhero?

Gravitational waves



- ◆ Merging of two giant black holes
- ◆ 1400000000 light years
- ◆ 1.5 billion €

Standard model of elementary particles



- ◆ 238 particles
- ◆ More than one million experiments
- ◆ 13 billion €

Outline

- ◆ Colours
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Colour of life (porphyrins)



Colour of pigments (minerals)

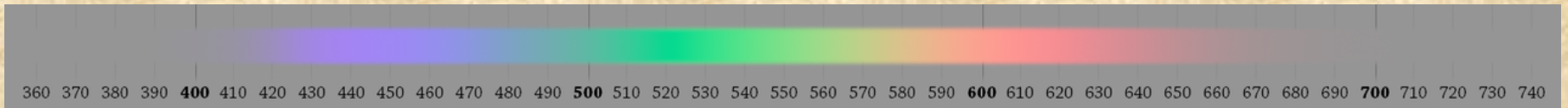


Colour of gemstones (minerals)



Colours

- ◆ Visible range: 400 nm to 700 nm or 1.8 eV to 3.0 eV

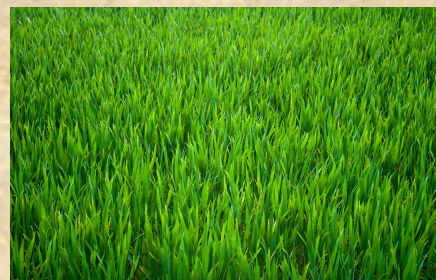


- ◆ The eye distinguishes 150 hues: < 10 meV

Outline

- ◆ Colours
- ◆ State of the art
- ◆ Why is it difficult?
- ◆ Do you need to be a superhero?

The colour of grass



- ◆ *Time-dependent density functional theory study of the electronic excitation spectra of Chlorophyllide a and Pheophorbide a in solvents, Z-W Qu, H. Zhu, V May, R Schinke, J. Phys. Chem. B. (2009) 113 4817*
- ◆ *The predicted excitation energies and oscillator strengths now agree much better with experiments*

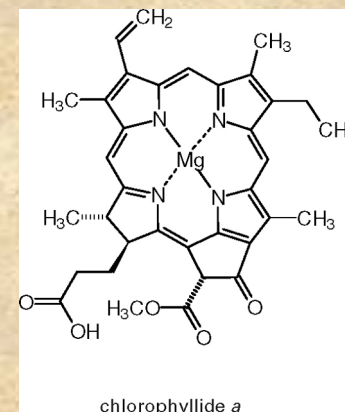
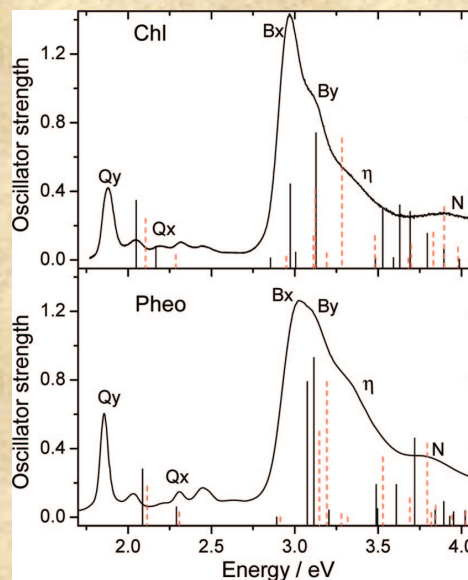
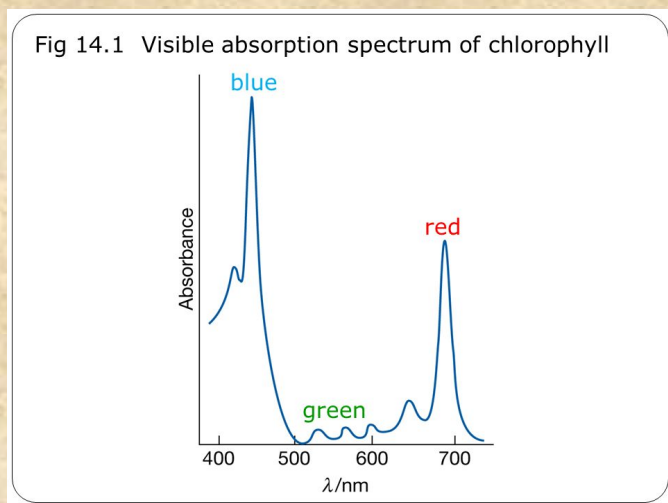
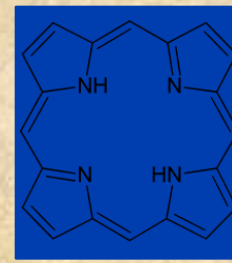
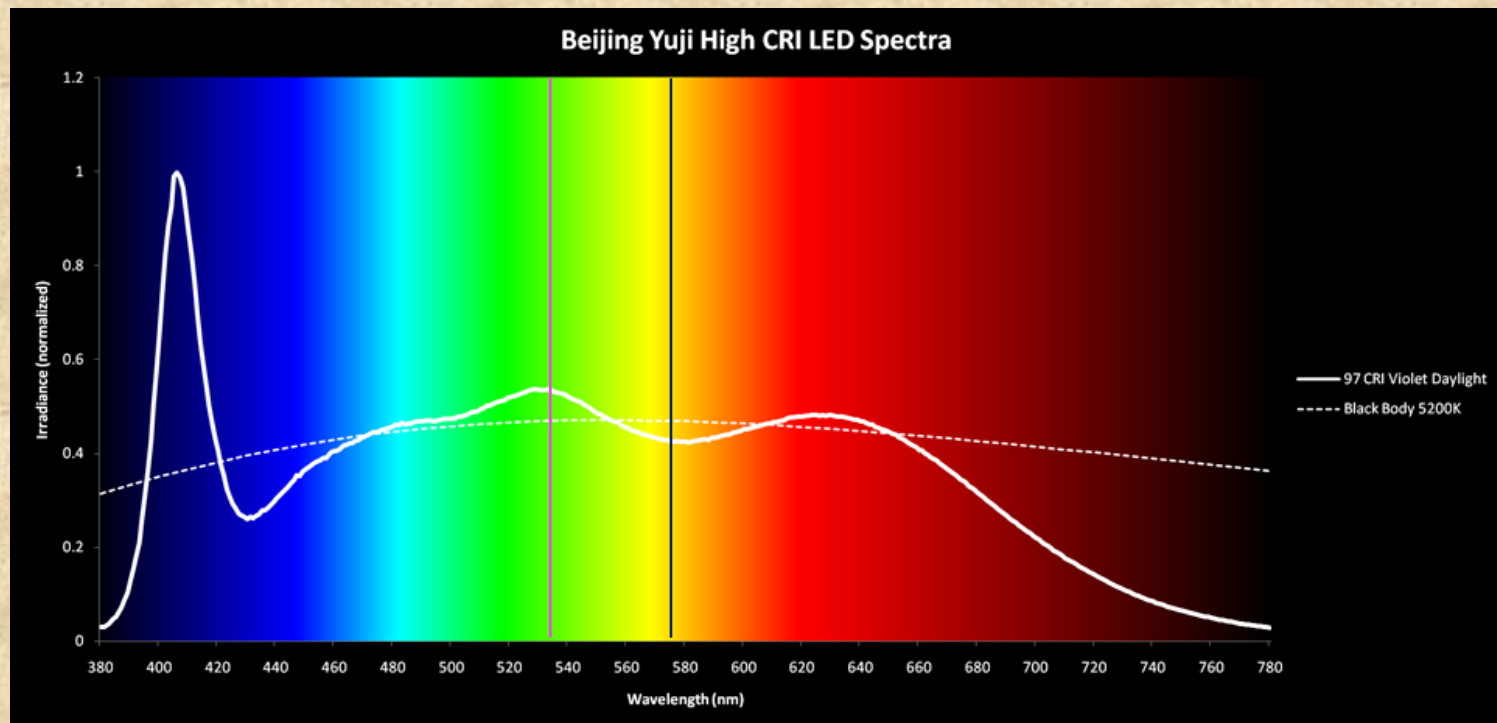


Figure 3. TDDFT predicted electronic absorption spectra in gas phase (in red dashed sticks) and in ethanol for pheophorbide *a* and in methanol for chlorophyllide *a* (in black solid sticks) within PCM model. The corresponding experimental spectra in solvents from refs 2 and 3 (in black solid lines) are also included for comparison.

