ab initio colors

Stefano Baroni

SISSA — Scuola Internazionale Superiore di Studi Avanzati — Trieste, Italy

Fifth International workshop and school on *Time-dependent Density-Functional Theory: Prospects and Applications*,
Benasque, January 3-17, 2012

ab initio colors

(and a few thoughts on functionals for spectroscopy)

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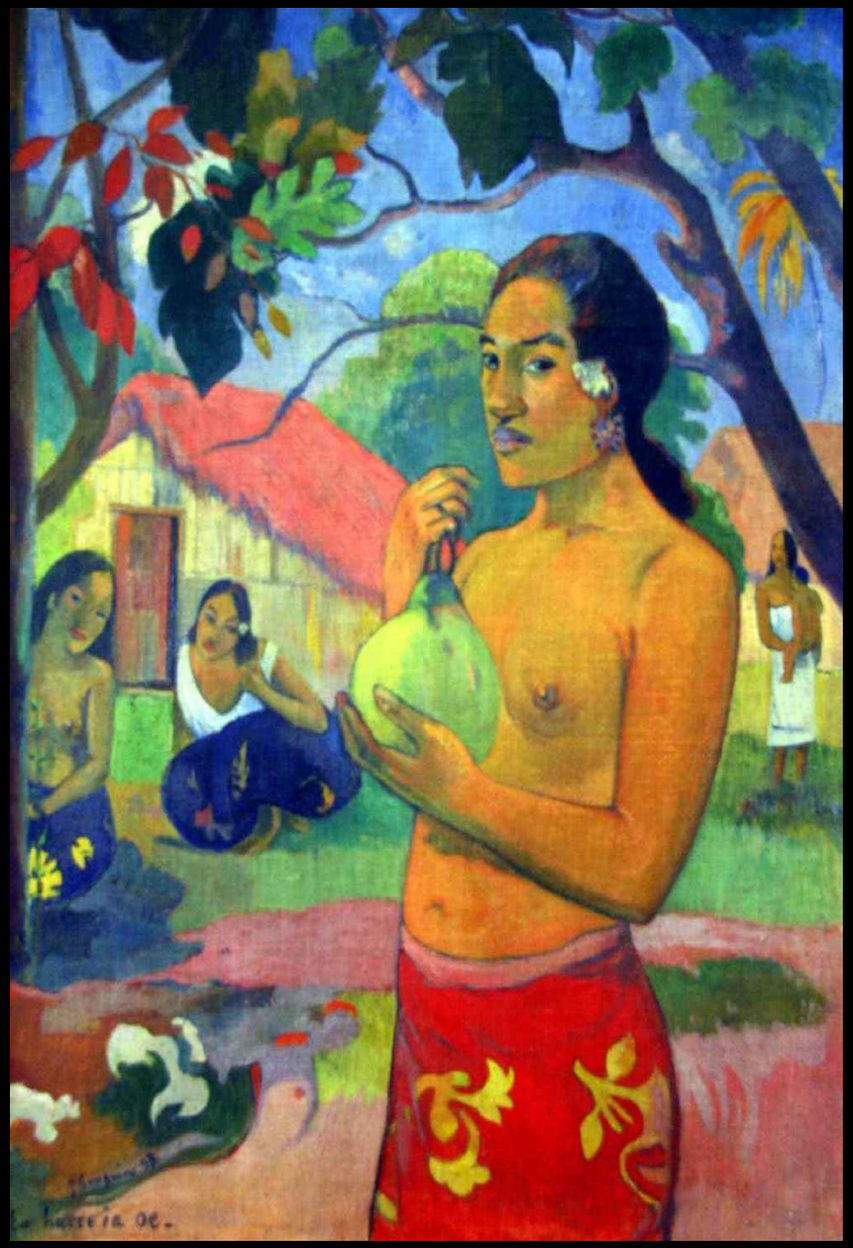
what color is all about



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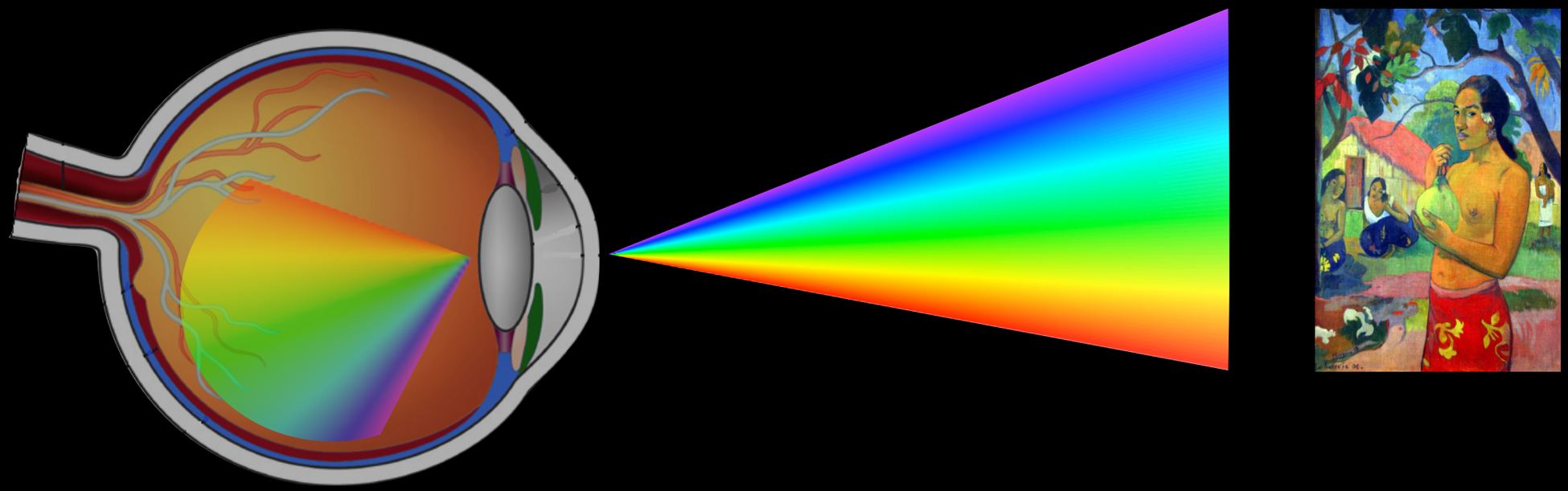

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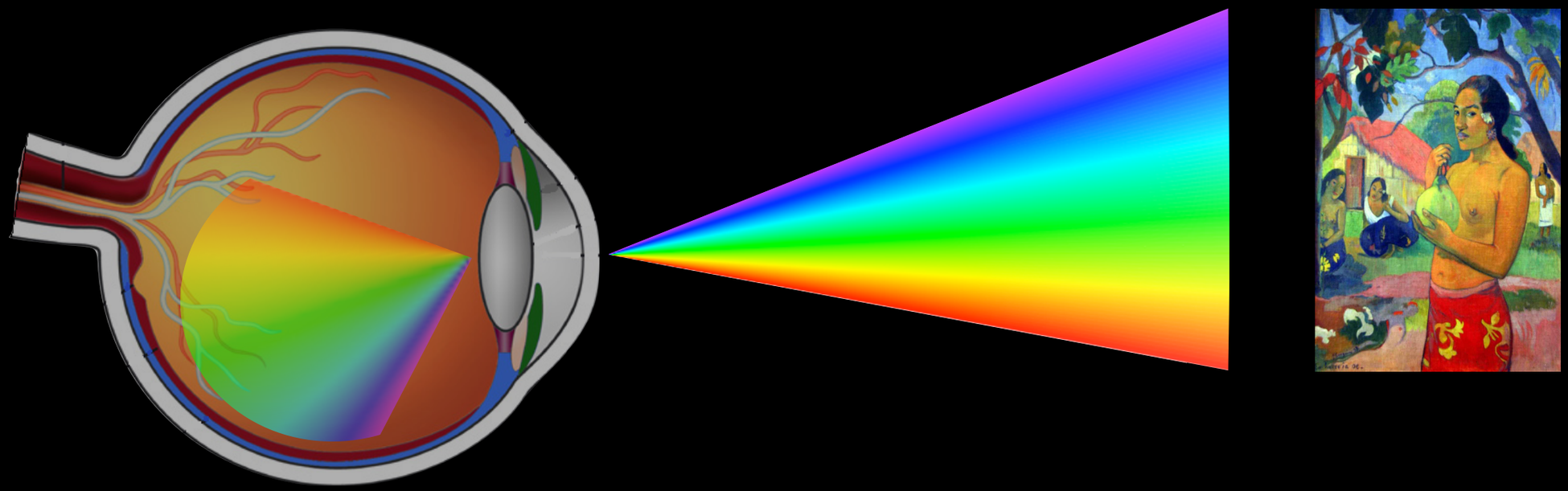

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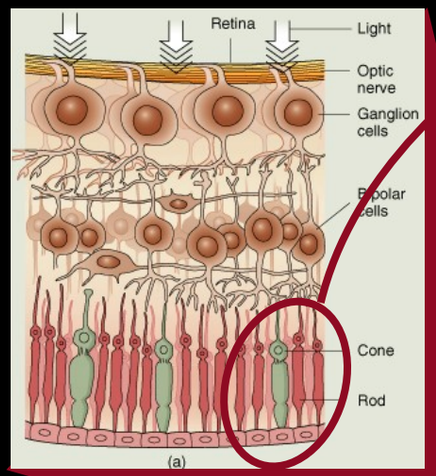

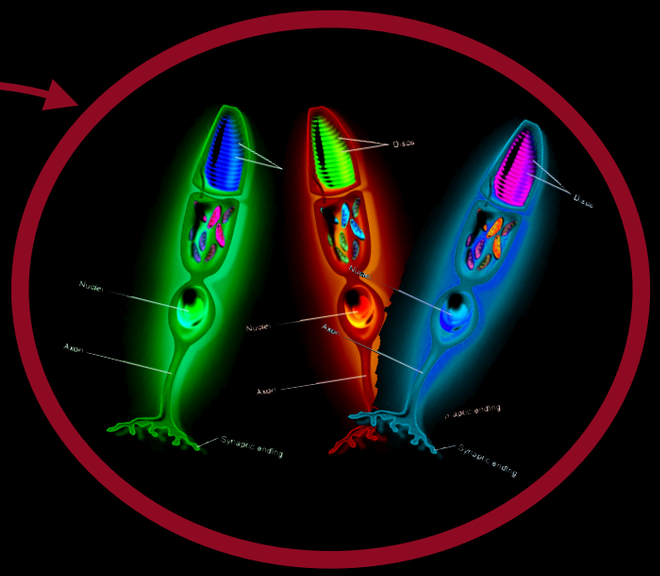

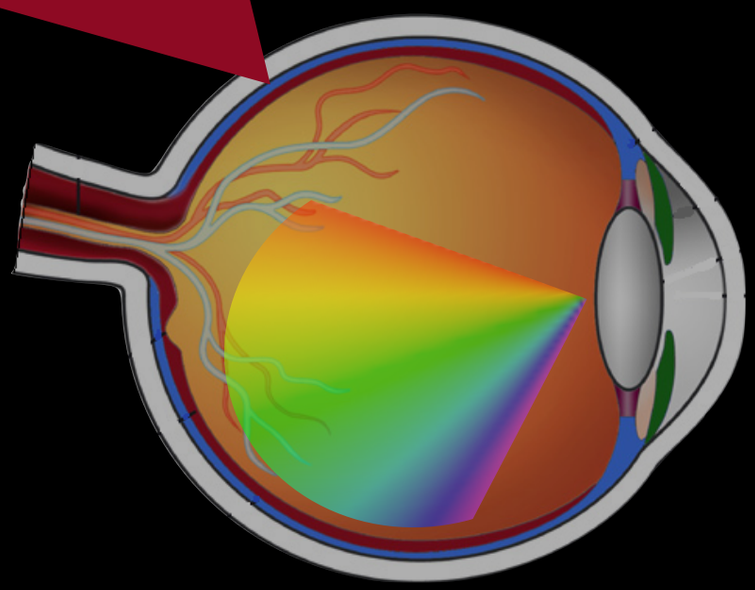

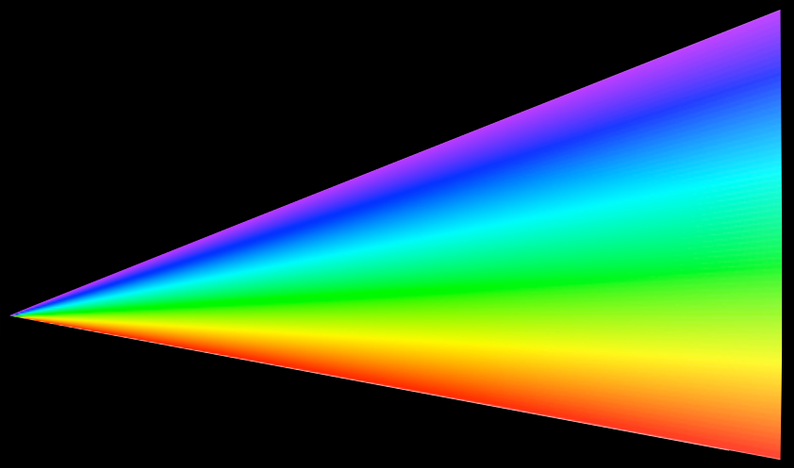

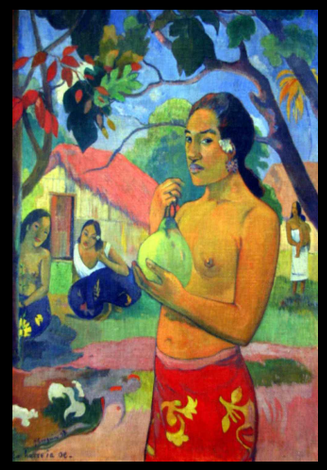

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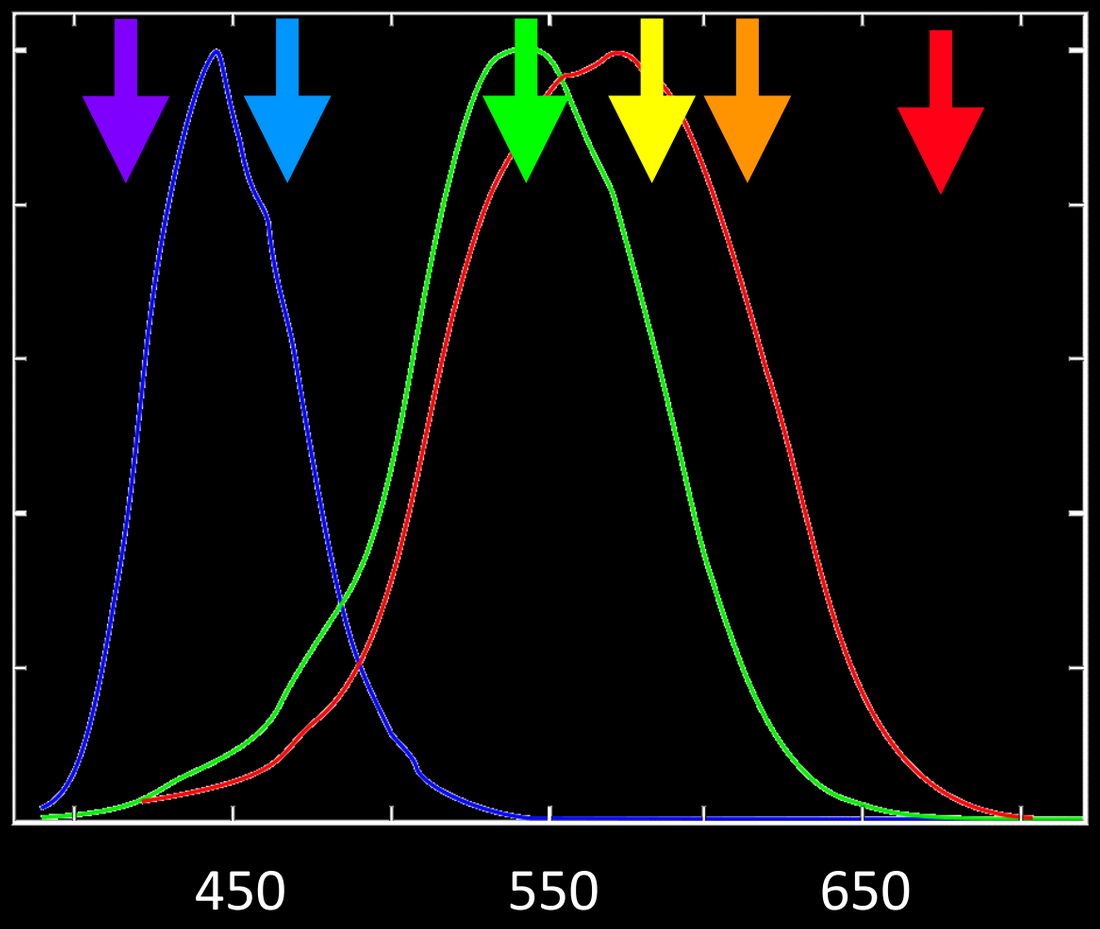
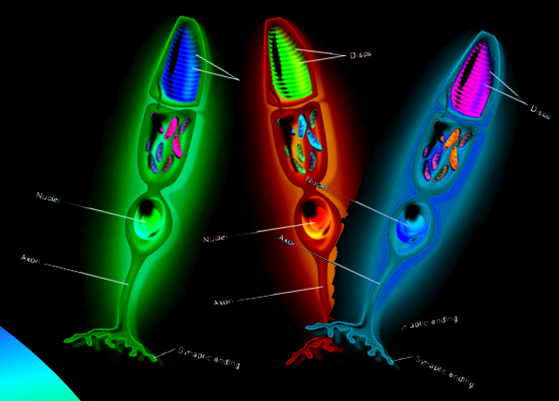
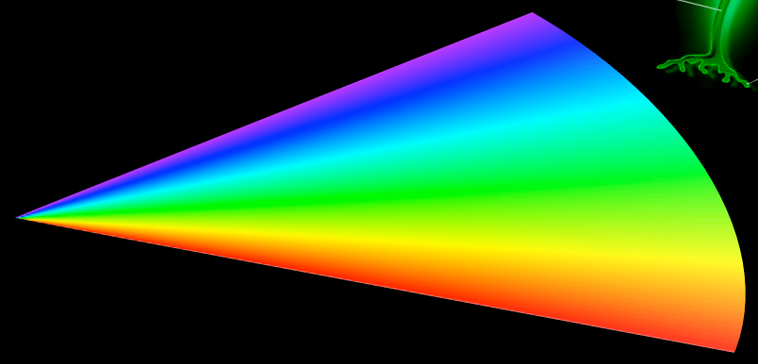