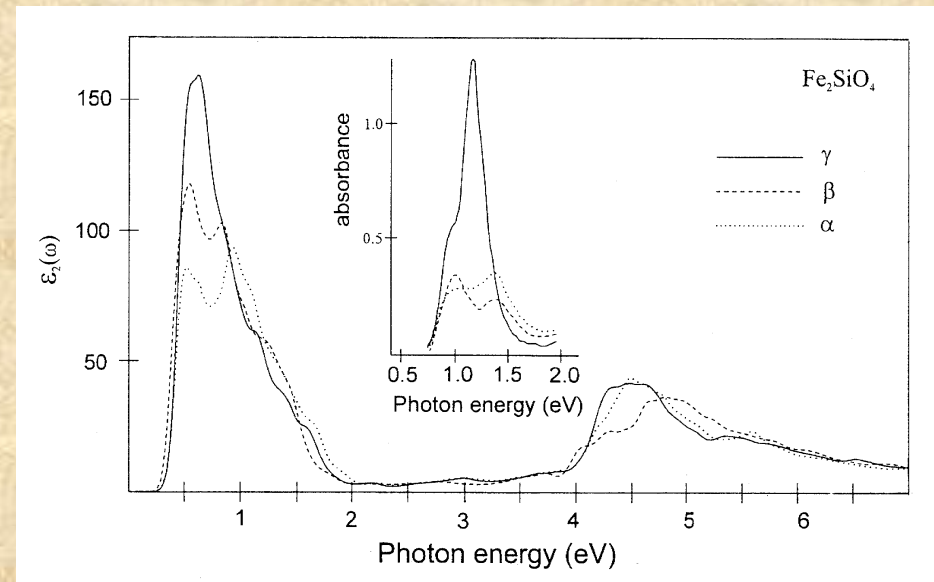
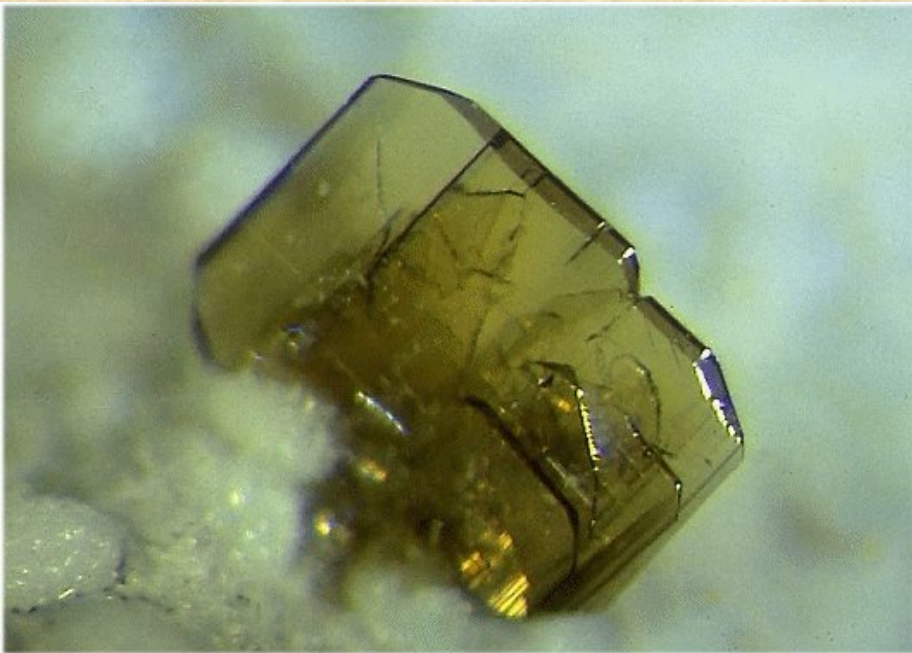
Porphyrins



- ◆ *Challenging density functional theory calculations with hemes and porphyrins, S. P. de Visser, M. J. Stillman, Int. J. Mol. Sci. (2016) 17 519*
- ◆ *Abstract: In recent years computational tools have improved considerably and now can reproduce experimental spectroscopic studies*
- ◆ *The Q-band is predicted to be at 535 nm, but is observed at 578 nm (0.17 eV)*



Colour of fayalite Fe_2SiO_4



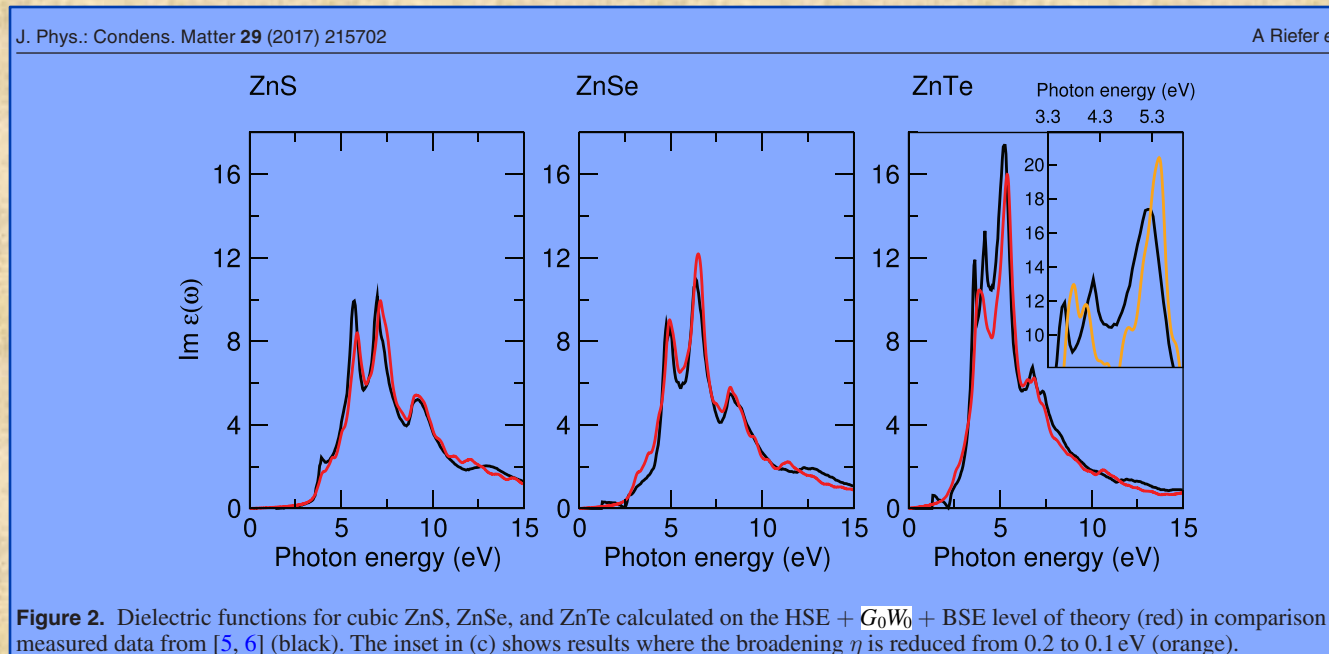
O.V. Krasovska et al., *Am. Min.*
82 (1997) 672

What colour can we compute?

- ◆ *Perspective: Fundamental aspects of time-dependent density functional theory*, N. T. Maitra, J. Chem. Phys. (2016) **144**, 220901
- ◆ *Fully parameter-free calculation of optical spectra for insulators, semiconductors and metals from a simple polarization functional*, J. A. Berger, Phys. Rev. Lett. (2015), **115**, 137402
- ◆ *Time-dependent density functional theory calculations for the excitation spectra of III-V ternary alloys*, Zhenhua Ning, Ching-Tarng Liang, Yia-Chung Chang, Phys. Rev. B (2017), **96**, 085202
- ◆ *Solution of the Bethe-Salpeter equation without empty electronic states: Application to the absorption spectra of bulk systems*, D. Rocca, Yuan Ping, R. Gebauer, G. Galli, Phys. Rev. B (2012), **85**, 045116
- ◆ *Zn-VI quasiparticle gaps and optical spectra from many-body calculations*, A. Riefer, N. Weber, J. Mund, D.R. Yakovlev, M. Bayer, A. Schindlmayr, C. Meier W.G. Schmidt, J. Phys.: Cond. Matt. (2017), **85**, 045116

Semiconductors

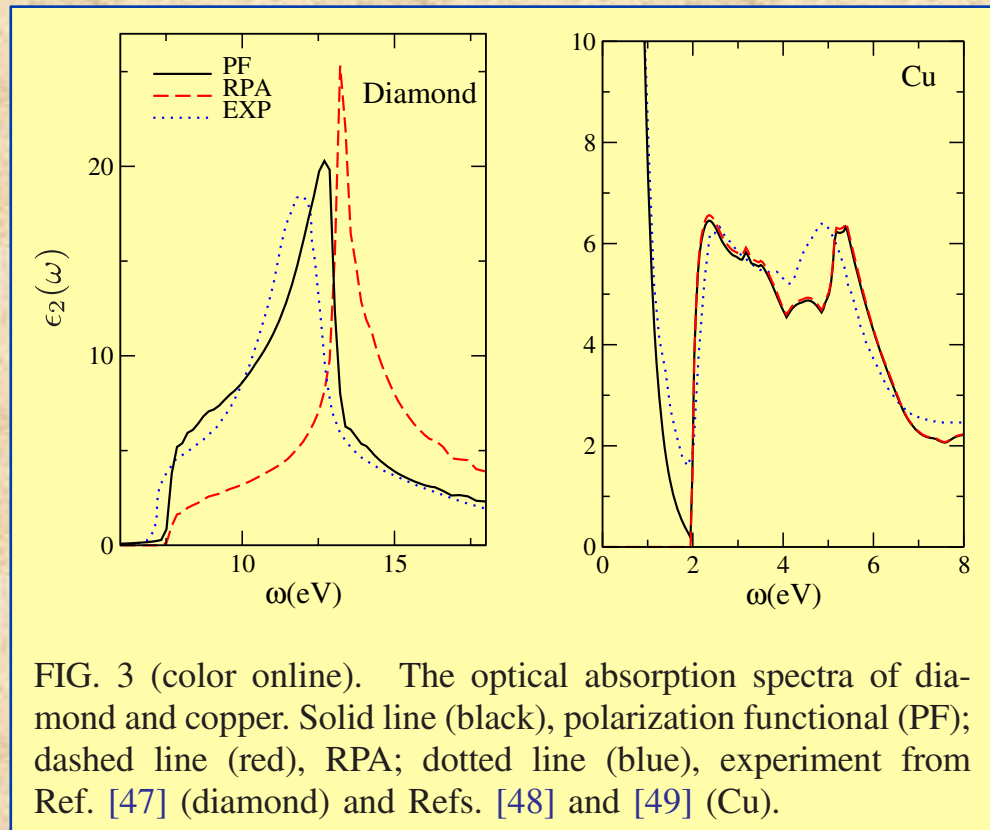
- ◆ *Zn-VI quasiparticle gaps and optical spectra from many-body calculations, A. Riefer, N. Weber, J. Mund, D.R. Yakovlev, M. Bayer, A. Schindlmayr, C. Meier W.G. Schmidt, J. Phys.: Cond. Matt. (2017), 85, 045116*



Metals

- ◆ *Fully parameter-free calculation of optical spectra for insulators, semiconductors and metals from a simple polarization functional, J. A. Berger, Phys. Rev. Lett. (2015), **115**, 137402*

excitons

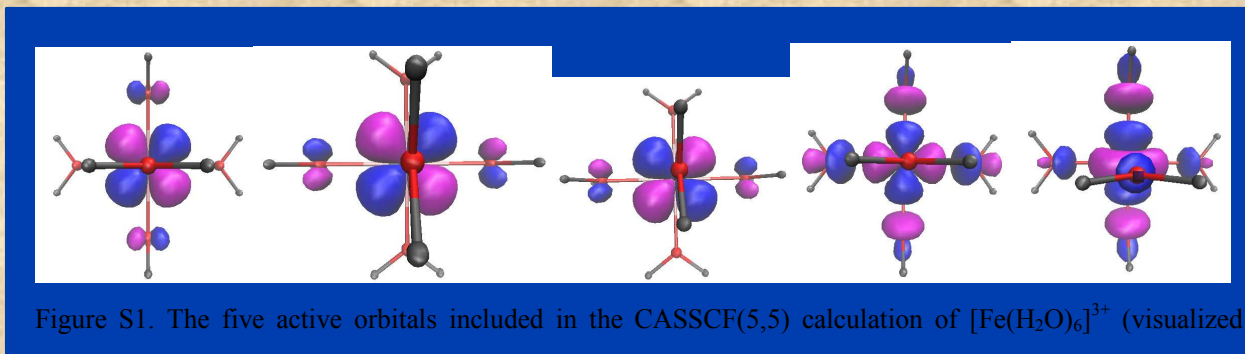


Drude tails

FIG. 3 (color online). The optical absorption spectra of diamond and copper. Solid line (black), polarization functional (PF); dashed line (red), RPA; dotted line (blue), experiment from Ref. [47] (diamond) and Refs. [48] and [49] (Cu).

Transition metal oxides $[\text{M}(\text{H}_2\text{O})_6]^{n+}$

- ◆ *Multireference ab initio study of ligand field d-d transitions in octahedral transition-metal oxide clusters*, Yang Yang, M.A. Ratner, G.C. Schatz, J. Phys. Chem. (2014), **118**, 29196
- ◆ Multiconfigurational multireference methods (CASSCF, CASPT2, MRCI)



- ◆ Good bond length
- ◆ Good ligand-to-metal charge transfer energy

Transition metal oxides $[\text{M}(\text{H}_2\text{O})_6]^{n+}$

- ◆ *Multireference ab initio study of ligand field d-d transitions in octahedral transition-metal oxide clusters*, Yang Yang, M.A. Ratner, G.C. Schatz, *J. Phys. Chem.* (2014), **118**, 29196

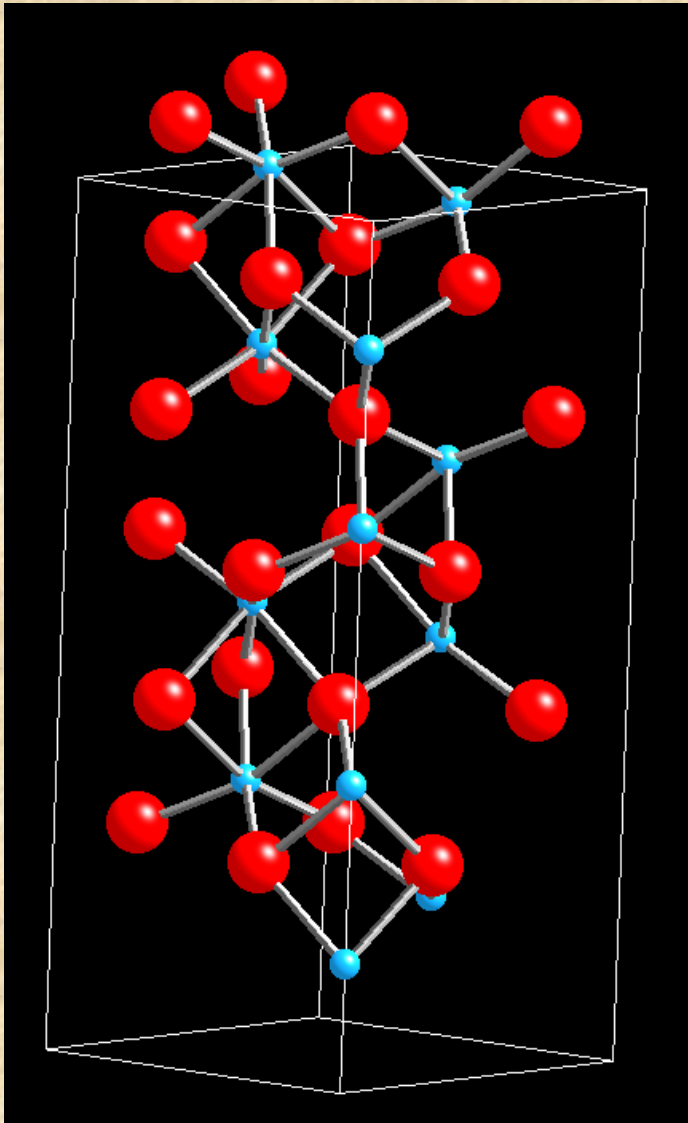
Table 3. Multireference d–d Transition Energies for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ (eV)

state	CASPT2(5,5)	CASPT2(5,10)	MRCI(5,5)	exp
$^6\text{A}_g$	0.00	0.00	0.00	0.00
$^4\text{B}_{1g}$	2.89	2.85	3.02	1.56
$^4\text{B}_{1g}$	n/a	n/a	3.74	2.29
$^4\text{A}_g$	3.78	3.80	4.08	3.01
$^4\text{A}_g$	3.82	3.84	4.13	3.05
$^4\text{A}_g$	3.82	3.84	4.13	

Table 13. Calculated d–d Transition Energies for d^3 $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (eV)