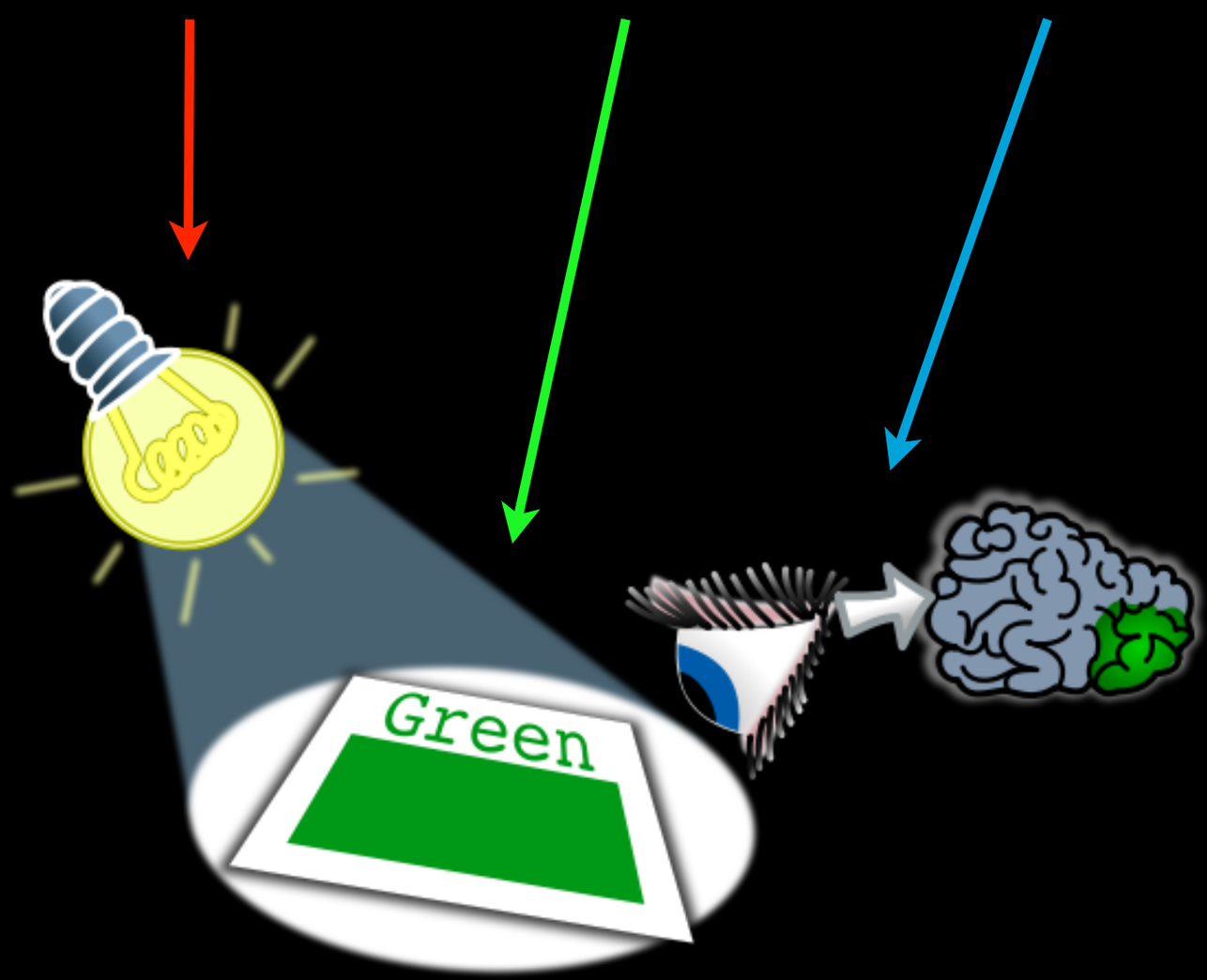


anycolor(λ) = r(λ) + g(λ) + b(λ)



what makes things look the color they have

stimulus =
illuminant × trasmission × sensitivity



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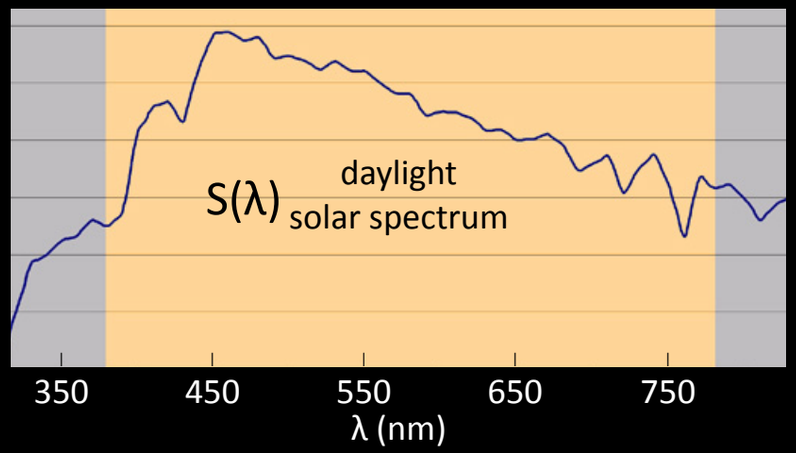

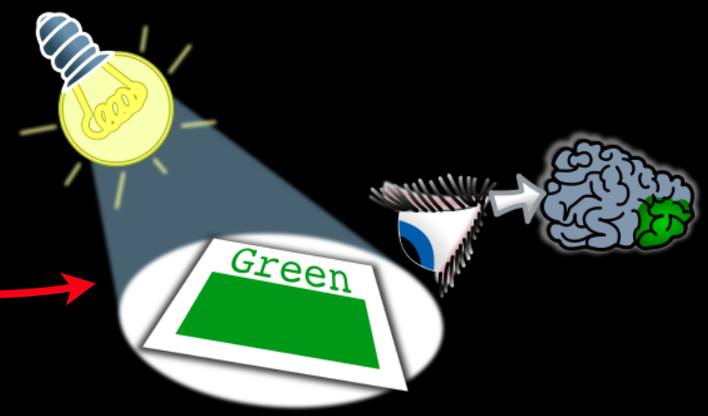

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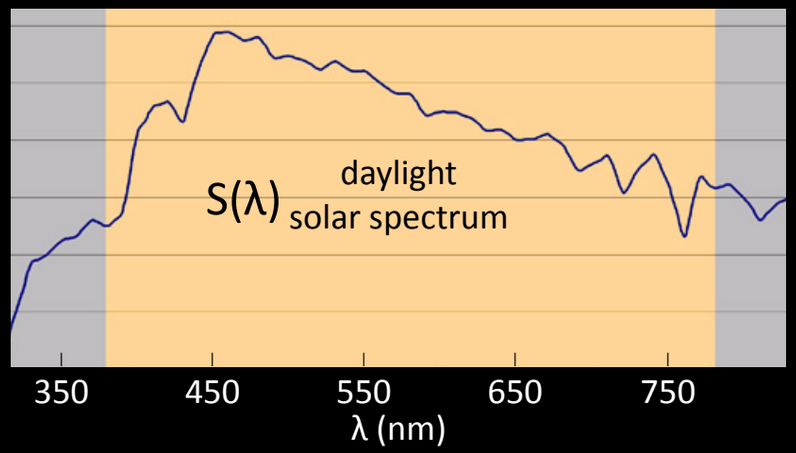
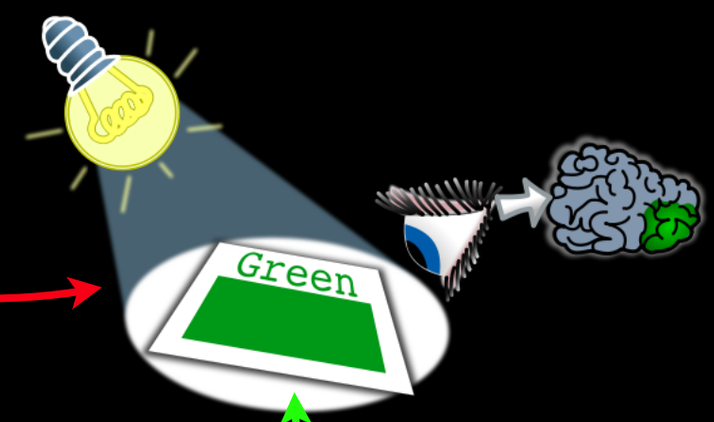
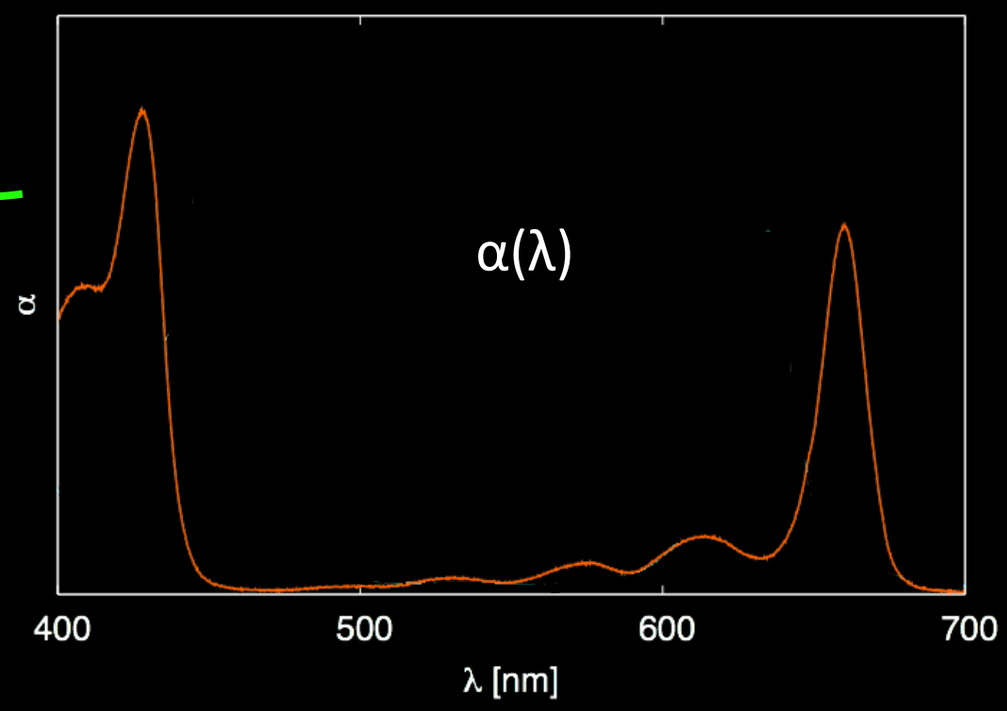




stimulus =
illuminant × trasmission × sensitivity

$$\mathsf{T}(x,\lambda) = \mathsf{S}(\lambda)\mathrm{e}^{-\alpha(\lambda)x}$$



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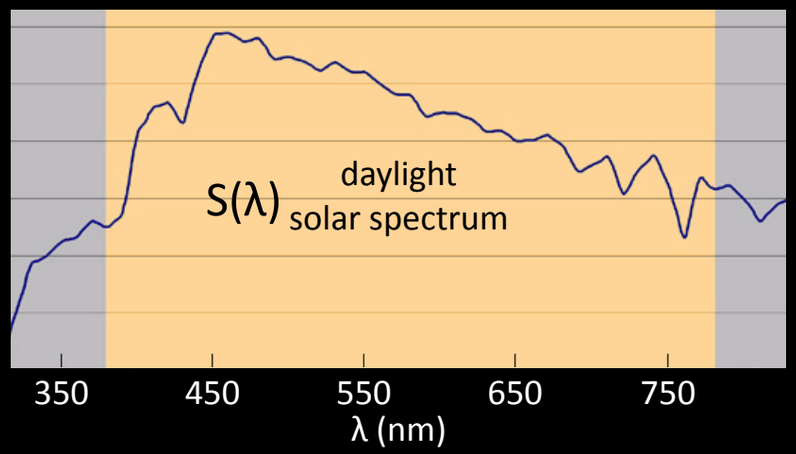

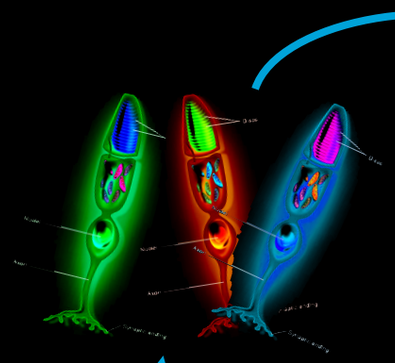

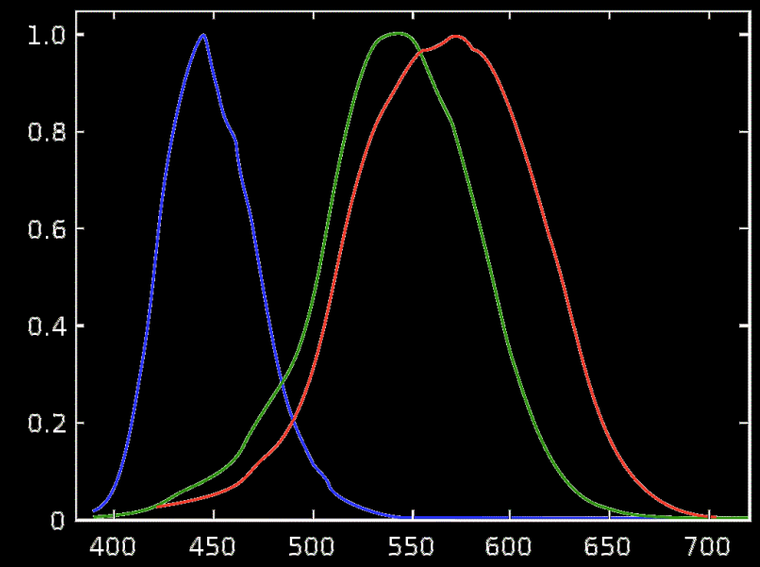

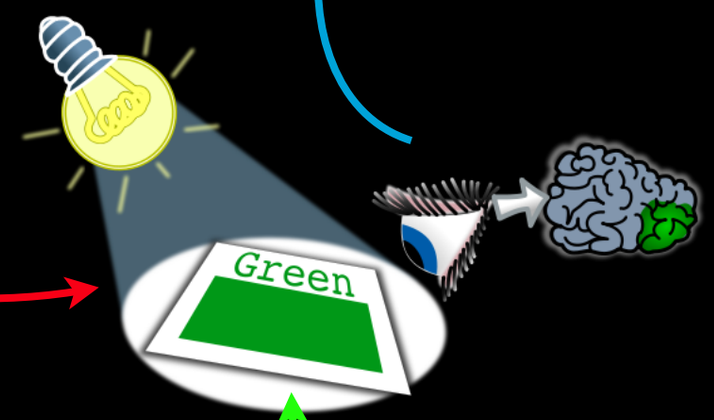

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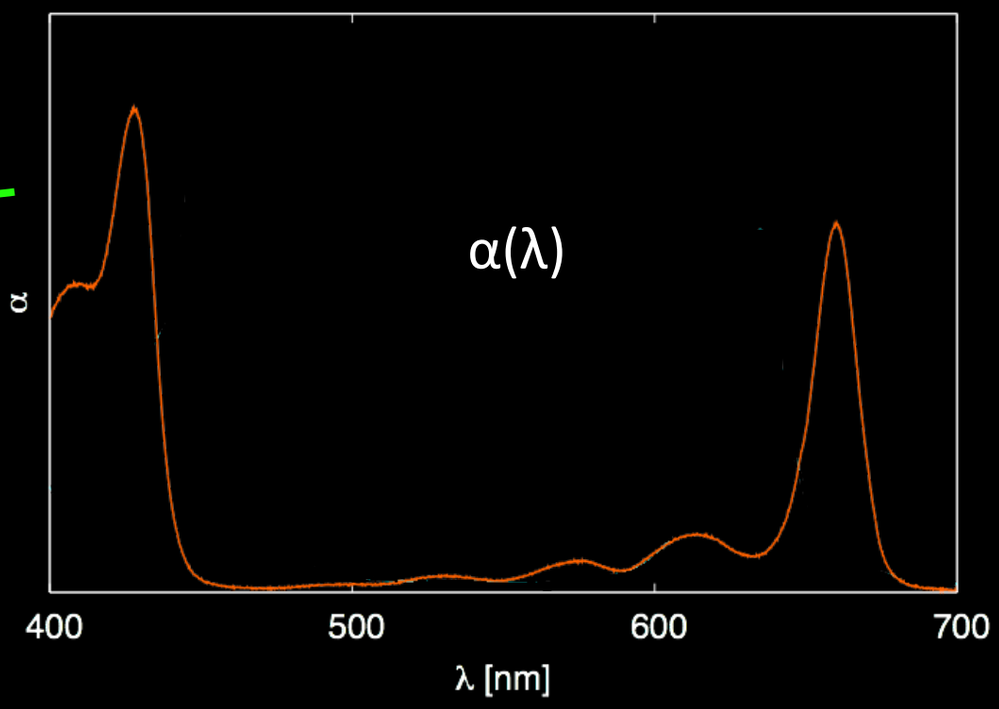
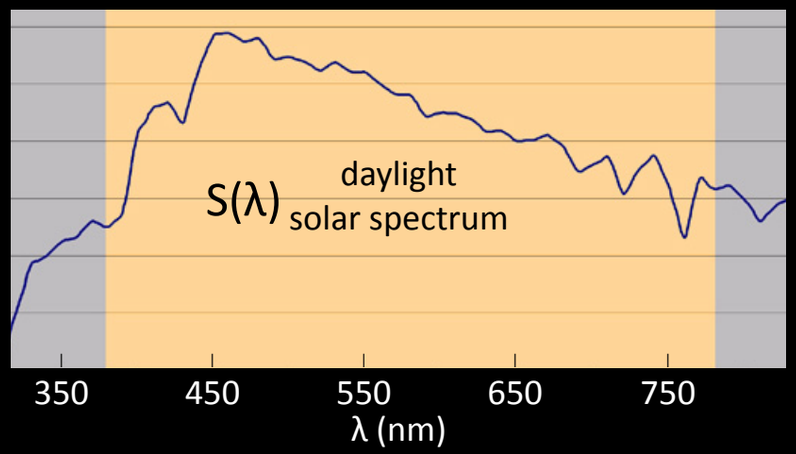
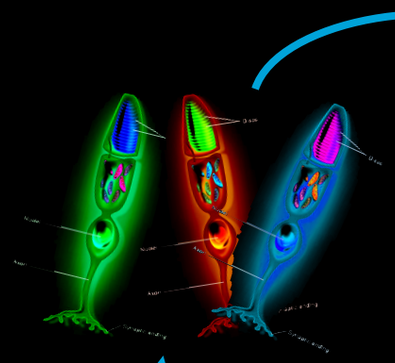
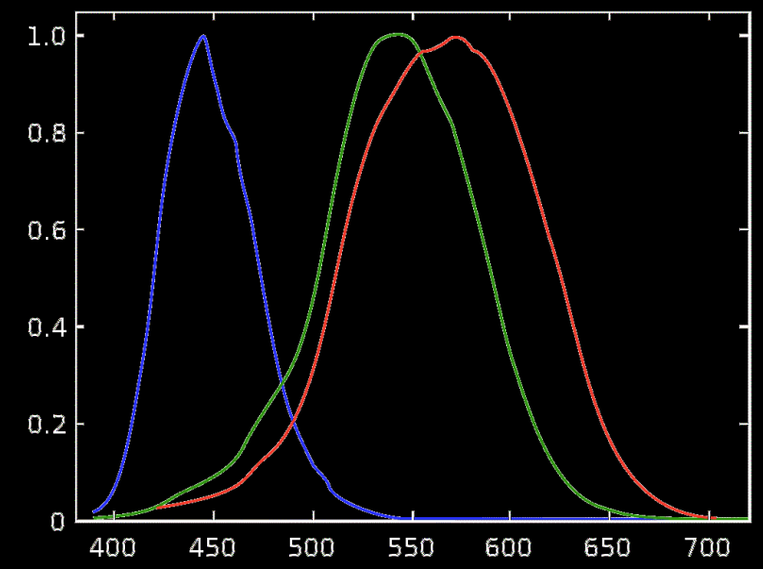
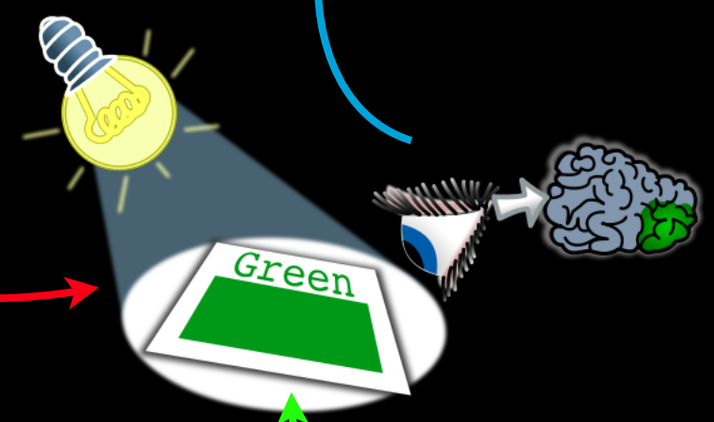


what makes things look the color they have

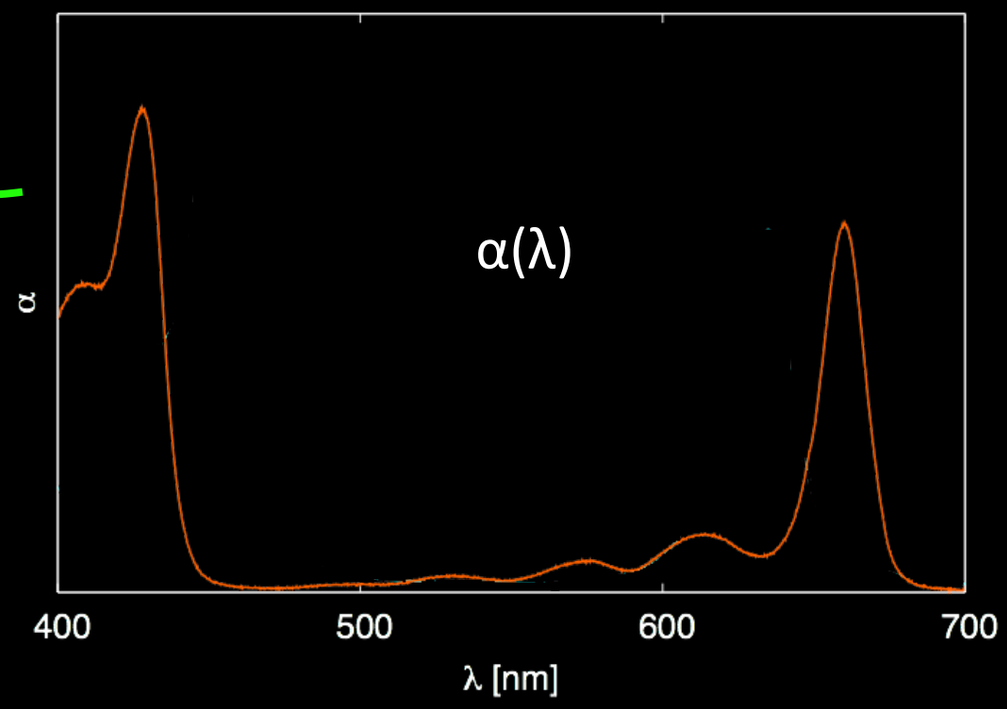




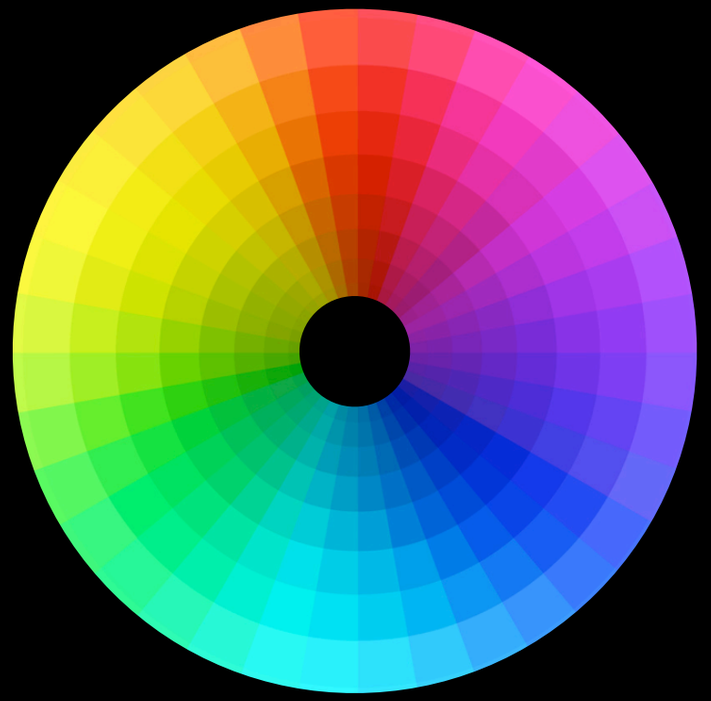




$$\mathrm{RGB}(x) = \int \mathrm{S}(\lambda)\mathrm{e}^{-\alpha(\lambda)x}\,\mathrm{rgb}(\lambda)d\lambda$$



a puzzle for you



optical spectra from TDDF (perturbation) T

$$i\frac{\partial \phi_v(\mathbf{r},t)}{\partial t} = \big(-\Delta + v_{KS}(\mathbf{r},t)\big)\phi_v(\mathbf{r},t)$$

$$v_{KS}(\mathbf{r},t) = v(\mathbf{r},t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}[n](\mathbf{r},t)$$

$$n(\mathbf{r},t) = \sum_v |\phi_v(\mathbf{r},t)|^2$$

E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984)

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E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984)

$$\rho(t) = \sum_v |\phi_v(t)\rangle\langle\phi_v(t)|$$

$$\langle A(t)\rangle = \mathsf{Tr}\big(\rho(t)A\big)$$

$$i\dot{\rho}(t) = \big[H_{KS}(t), \rho(t)\big]$$

optical spectra from TDDF (perturbation) T

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optical spectra from TDDF (perturbation) T

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$$\rho(t) = \rho^{\circ} + \rho'(t)$$
$$H_{KS}(t) = H^{\circ} + V'_{ext}(t) + V'_{HXC}(t)$$

$$i\ \dot{\rho}' = [H^{\circ},\rho'] + [V'_{HXC}, \rho^{\circ}] + [V'_{ext}, \rho^{\circ}] + \mathcal{O}\left(V'^{2}\right)$$

optical spectra from TDDF (perturbation) T

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$$i\ \dot{\rho}' = \mathcal{L}\ \rho' + [V'_{ext}, \rho^{\circ}]$$

optical spectra from TDDF (perturbation) T

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$$i\ \dot{\rho}' = [H^{\circ},\rho'] + [V'_{HXC}(\rho'), \rho^{\circ}] + [V'_{ext}, \rho^{\circ}]$$

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^{\circ}]$$

optical spectra from TDDF (perturbation) T

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free oscillations

$$\mathcal{L}\ \tilde{\rho}' = \omega\tilde{\rho}'$$

optical spectra from TDDF (perturbation) T

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^{\circ}]$$

free oscillations

$$\mathcal{L}\ \tilde{\rho}' = \omega\tilde{\rho}' \longrightarrow$$

excitation energies
and oscillator strenghts

optical spectra from TDDF (perturbation) T

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optical spectra from TDDF (perturbation) T

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^{\circ}]$$

$$\boldsymbol{\alpha}(\omega) \quad = \quad \mathsf{Tr}\big(\mathbf{d}\tilde{\rho}'(\omega)\big)$$

optical spectra from TDDF (perturbation) T

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^{\circ}]$$

$$\begin{aligned} \boldsymbol{\alpha}(\omega) &= \mathsf{Tr}\big(\mathbf{d}\tilde{\rho}'(\omega)\big) \\ &= \big(\mathbf{d}, (\omega - \mathcal{L})^{-1} \cdot [\tilde{V}'_{ext}(\omega), \rho^{\circ}]\big) \end{aligned}$$

optical spectra from TDDF (perturbation) T

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^{\circ}]$$

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&= \big(\mathbf{d}, (\omega - \mathcal{L})^{-1} \cdot [\tilde{V}'_{ext}(\omega), \rho^{\circ}]\big) \\
&\equiv \big(u, (\omega - \mathcal{L})^{-1} \cdot v\big)
\end{aligned}$$

the Lanczos connection

$$g(\omega) = \langle \phi_0 | (\omega - \mathcal{H})^{-1} | \phi_0 \rangle$$

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J. Phys. C: Solid State Phys., Vol. 5, 1972. Printed in Great Britain. © 1972

Electronic structure based on the local atomic environment for tight-binding bands

R HAYDOCK, VOLKER HEINE and M J KELLY
Cavendish Laboratory, Cambridge, UK

the Lanczos connection

$$g(\omega) = \langle \phi_0 | (\omega - \mathcal{H})^{-1} | \phi_0 \rangle$$

$$\begin{aligned}
\phi_{-1} &= 0 \\
b_{n+1}\phi_{n+1} &= (\mathcal{H} - a_n)\phi_n - b_n\phi_{n-1} \\
\langle \phi_{n+1} | \phi_{n+1} \rangle &= 1 \\
a_n &= \langle \phi_n | \mathcal{H} | \phi_n \rangle
\end{aligned}$$

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a_n &= \langle \phi_n | \mathcal{H} | \phi_n \rangle
\end{aligned}$$

$$\mathcal{H} = \begin{pmatrix}
a_0 & b_1 & 0 & \cdots & 0 \\
b_1 & a_1 & b_2 & 0 & \vdots \\
0 & b_2 & a_2 & \ddots & 0 \\
\vdots & 0 & \ddots & \ddots & b_n \\
0 & \cdots & 0 & b_n & a_n
\end{pmatrix}$$

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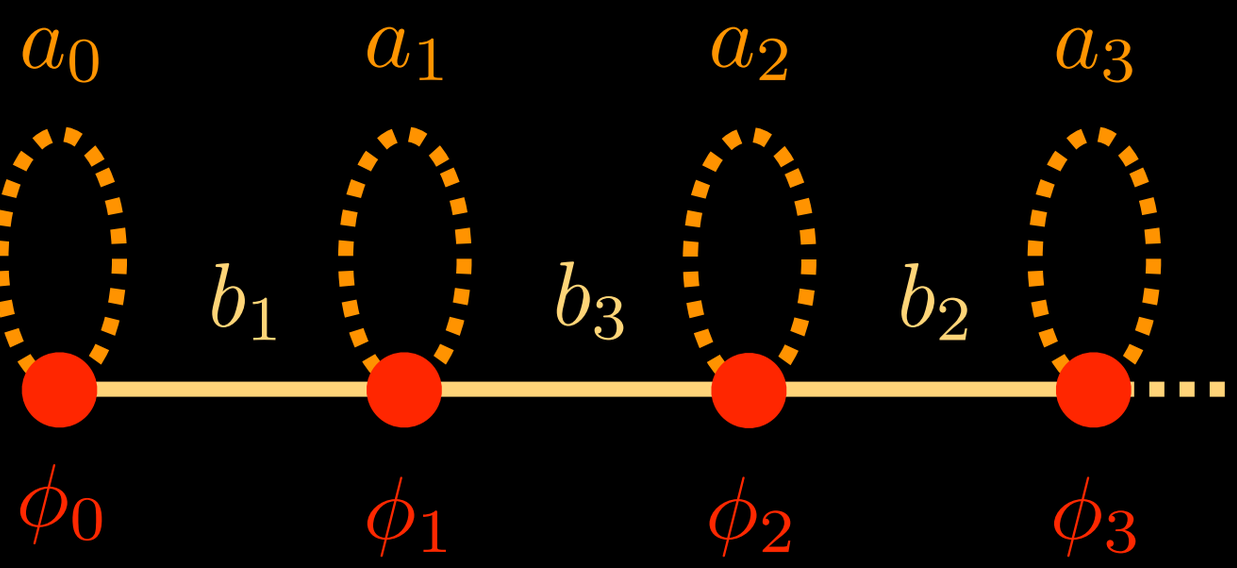

$$\mathcal{H} = \begin{pmatrix} a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & 0 & \vdots \\ 0 & b_2 & a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & b_n \\ 0 & \cdots & 0 & b_n & a_n \end{pmatrix}$$

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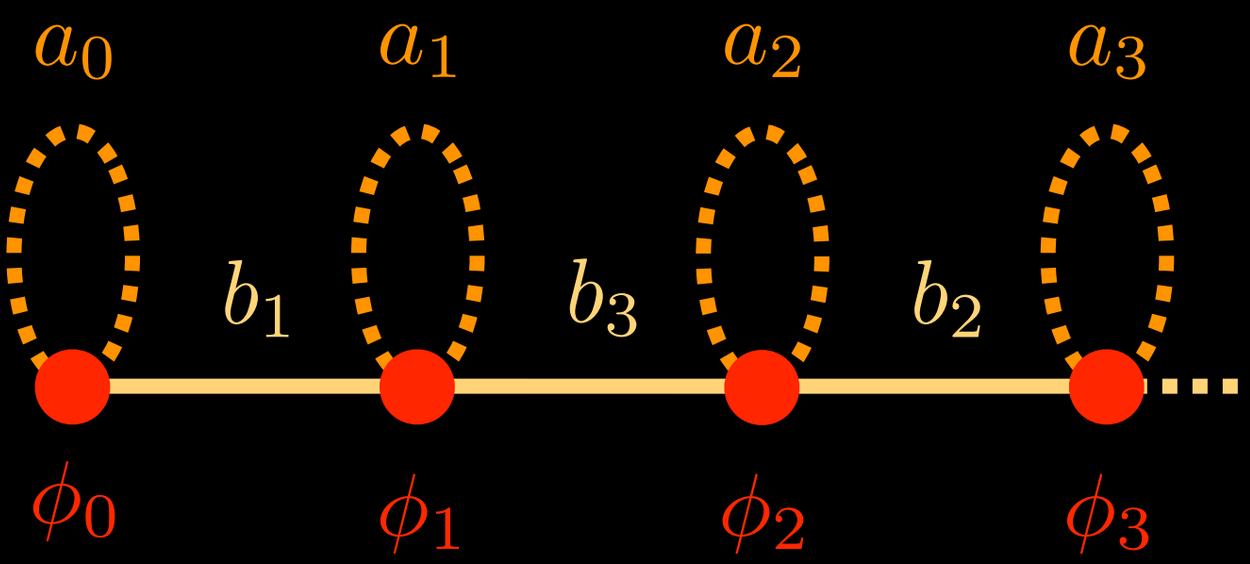

$$g(\omega) = \cfrac{1}{\omega - a_0 + \cfrac{b_1^2}{\omega - a_1 + \cfrac{b_2^2}{\omega - a_2 + \cdots}}}$$

the DFPT representation

$$\tilde{\rho}'(\omega) = \sum_v \Big(|\varphi'_v(\omega)\rangle\langle\varphi^\circ_v| + |\varphi^\circ_v\rangle\langle\varphi'_v(-\omega)| \Big)$$