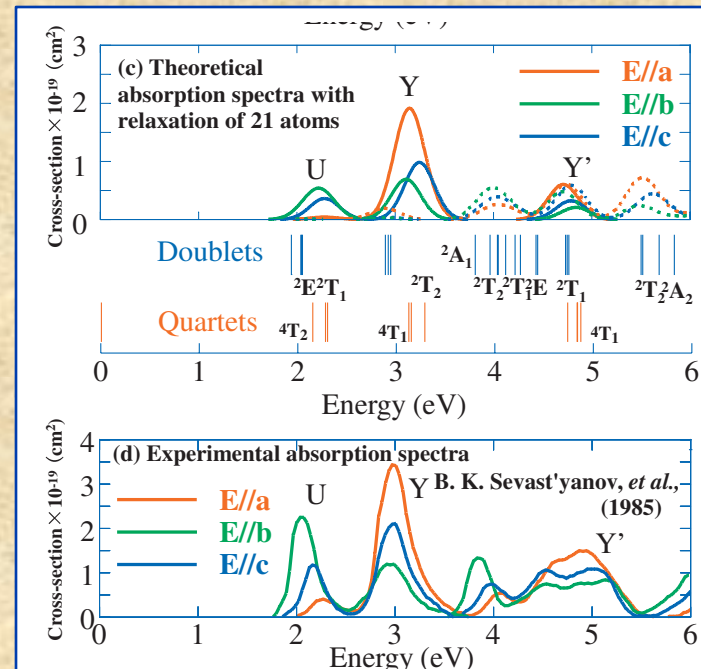
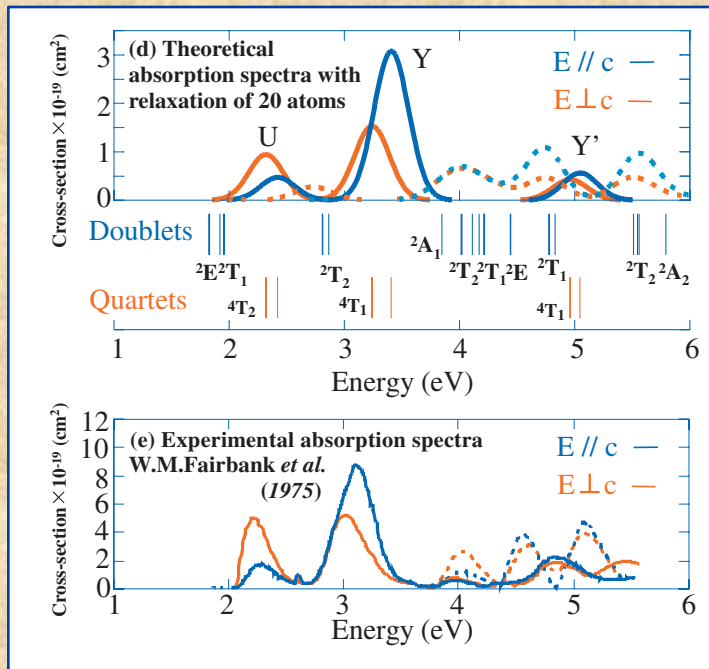
state	CASSCF(3,5)	CASPT2(3,5) ^a	MRCI(3,5)	exp
$^4\text{A}_g$	0.00	0.00	0.00	0.00
$^4\text{B}_{1g}/\text{B}_{2g}/\text{B}_{3g}$	1.69	1.77	1.79	2.16
$^4\text{B}_{1g}/\text{B}_{2g}/\text{B}_{3g}$	2.70	2.68	2.77	3.05
$^4\text{B}_{1g}/\text{B}_{2g}/\text{B}_{3g}$	4.36	4.28	4.42	4.69
$^2\text{A}_g$	2.41	2.23	2.35	2.60
$^2\text{A}_g$	2.41	2.23	2.35	2.60
$^2\text{A}_g$	3.71			

Ruby : Cr^{3+} in Al_2O_3



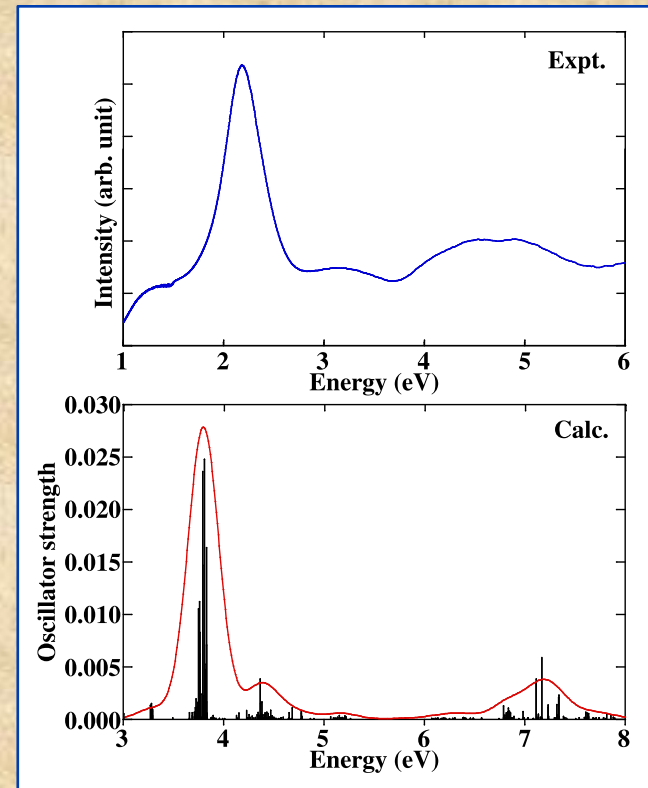
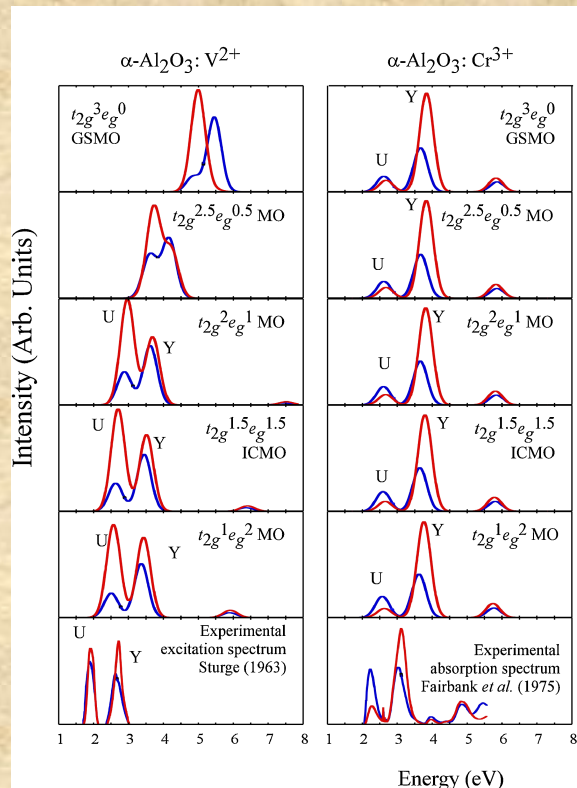
Optical spectra of ruby

- ◆ *First-principles calculation of ground and excited-state absorption spectra of ruby and alexandrite considering lattice relaxation, S. Watanabe, T. Sasaki, R. Taniguchi, T. Ishii, K. Ogasawara, Phys. Rev. B (2009), 79, 075109*



Further calculations

- ◆ *Comparative study of absorption spectra of V^{2+} , Cr^{3+} , and Mn^{4+} in $\alpha-Al_2O_3$ based on first-principles configuration-interaction calculations*, M. Novita and K. Ogasawara, J. Phys. Soc. Japan (2012) **81** 104709 + 4 other papers until 2016
- ◆ *Intra- and inter-atomic optical transitions of Fe, Co, and Ni ferrocyanides studied using first-principles many-electron calculations*, S. Watanabe, Y. Sawada, M. Nakaya, M. Yoshino, T. Nagasaki, T. Kamemaya, T. Torimoto, Y. Inaba, H. Takahashi, K. Takeshita, J. Once, J. Appl. Phys. (2016) **119** 235102



Outline

- ◆ Colours
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Ruby and emerald