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$$= \sum_{cv} \Big(X_{cv}(\omega)|\varphi^\circ_c\rangle\langle\varphi^\circ_v| + Y_{cv}(\omega)|\varphi^\circ_v\rangle\langle\varphi^\circ_c| \Big)$$

the DFPT representation

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$$= \sum_v \Big(|x_v\rangle\langle\varphi^\circ_v| + |\varphi^\circ_v\rangle\langle y_v| \Big) \qquad \rightarrow \begin{pmatrix} \{x_v\} \\ \{y_v\} \end{pmatrix}$$

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$$x_v(\mathbf{r}) \xrightarrow{\mathcal{L}} (H^\circ - \epsilon_v)x_v(\mathbf{r}) + P_c \sum_{v'} \int K_{vv'}(\mathbf{r},\mathbf{r}')\big(x_{v'}(\mathbf{r}') + y_{v'}(\mathbf{r}')\big)d\mathbf{r}'$$

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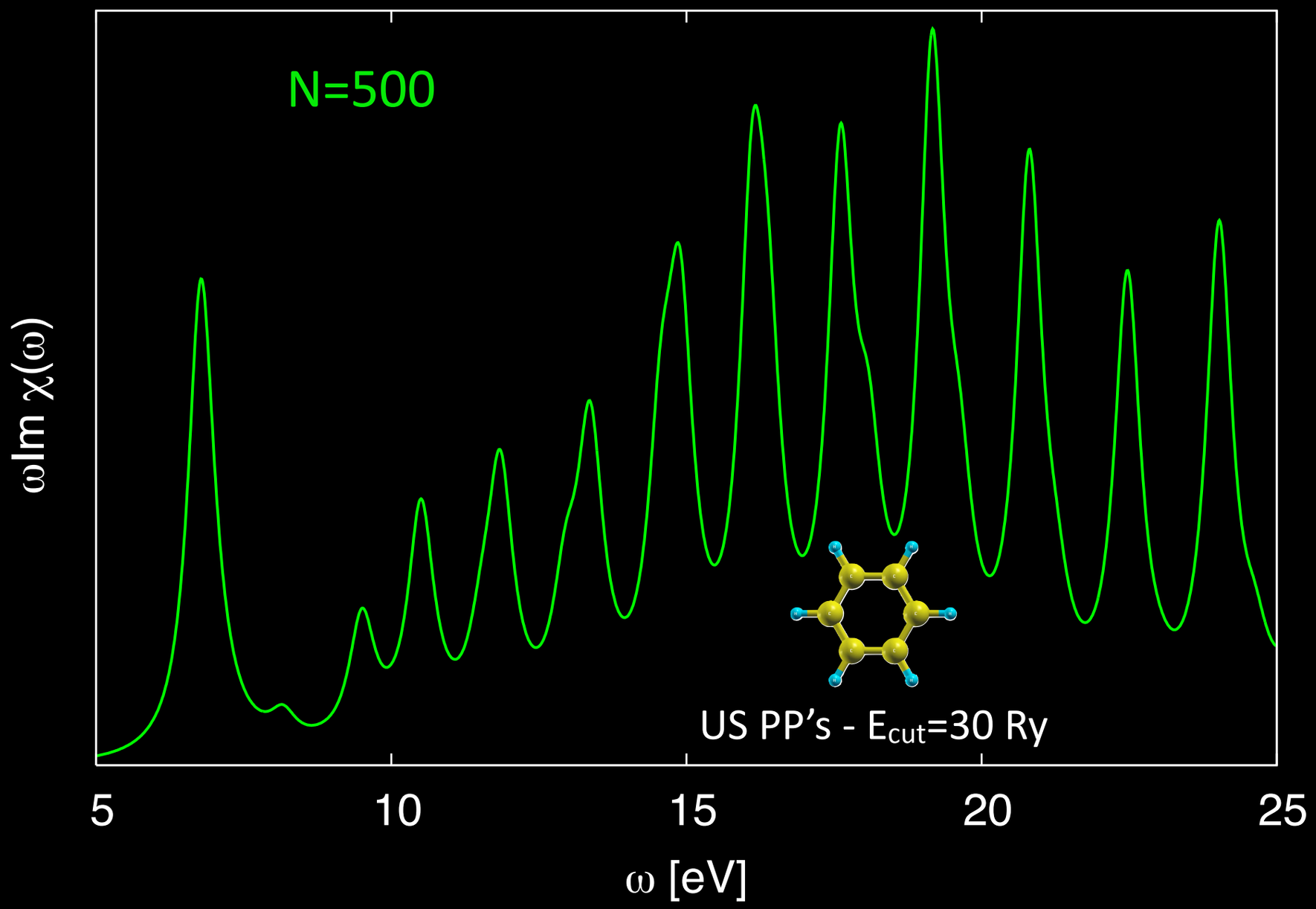
$$2\varphi^\circ_v(\mathbf{r})\varphi^\circ_{v'}(\mathbf{r}') \times \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \kappa_{XC}(\mathbf{r}-\mathbf{r}') \right)$$

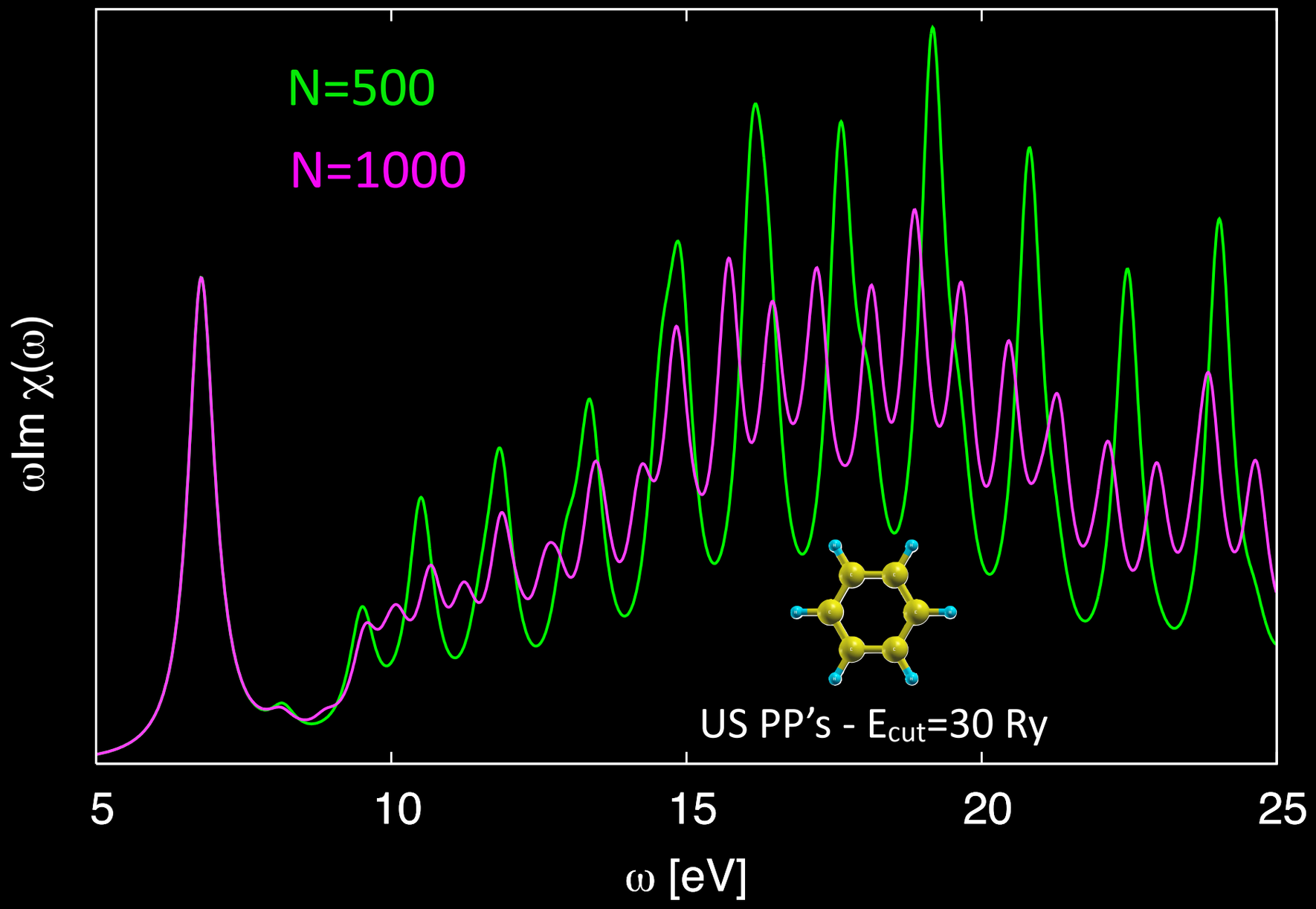
$$x_v(\mathbf{r}) \xrightarrow{\mathcal{L}} (H^\circ - \epsilon_v)x_v(\mathbf{r}) + P_c \sum_{v'} \int K_{vv'}(\mathbf{r},\mathbf{r}') \big(x_{v'}(\mathbf{r}') + y_{v'}(\mathbf{r}') \big) d\mathbf{r}'$$

$$= (H^\circ - \epsilon_v)x_v(\mathbf{r}) + P_c V'_{HXC}(\mathbf{r})\varphi^\circ_v(\mathbf{r})$$