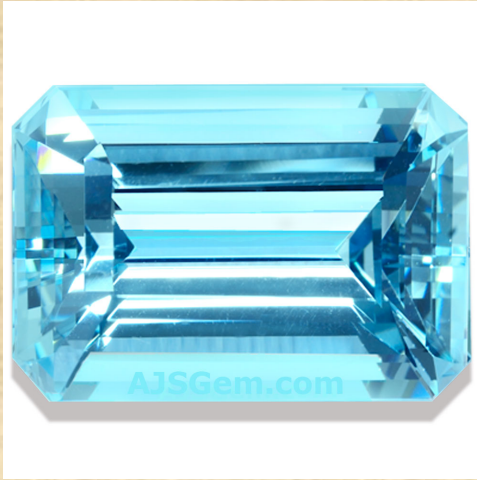


◆ Chromium in alumina



◆ Chromium in beryl

Aquamarine and heliodore



◆ Iron in beryl



◆ Iron in beryl

Transition metals

- ◆ Transitions in the range 1.8 eV to 3 eV:
- ◆ 3d orbitals are localized
- ◆ 3d orbitals are extended
- ◆ 3d orbitals are almost degenerate

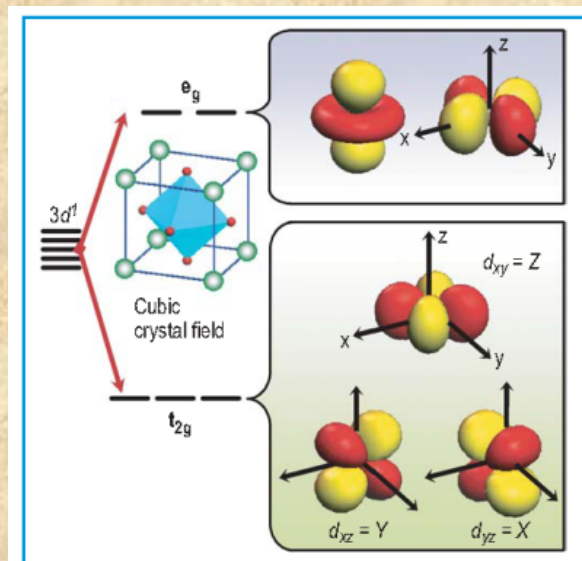


Fig. 1. A schematic view of the splitting of the five-fold 3d orbitals under cubic crystal field. The transition metal is located at the center of the oxygen octahedra (shown in blue).

Calculation of transition energies

- ◆ Transitions in the range 1.8 eV to 3 eV:
 - Accuracy in the 10 meV range
 - No low-energy effective Hamiltonian like in magnetism
- ◆ 3d orbitals are localized
 - Strong interaction (many-body techniques)
 - Strong excitonic (electron-hole) interaction (Bethe-Salpeter)
- ◆ 3d orbitals are extended
 - Influence of the crystal host
 - Coupling between transition metals (sapphire)

Calculation of transition energies

- ◆ 3d orbitals are almost degenerate
 - Green function techniques are not applicable
 - High sensitivity to external perturbation
- ◆ Transitions metal impurities
 - Position of the TM atom in the structure (heliodore and aquamarine)
 - Deformation of the crystal structure
 - Possible clustering

Calculation of transition intensities

- ◆ Which transition operator?
- ◆ Selection rules
- ◆ Role of vibrations

Electric dipole transitions

- ◆ *Calculated optical absorption spectra of Ni²⁺-bearing compounds, S. Rossano, C. B., Phys. Chem. Min. (2000) 27 170*

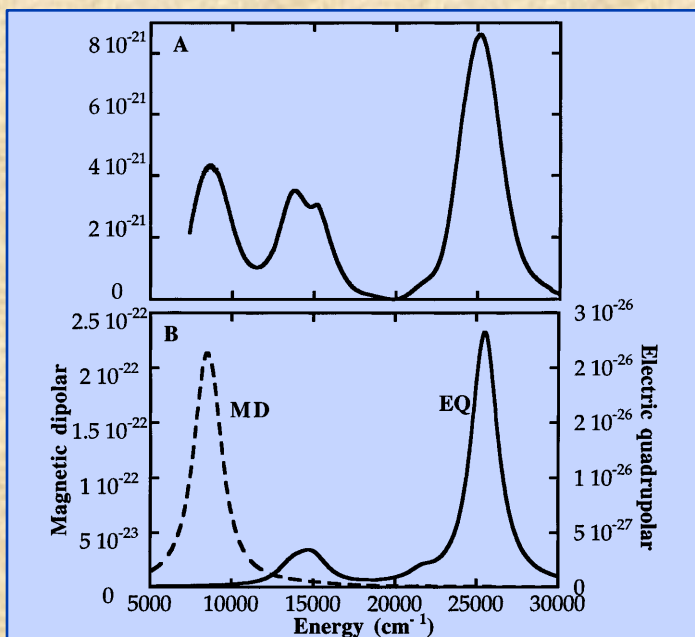


Fig. 1 **A** Optical absorption spectrum of a 0.25 mol l⁻¹ solution of Ni(H₂O)₆²⁺ has been recorded in the UV-visible range on a CARY 5 spectrophotometer. Absorbance values have been transformed to absorption cross-section, σ (cm²) according to $\sigma = \ln(I_0/I)/dN_{at}$, where d is the cell size and N_{at} is the number of Ni atoms per m³. **B** Magnetic dipolar (MD) and electric quadrupolar (EQ) contribution to the theoretical absorption spectrum of Ni²⁺ ion in a regular octahedron. Parameter values are given in text

- Peak positions are correct
- Peak intensities are wrong

Selection rules

- ◆ 3d-3d dipole transitions are forbidden
- ◆ In non-centrosymmetric sites, d and p states can mix by interacting with the ligands and dipole transitions are allowed
- ◆ In centrosymmetric sites, dipole transitions are still forbidden and transitions are allowed by **vibrations**
- ◆ Vibrations play a rôle in the width of the peaks
- ◆ Electron-phonon coupling

Outline

- ◆ Colours
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Do you need to be a superhero?



Monica Rambeau alias Photon alias Spectrum alias Captain Marvel

The roads to progress

◆ Energies

- TDDFT with improved kernel
- Multiplet approach with improved effective potential
- Many-body Green function techniques for quasi-degenerate systems

◆ Intensities

- Taking vibrations into account

◆ Spectral shapes

- Taking vibrations into account
- Inelastic effects

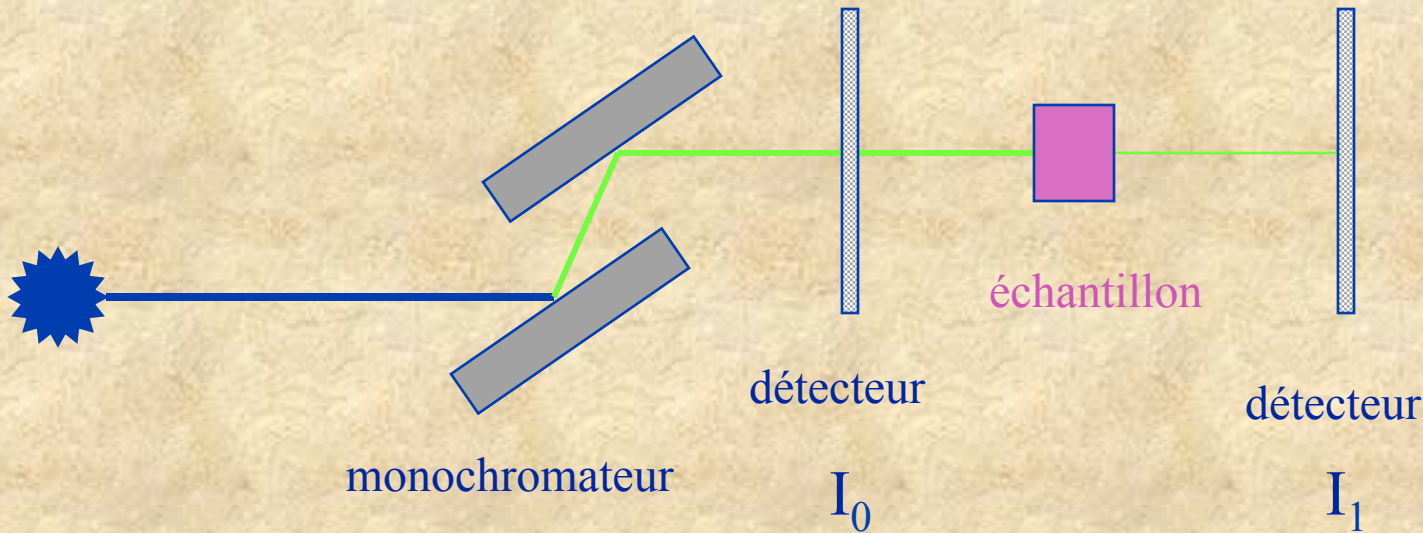
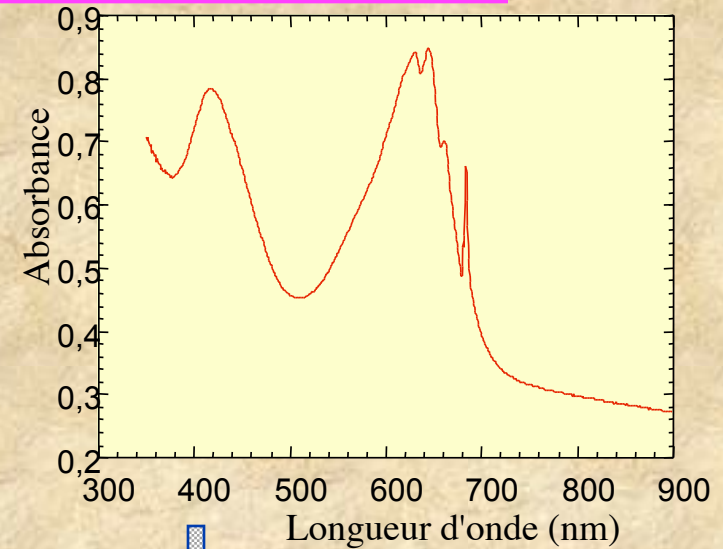
◆ First-order effect

FOR YOUR ATTENTION

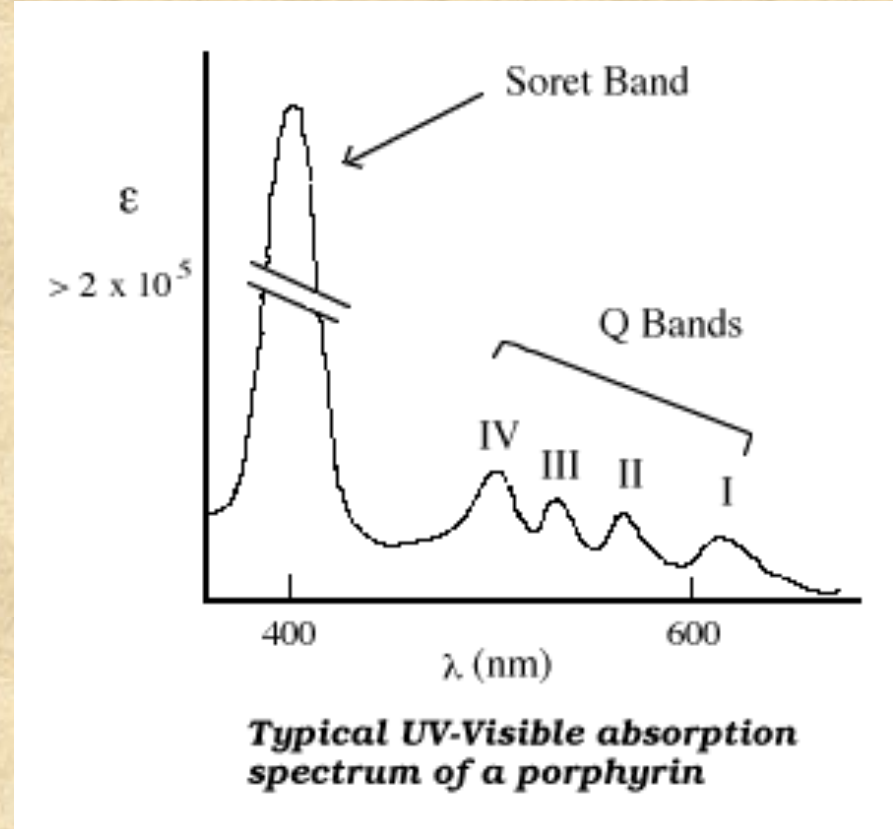
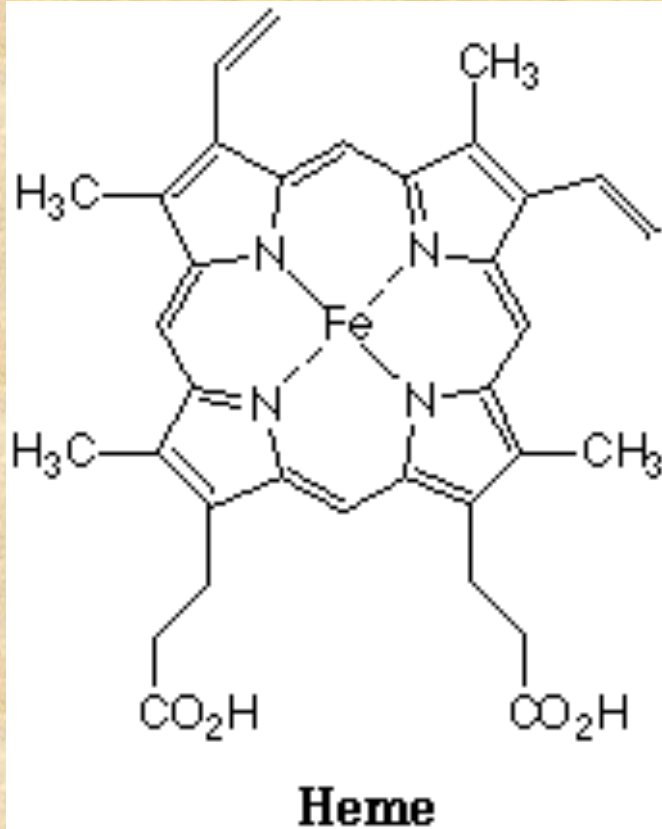