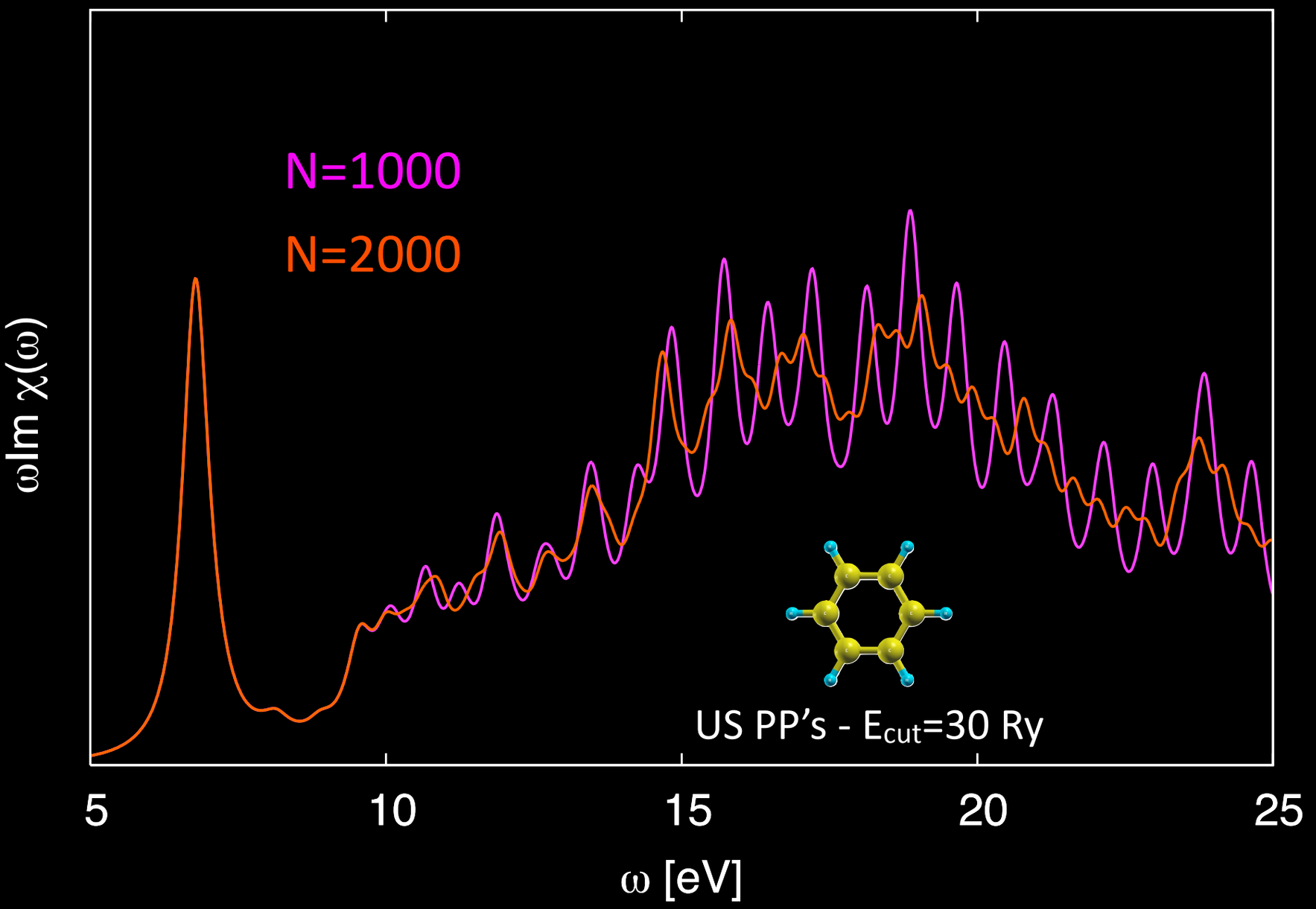
benzene, a benchmark



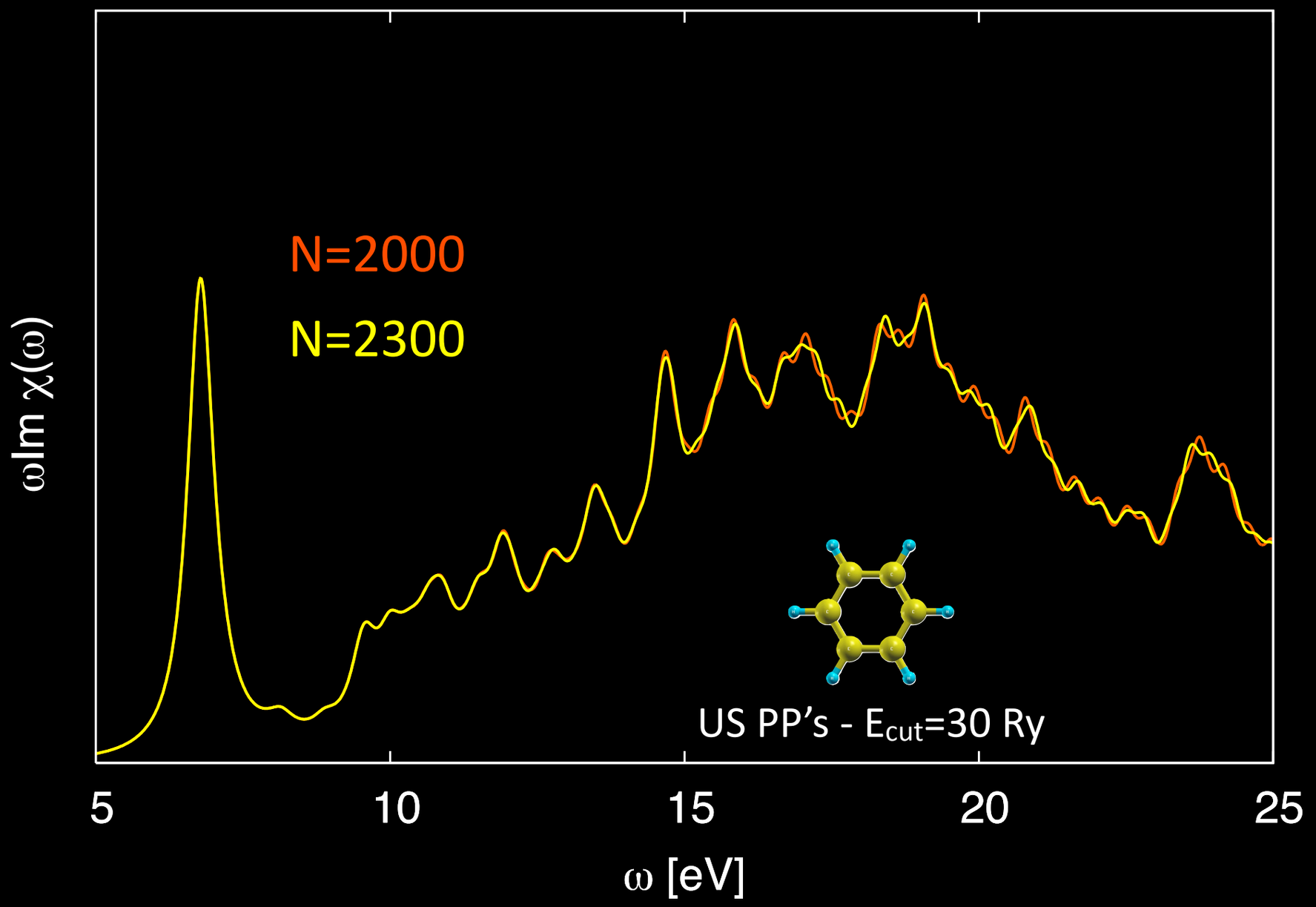
benzene, a benchmark



benzene, a benchmark



benzene, a benchmark



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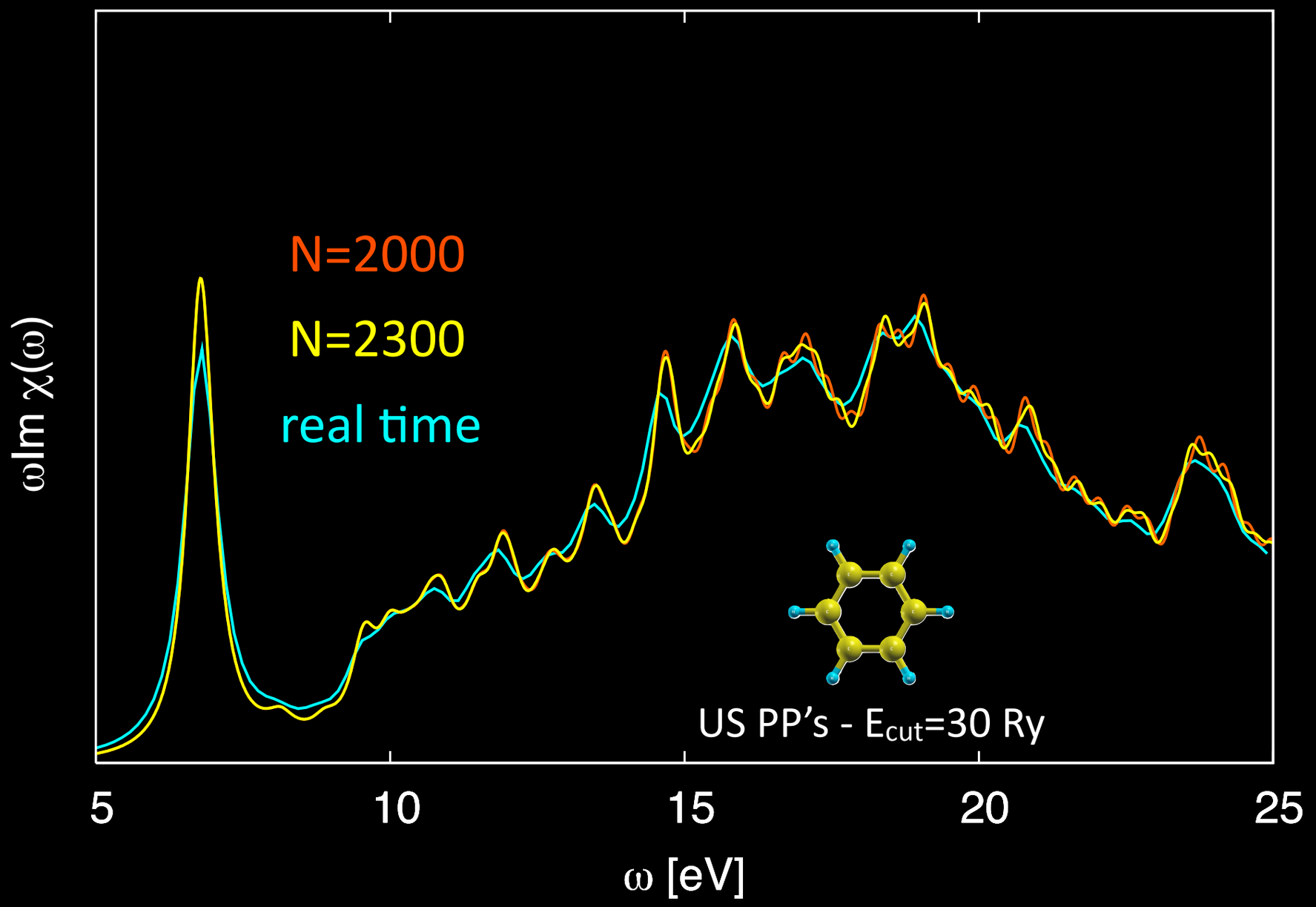

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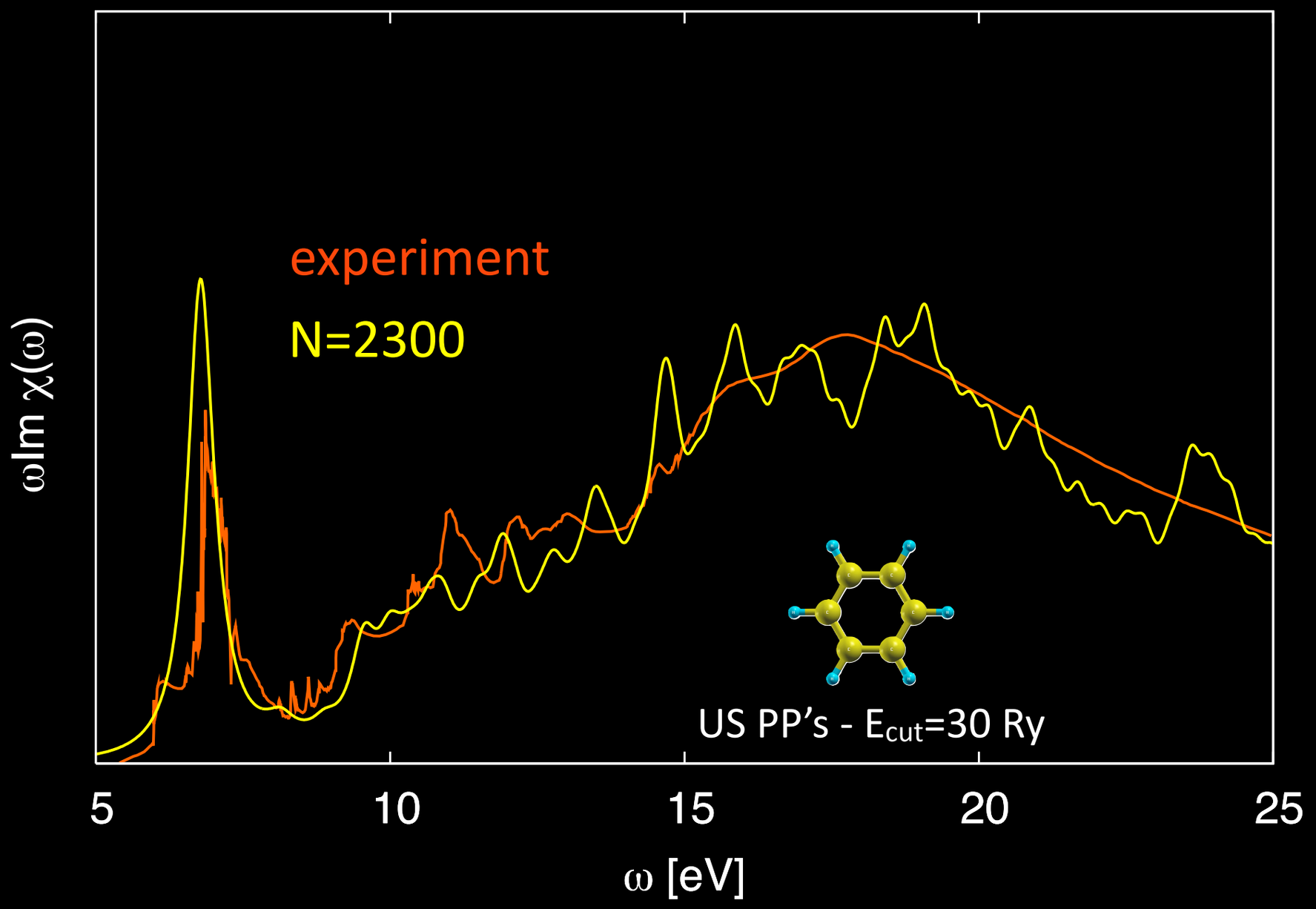
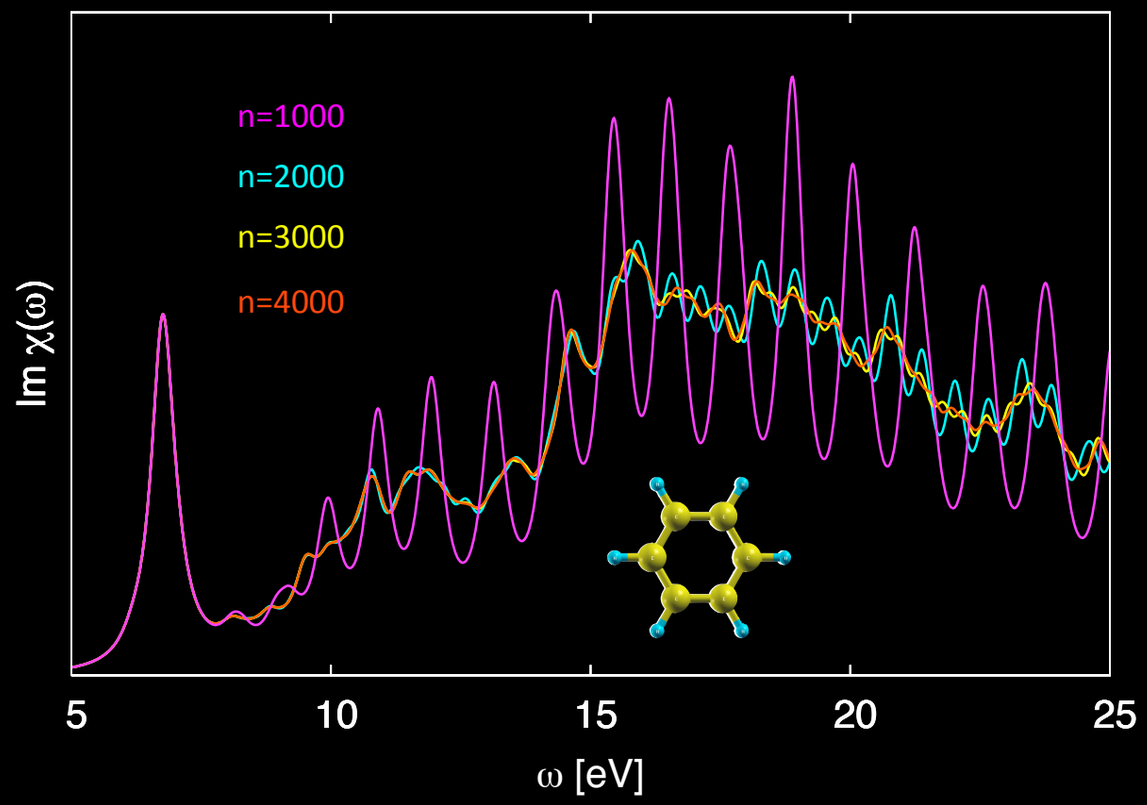


speeding up the convergence



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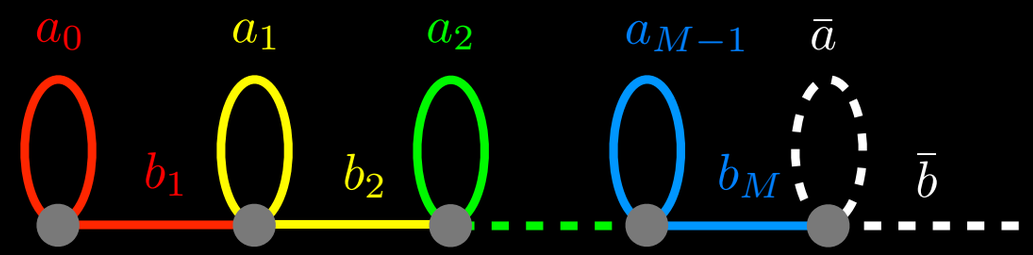

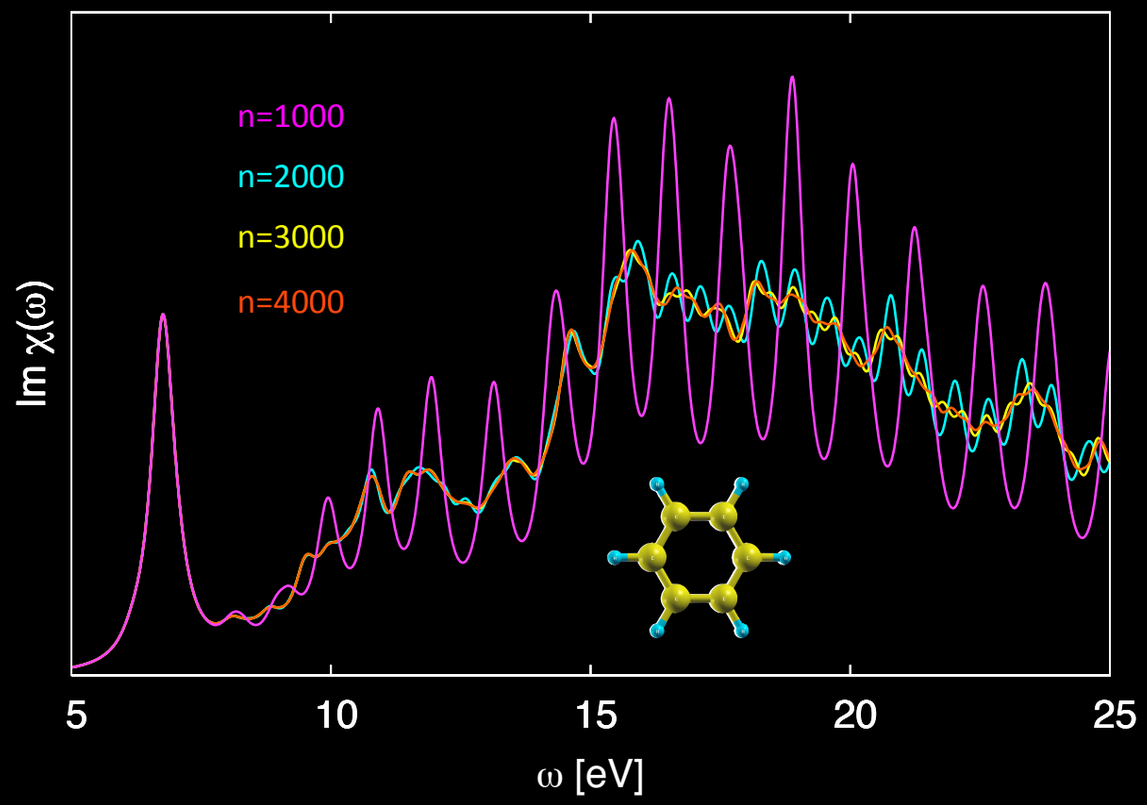

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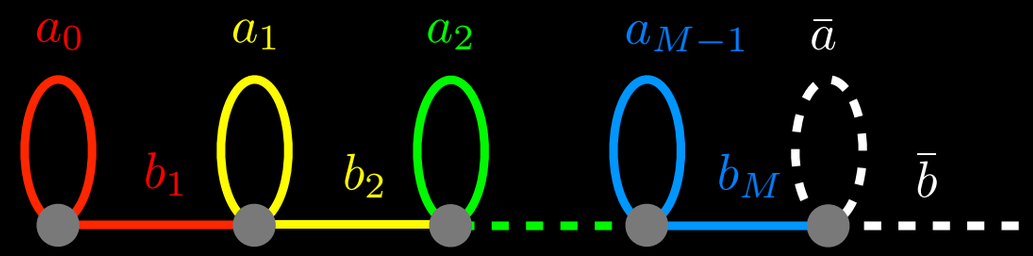
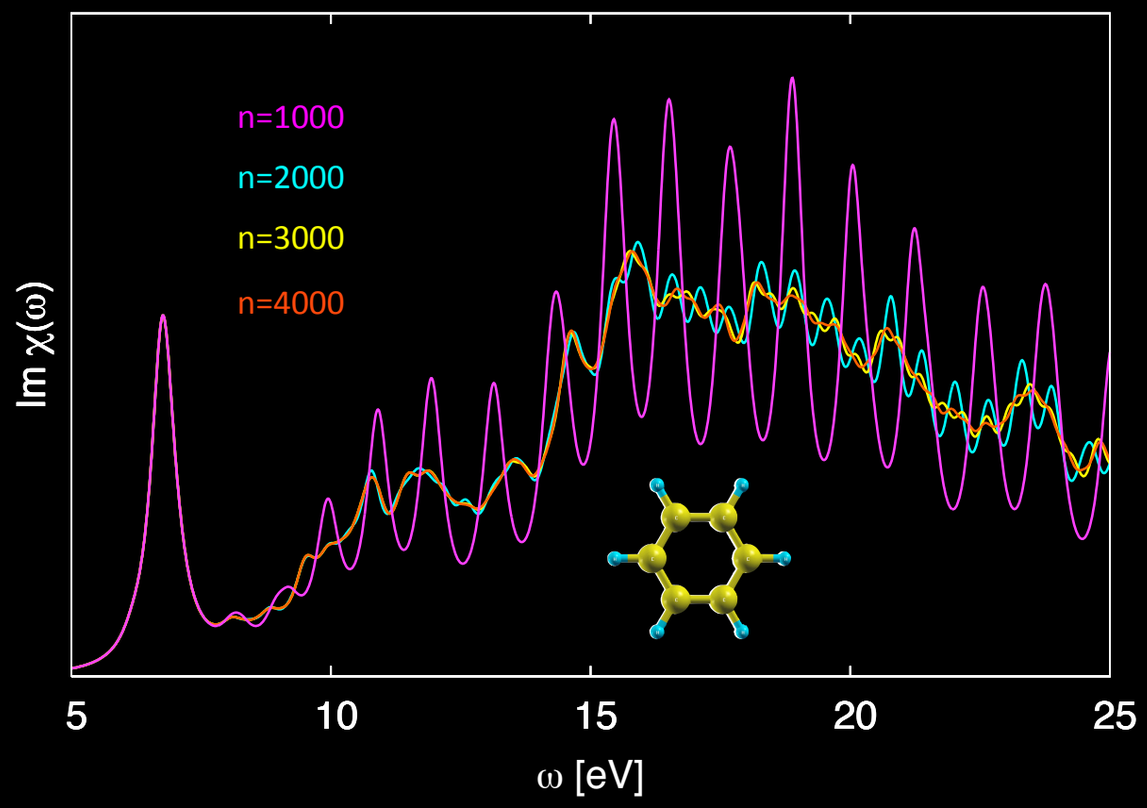
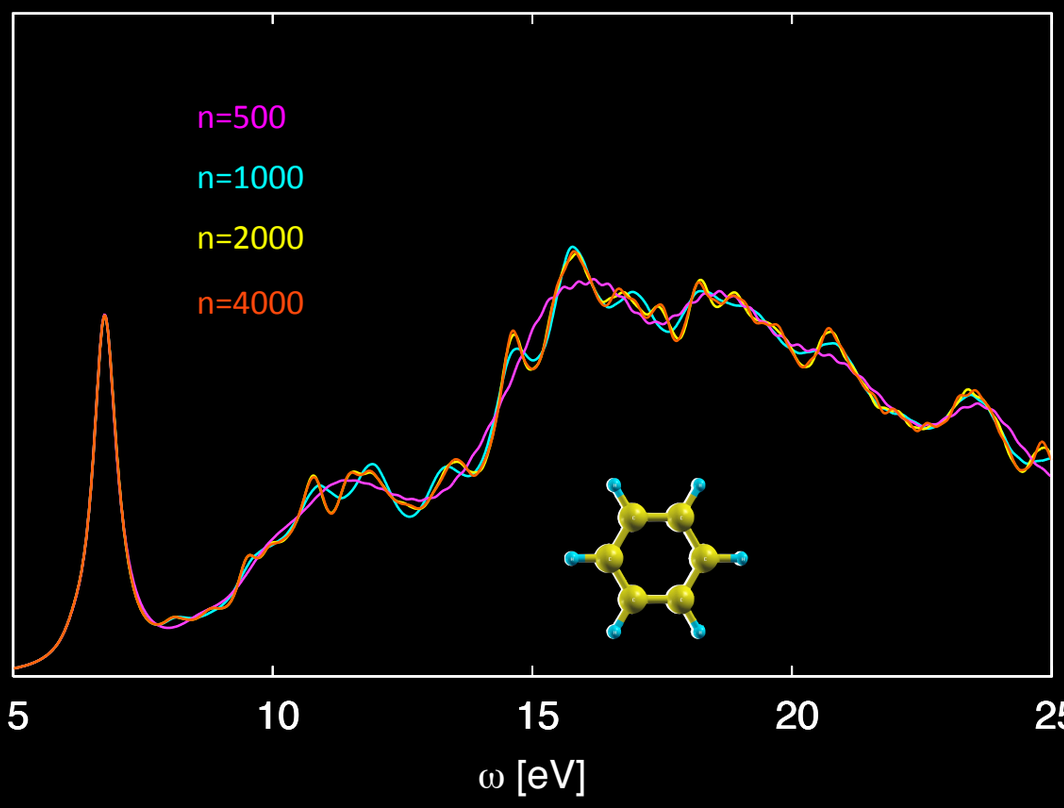


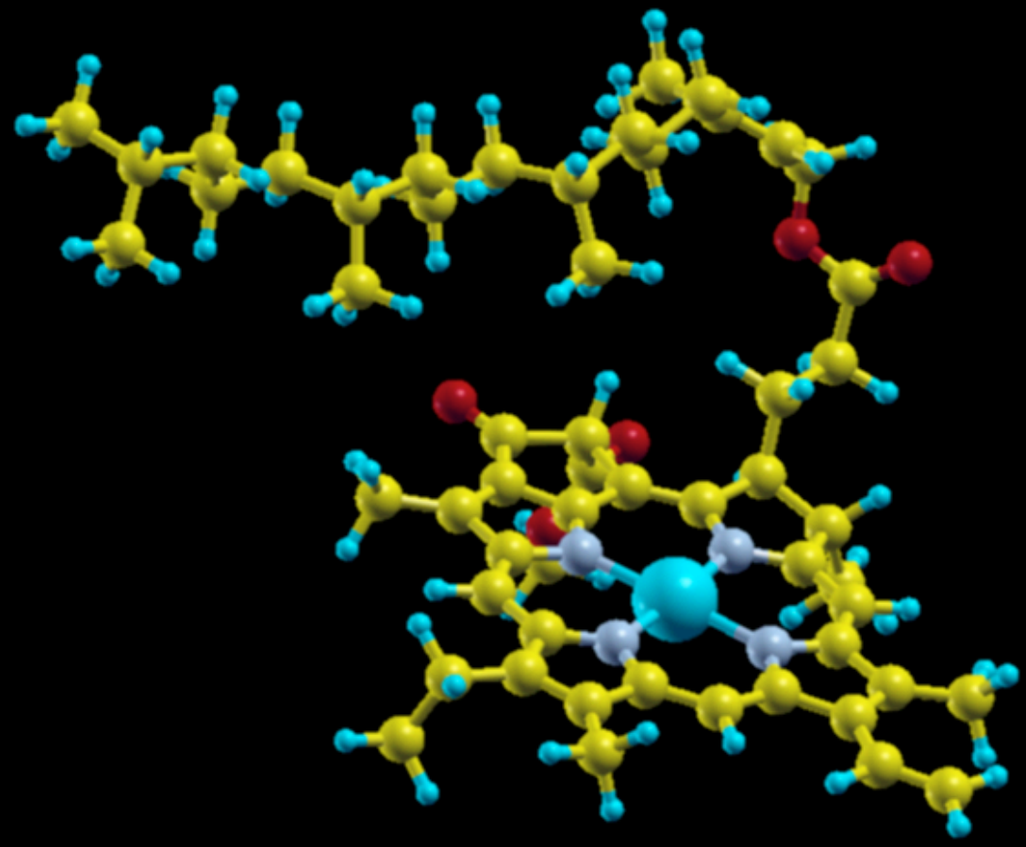




no extrapolation

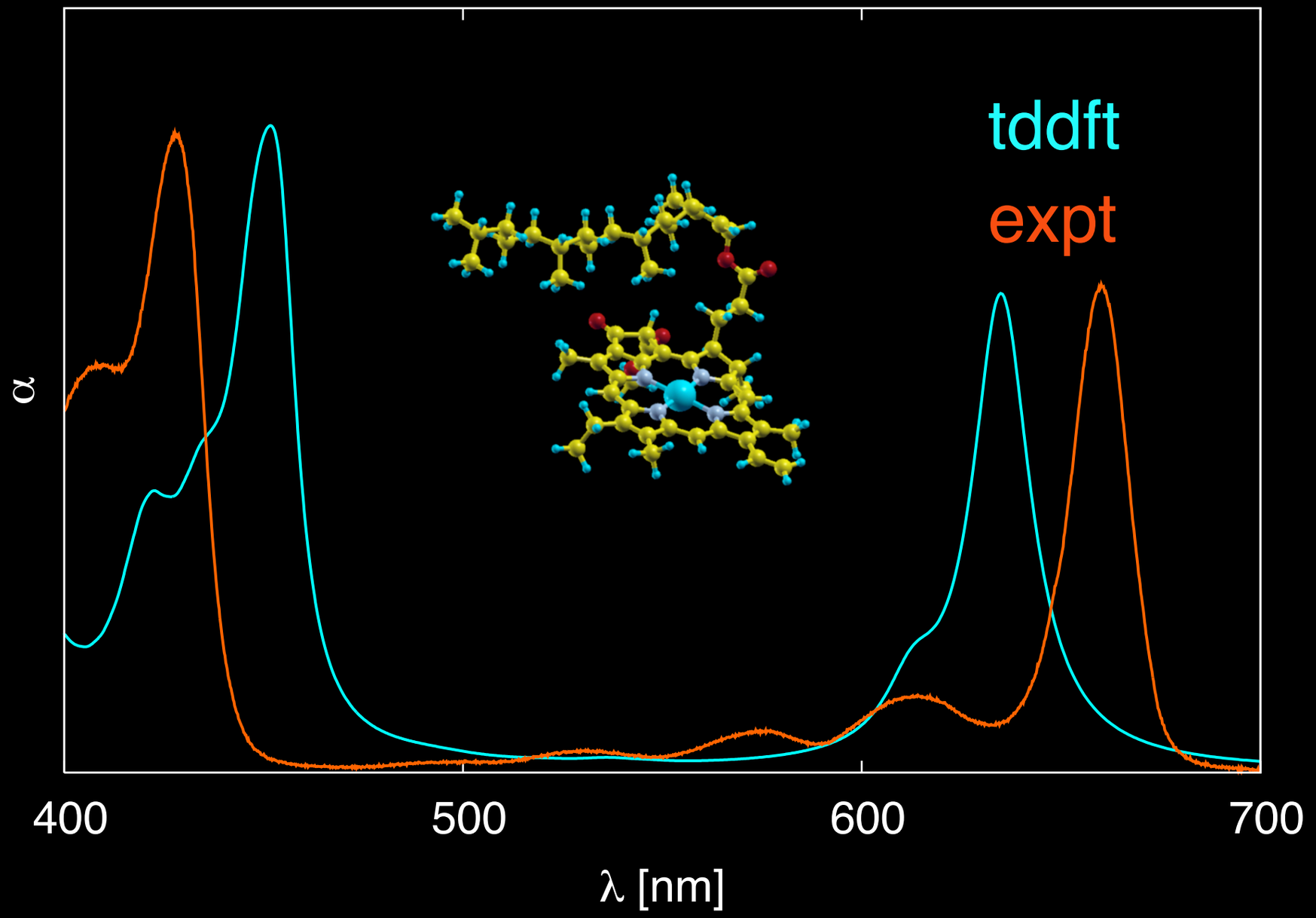
with extrapolation

chlorofyll a

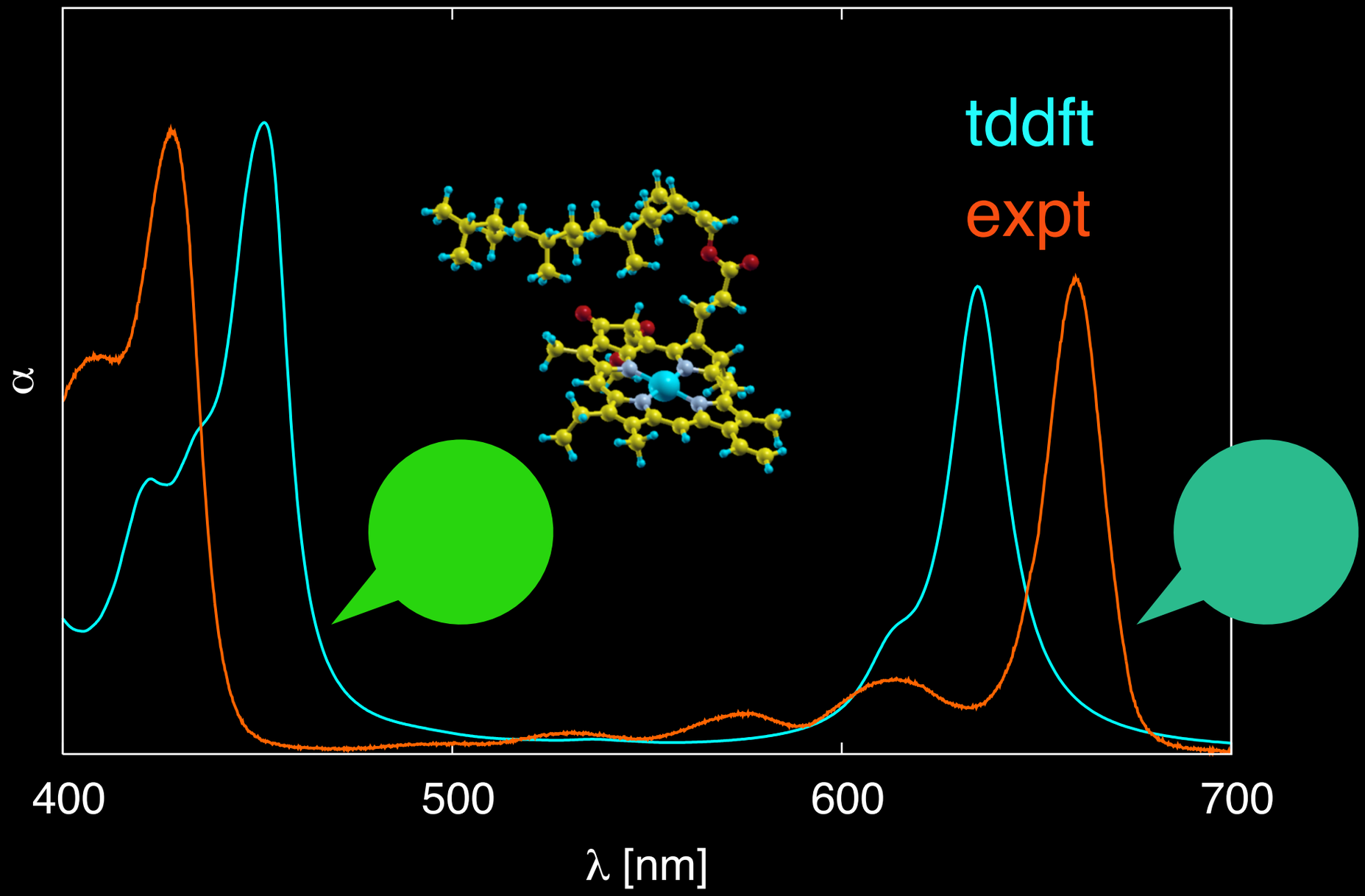


$C_{55}H_{72}MgN_4O$

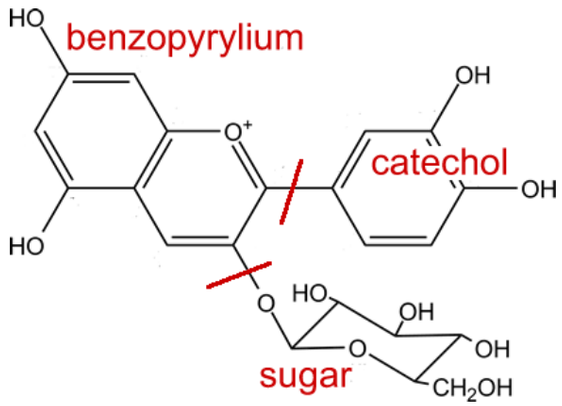
chlorofyll a



chlorofyll a

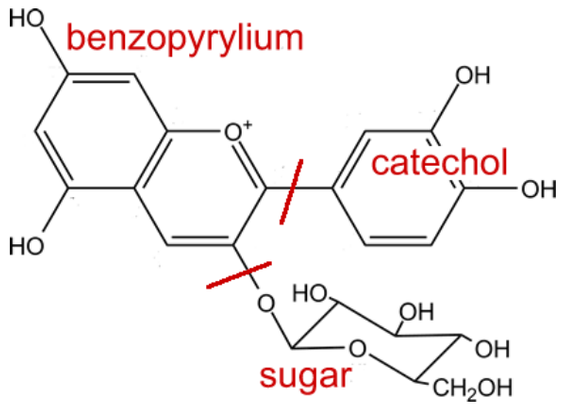


color and function of anthocyanins

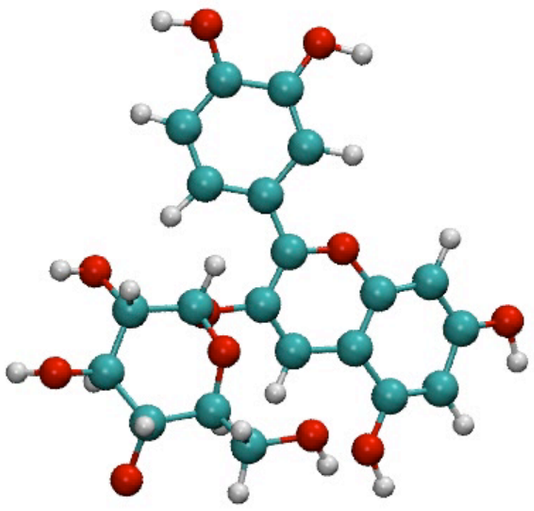


cyanidin-3-glucoside

color and function of anthocyanins

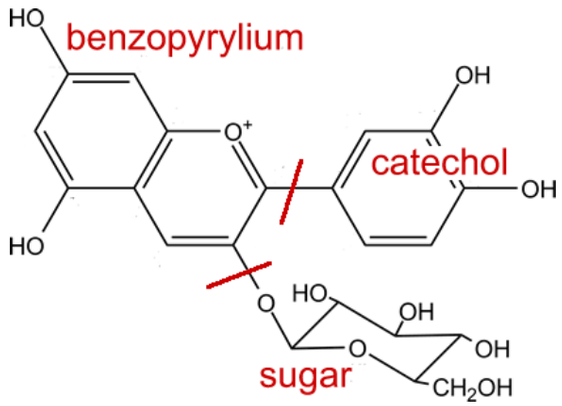


cyanidin-3-glucoside

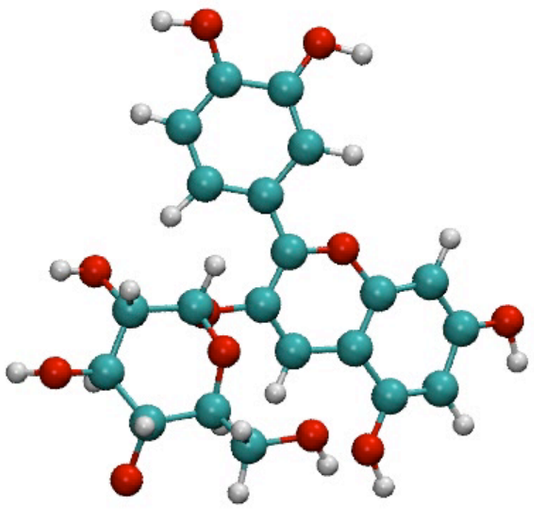


TDDFT ?