La mesure de l'absorption

Coefficient d'absorption : $\sigma = \log(I_0/I_1)$

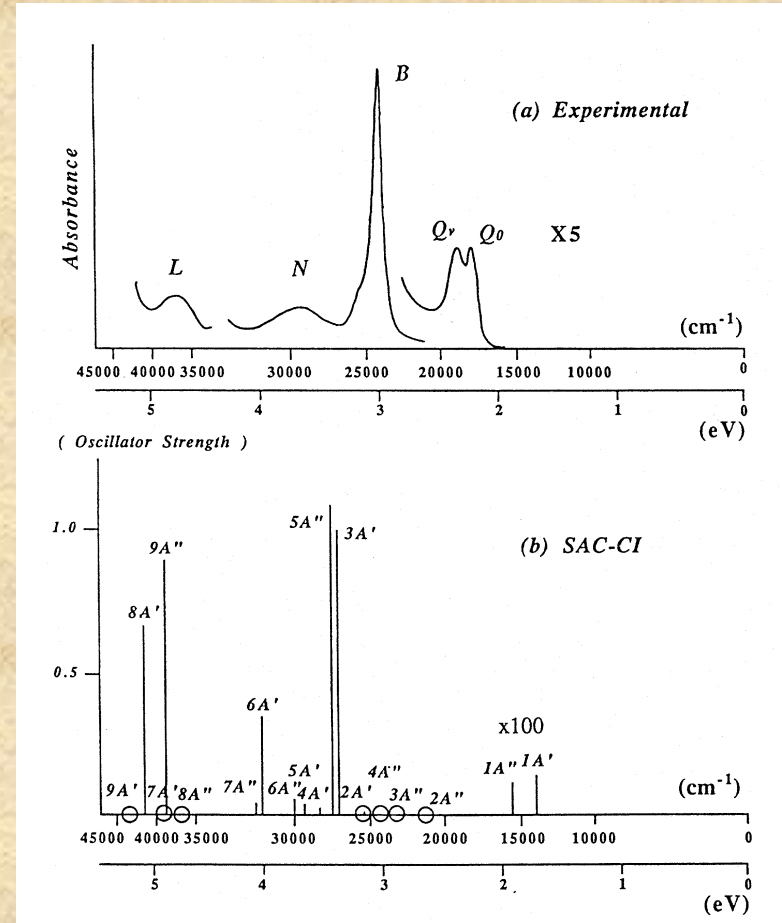


Couleur du sang



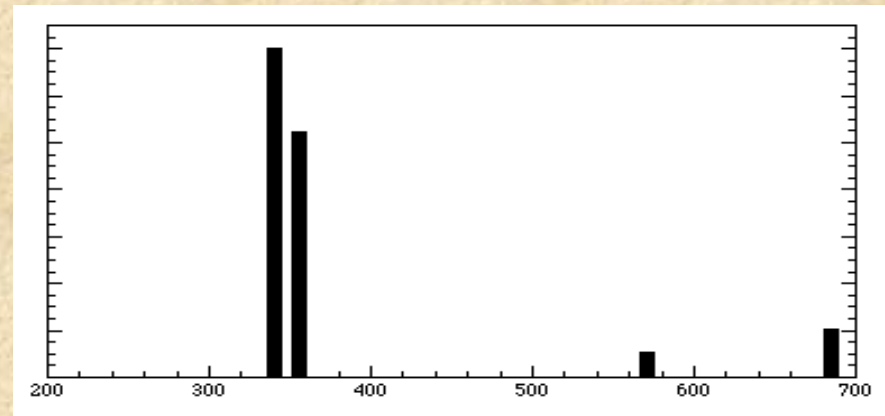
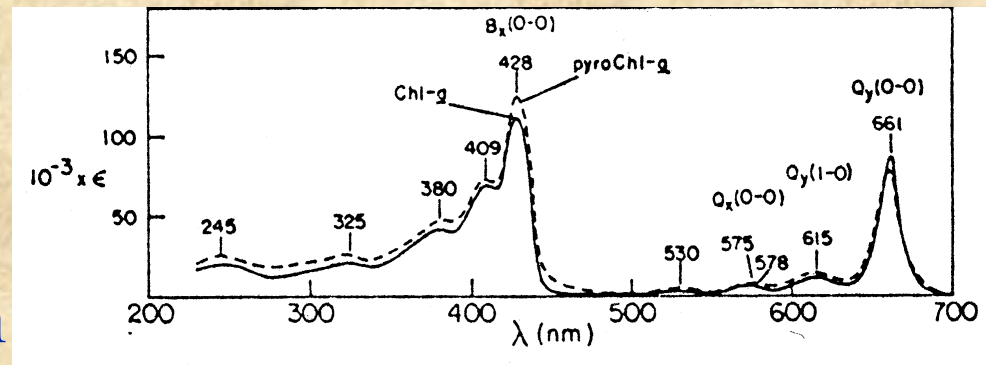
Calcul de la couleur du sang

- ◆ Nakatsuji et al. Chem. Phys. Lett. **256** (1996) 220
- ◆ Orbitales symétrisées et configuration d'interaction
- ◆ Symétrie Cs
- ◆ 48 atomes, 236 électrons
- ◆ 92350 états de symétrie A'
- ◆ 120182 états de symétrie A''



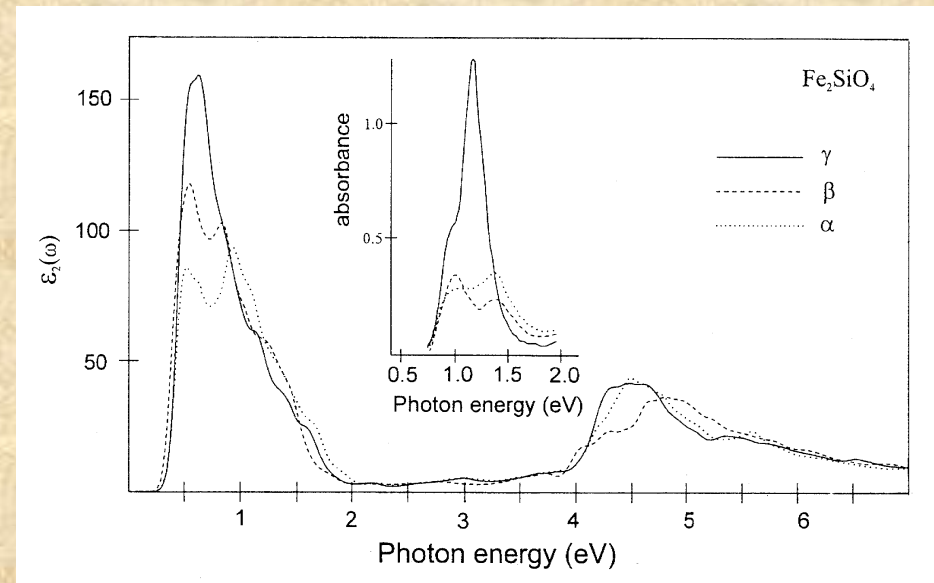
Calcul de la couleur de l'herbe

- ◆ Hasegawa et al. J. Phys. Chem. **102** (1998) 1320
- ◆ Orbitales symétrisées et configuration d'interaction
- ◆ Symétrie C1
- ◆ 24971 états (fondamental)
- ◆ 71422 états (excité)



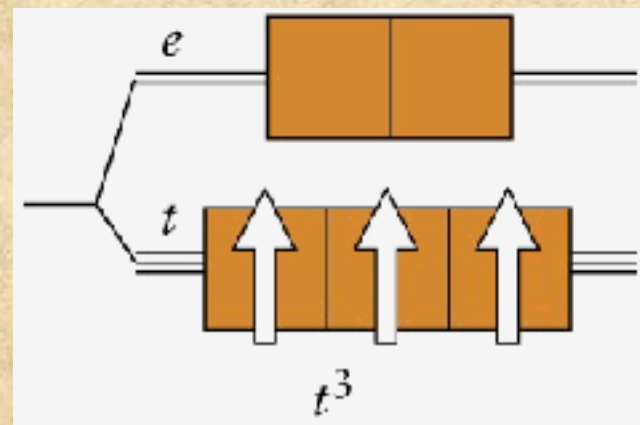
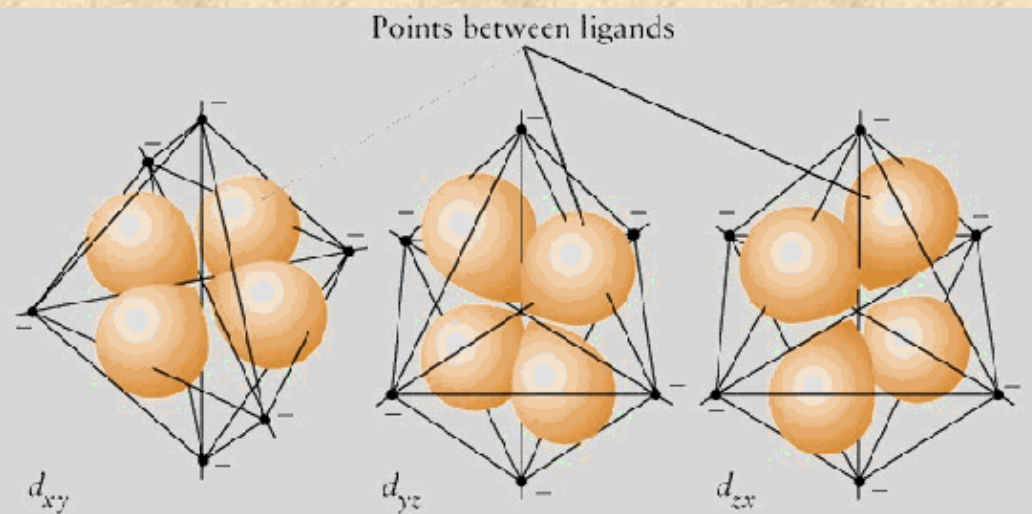
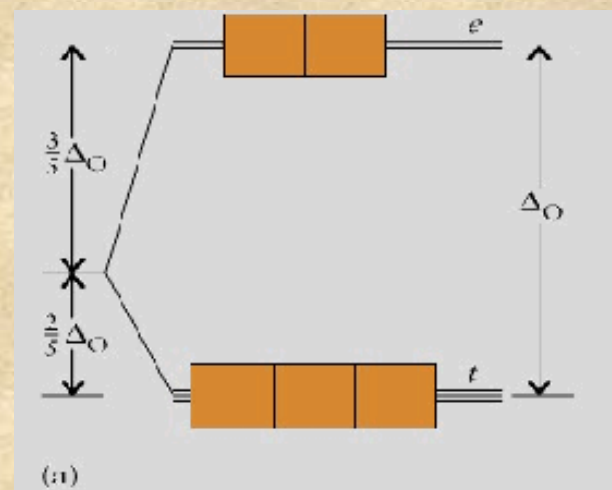
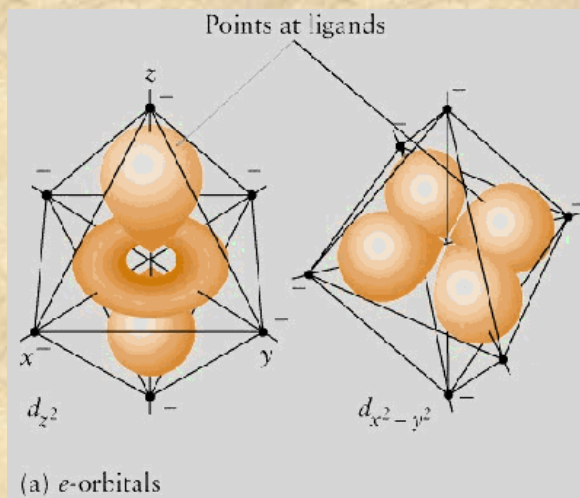
La couleur des minéraux