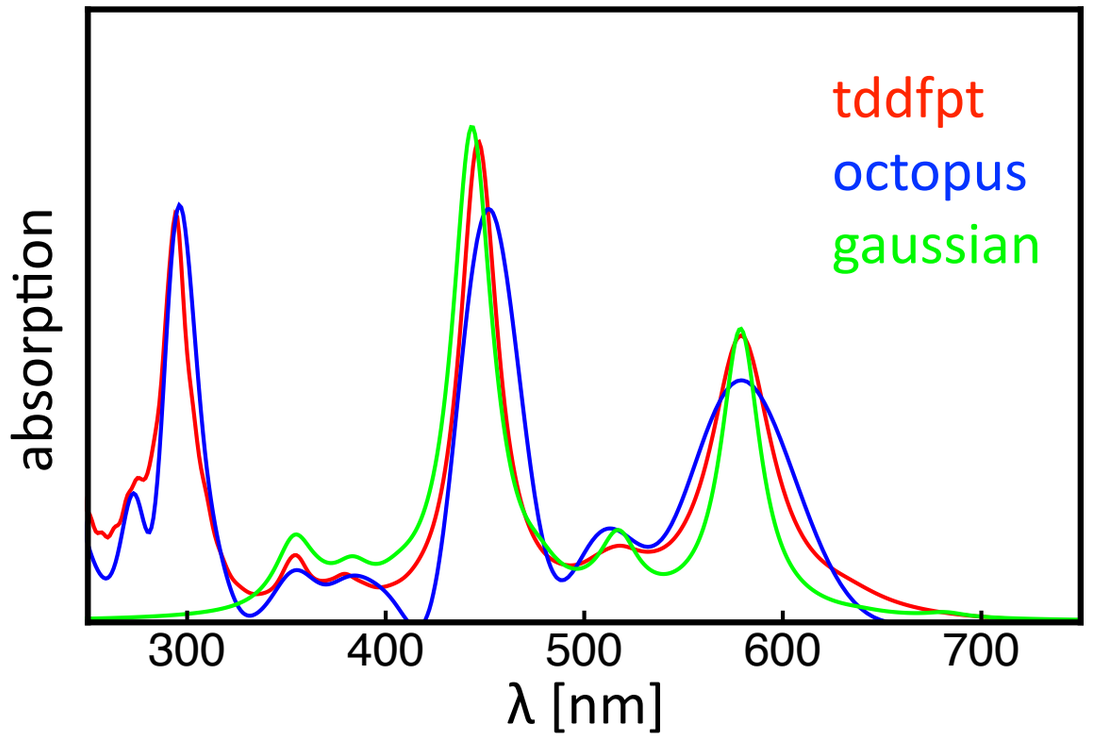
color and function of anthocyanins



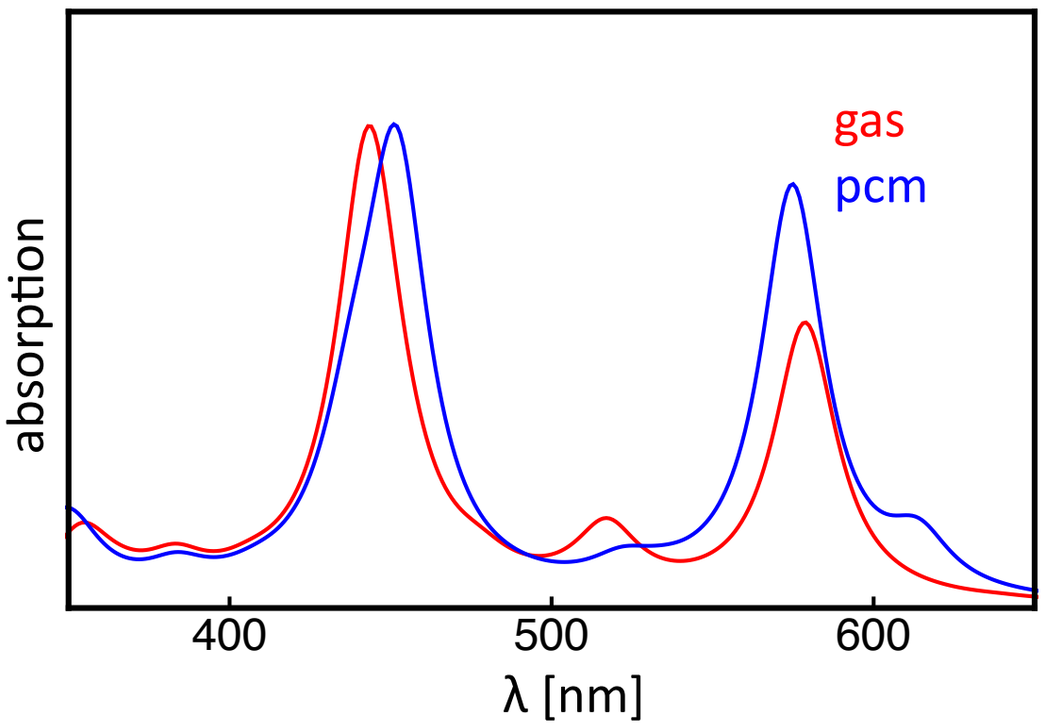
cyanidin-3-glucoside



TDDFT :-(



optical effect of the solvent



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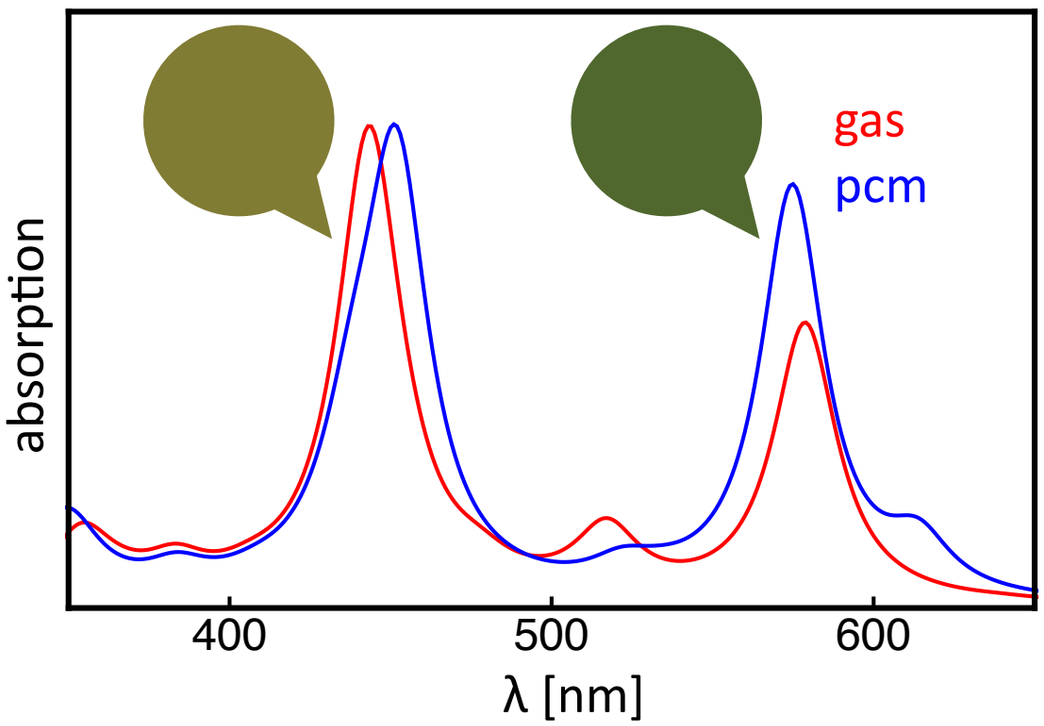
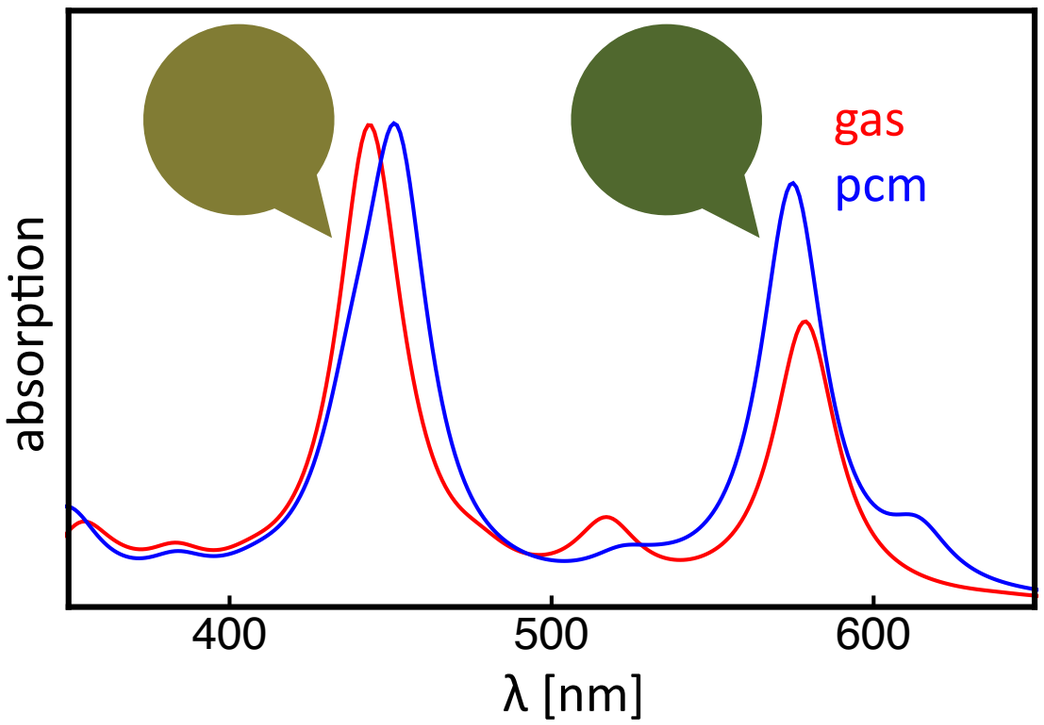
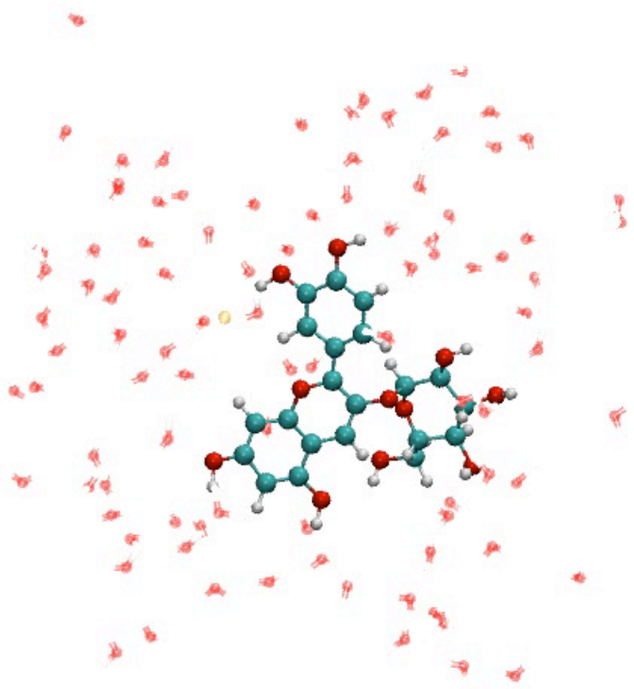