Couleur de la fayalite Fe_2SiO_4



O.V. Krasovska et al., *Am. Min.*
82 (1997) 672

Cr³⁺ (3d³) configuration t_{2g}³

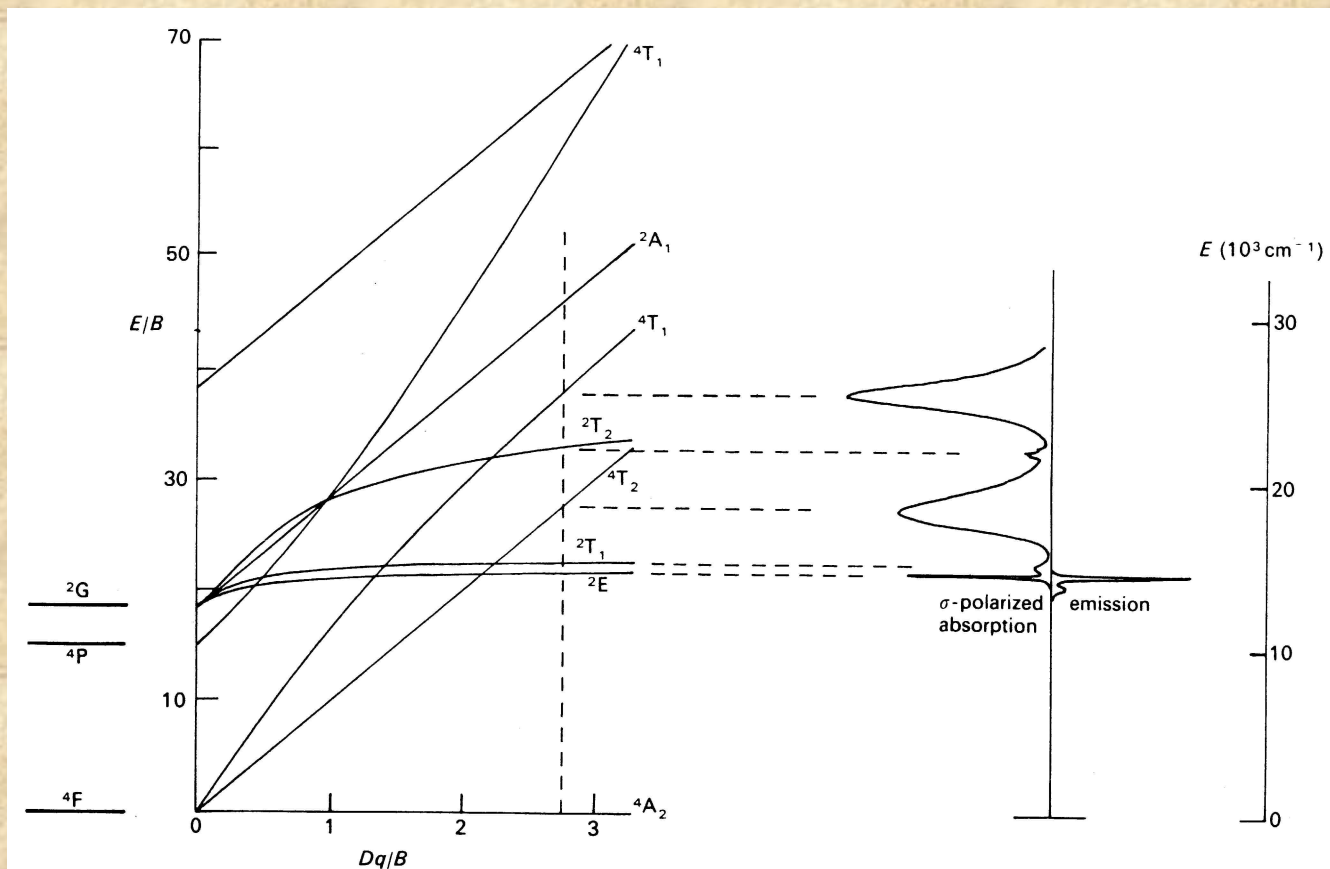


(b) *t*-orbitals

Hamiltonien effectif

- ◆ Regardez le tableau
- ◆ Ecoutez le monsieur

Cr³⁺ (3d³) terme ⁴F



Calculs perturbatifs

- ◆ Kristine Pierloot (2006)
- ◆ CASPT2 (complete active space with second order perturbation theory)
- ◆ La fonction de l' espace actif + les excitations simples et doubles.
- ◆ FeX_6 , avec $\text{X}=\text{H}_2\text{O}$ et $\text{X}=\text{NH}_3$
- ◆ Pour une précision de 1000 cm^{-1} , il faut aller jusqu' aux orbitales h sur le fer et aux orbitales f sur le ligand \rightarrow énorme calcul
- ◆ *The above conclusions may sound discouraging*

Excitation triplet-singulet

- ◆ Deux orbitales, deux spins, 4 états
- ◆ 4 états $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$ et $|\downarrow\downarrow\rangle$
- ◆ Déterminants de Slater
- ◆ $\langle\uparrow\uparrow|H|\uparrow\uparrow\rangle = \langle\downarrow\downarrow|H|\downarrow\downarrow\rangle = J-K$
- ◆ $\langle\uparrow\downarrow|H|\uparrow\downarrow\rangle = \langle\downarrow\uparrow|H|\downarrow\uparrow\rangle = J$
- ◆ Energie du triplet: $E_T = J-K$
- ◆ Energie du singlet: $E_S = J+K$
- ◆ $E_S = 2 \langle\uparrow\downarrow|H|\uparrow\downarrow\rangle - \langle\uparrow\uparrow|H|\uparrow\uparrow\rangle$

Fitter les multiplets: méthode

- ◆ Ziegler et al. Theor. Chim. Acta (1977)
- ◆ Daul (1993 - 2004), Moreno (1999-2008)
- ◆ Exemple e^2 . Les orbitales e sont α et β .
$$E(^1A_1) = A + 8B + 4C + 2\varepsilon_e = 4E(\alpha^+\alpha^-)/3 - E(\alpha^+\beta^+)/3$$
$$E(^3A_2) = A - 8B + 2\varepsilon_e = E(\alpha^+\beta^+)$$
$$E(^1E) = A + 2C + 2\varepsilon_e = 2E(\alpha^+\alpha^-)/3 + E(\alpha^+\beta^+)/3$$
- ◆ Calcul SCF sur une molécule avec occupation 1/10 de chaque orbitale d
- ◆ Calcul des énergies DFT des énergies des configurations
- ◆ Fit des paramètres A , B , C , ε_e et ε_{t_2}

Fitter les multiplets: résultats

- ◆ Garcia-Lastra et al. Phys. Rev. B 78, 085117 (2008)
- ◆ Accord pour 10Dq
 - Emeraude : 15739 cm^{-1} (théo) - 16130 cm^{-1} (exp)
 - Spinelle : 20627 cm^{-1} (théo) - 18520 cm^{-1} (exp)
 - Rubis : 18179 cm^{-1} (théo) - 18070 cm^{-1} (exp)
- ◆ Il est important d' avoir la bonne structure locale
- ◆ Le champ de Madelung doit être pris en compte
- ◆ Pas de calcul de l' intensité des transitions

Effet néphélauxétique

- ◆ La répulsion coulombienne n' est pas la même dans les orbitales e et t_2 .
- ◆ Vision DFT: Fazzio, Caldas, Zunger (1984)
- ◆ Watanabe, Kamimura (1987)
- ◆ Ogasawara et al. (1998-2004)

Conclusion

- ◆ Premier calcul ab initio convaincant
- ◆ Mais fondement théorique fragile
 - double-counting de la corrélation
 - prise en compte très approximative de l'influence des autres électrons
 - erreur sur l'intensité
 - réduction assez arbitraire des interactions électron-électron
- ◆ Spectre nul pour un système centrosymétrique

Perspective

- ◆ Traiter les systèmes centrosymétriques
 - tenir compte du couple électron-phonon
 - commencer par un calcul en absorption X
- ◆ Améliorer le hamiltonien effectif
 - traiter le solide (et plus une molécule)
 - améliorer le calcul du potentiel dû aux autres électrons
 - améliorer le traitement de l'interaction électron-électron écrantée
- ◆ Tenir compte des effets de champ local