optical effect of the solvent



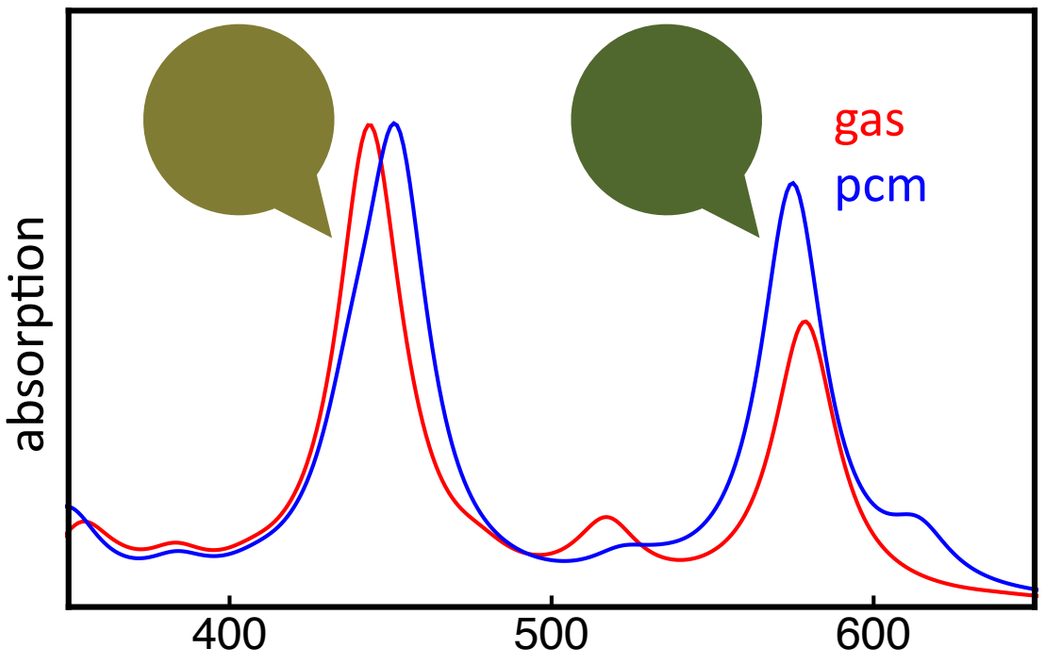


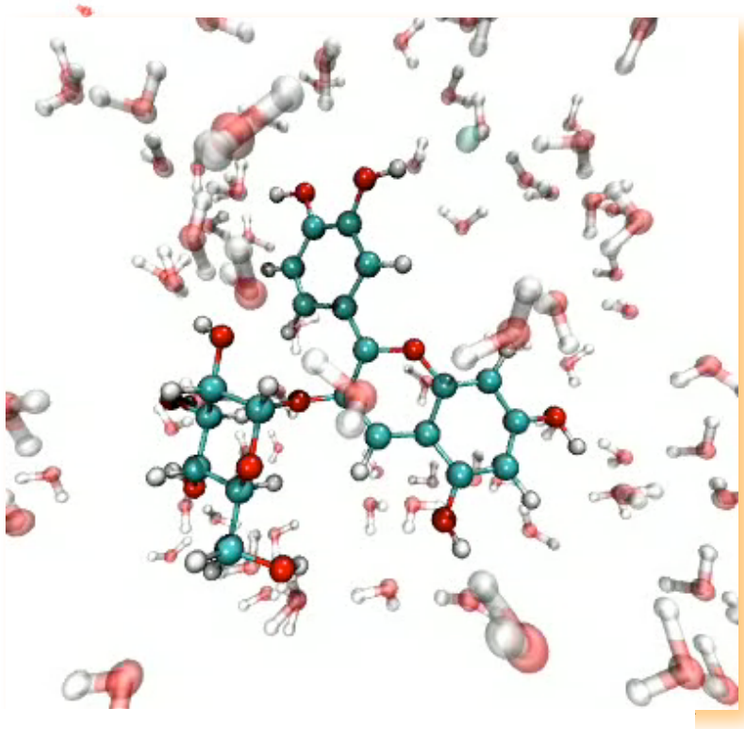
$C_{21}H_{21}O_{11}Cl@(H_2O)_{95}$

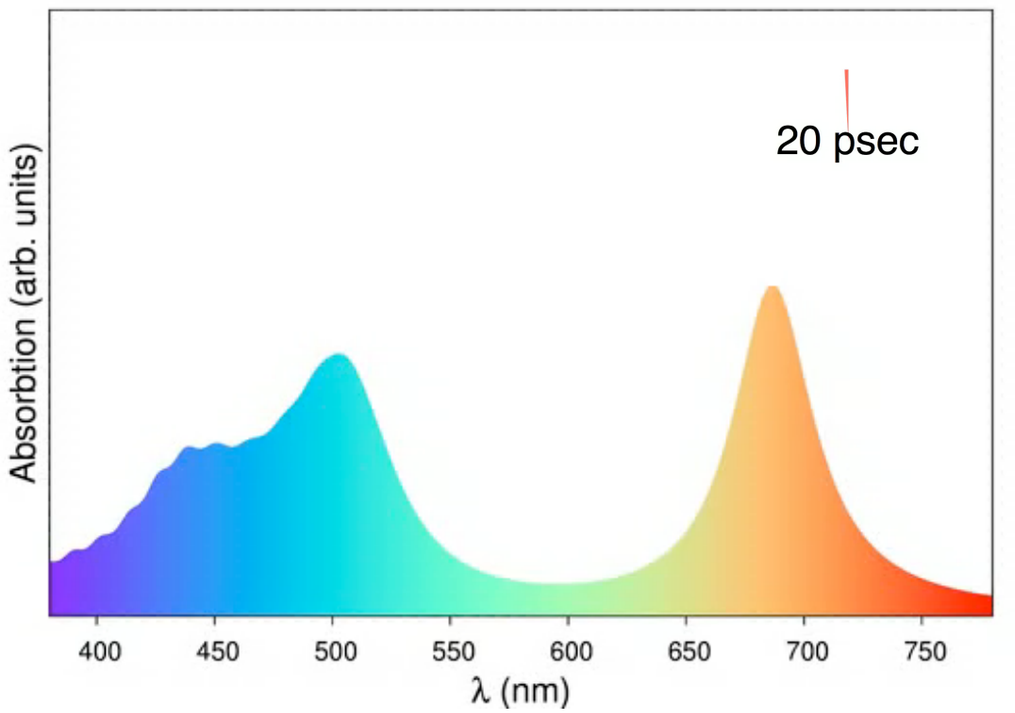
339 atoms

938 electrons

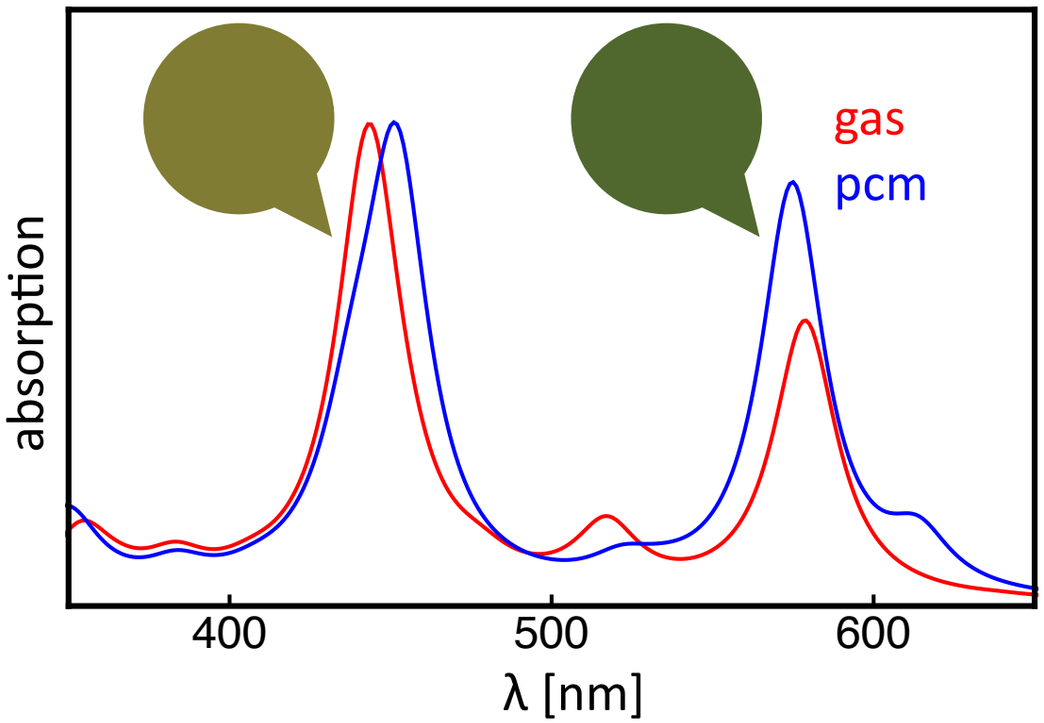
optical effect of the solvent

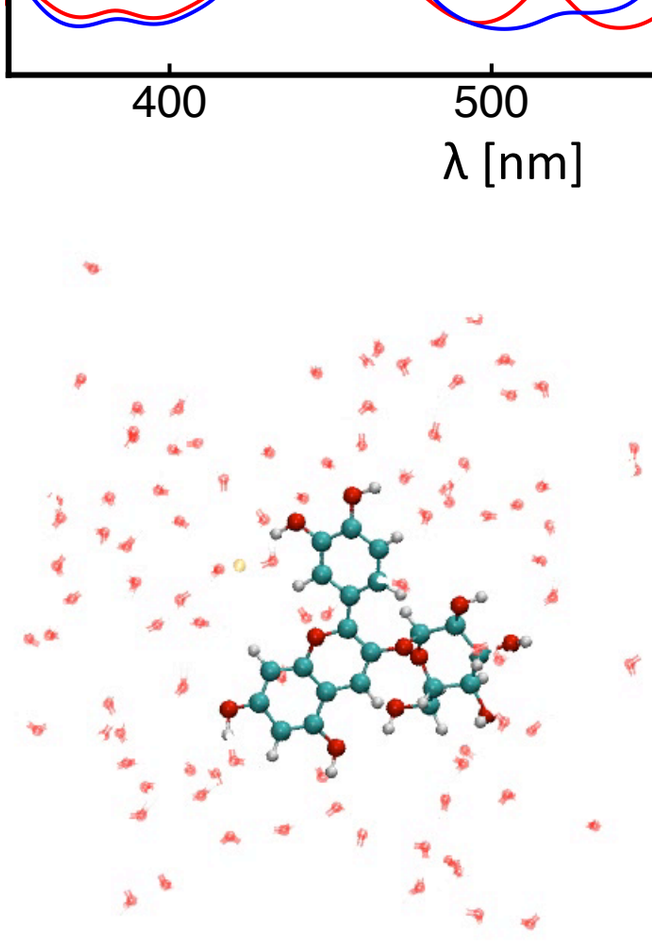


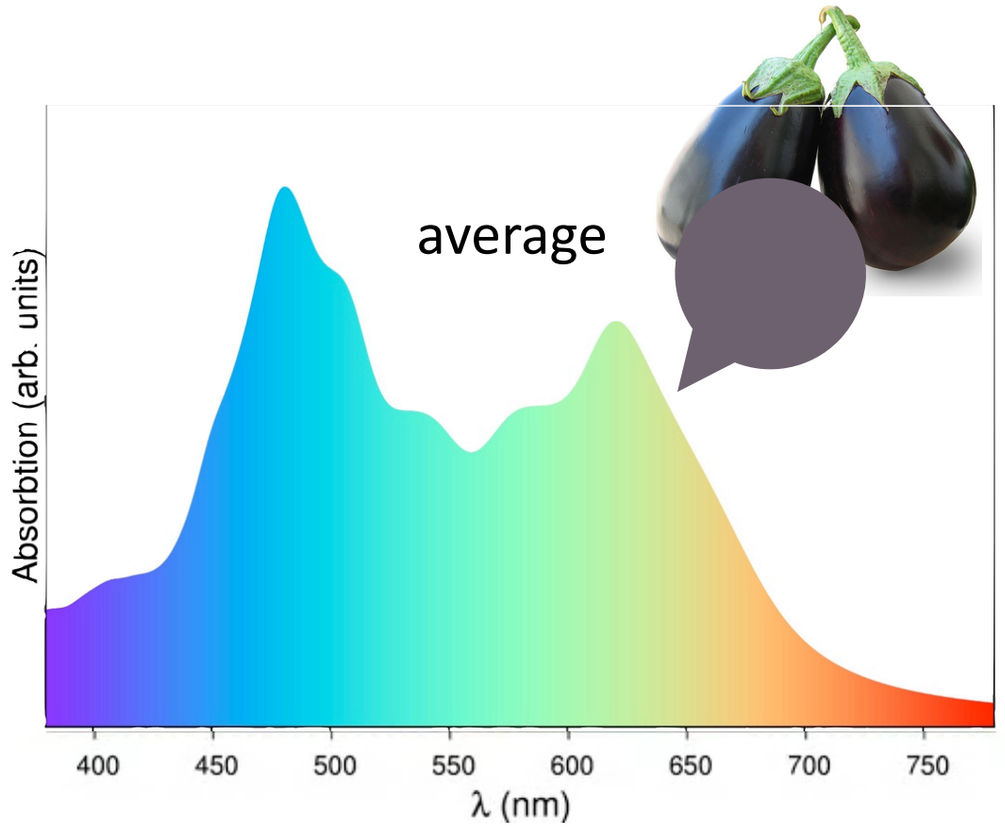


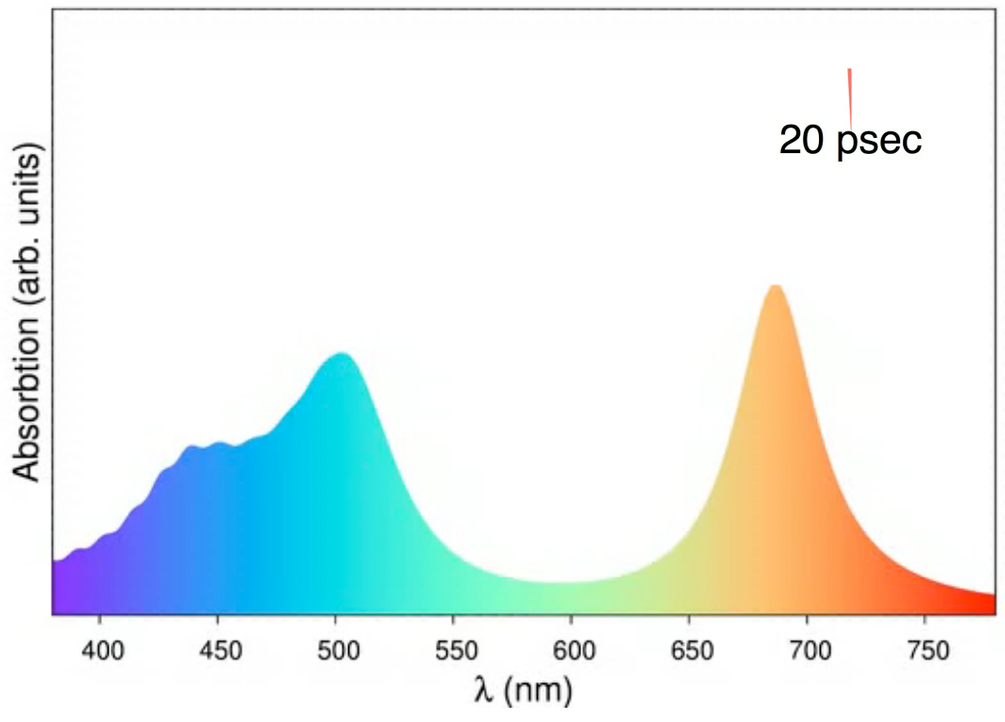


optical effect of the solvent

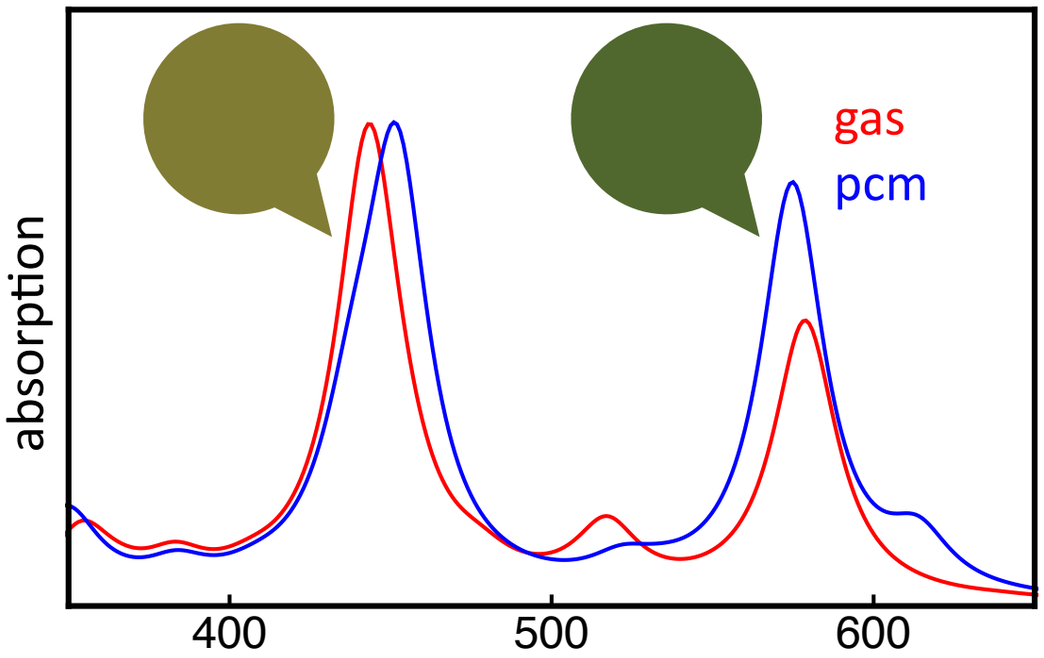


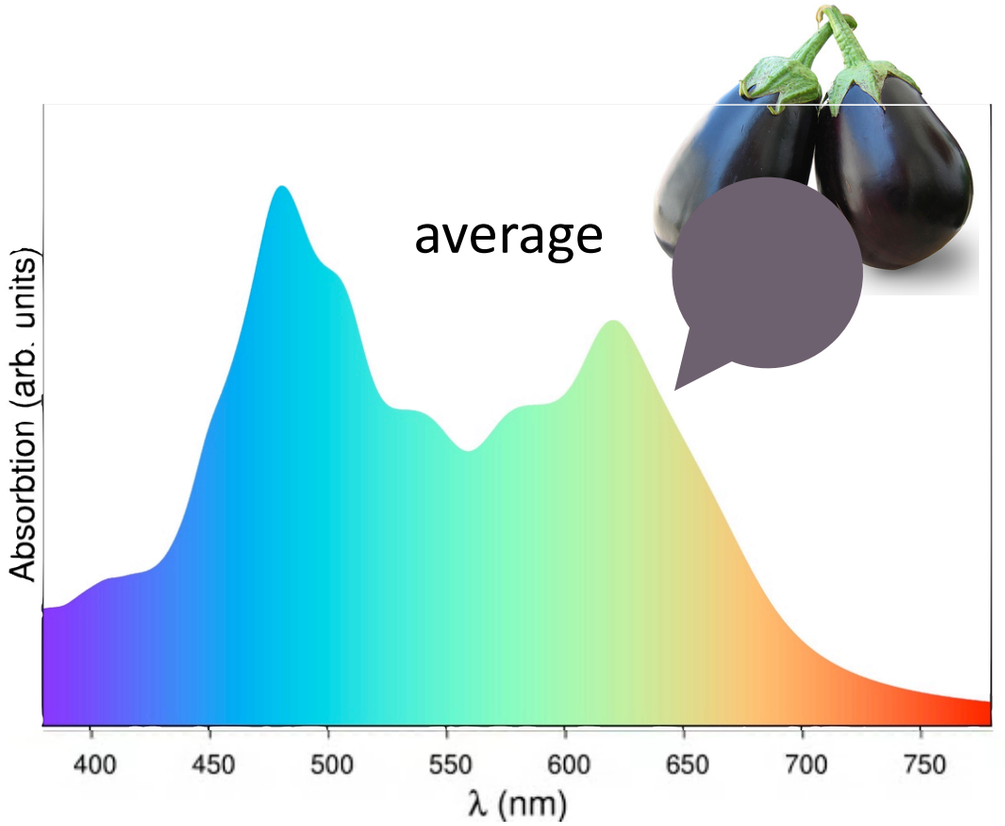


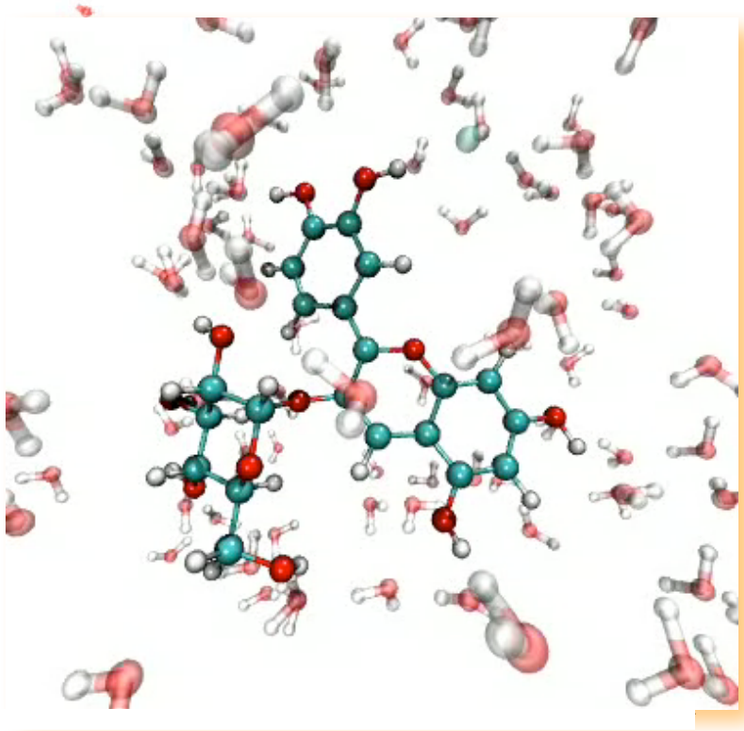


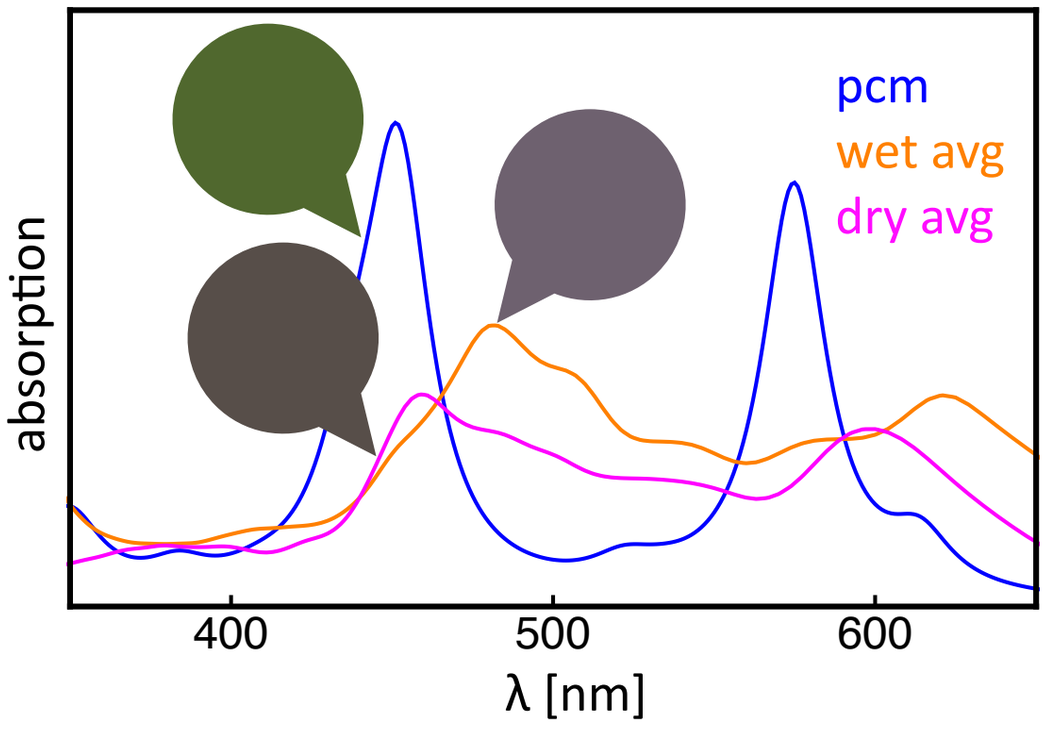


optical effect of the solvent

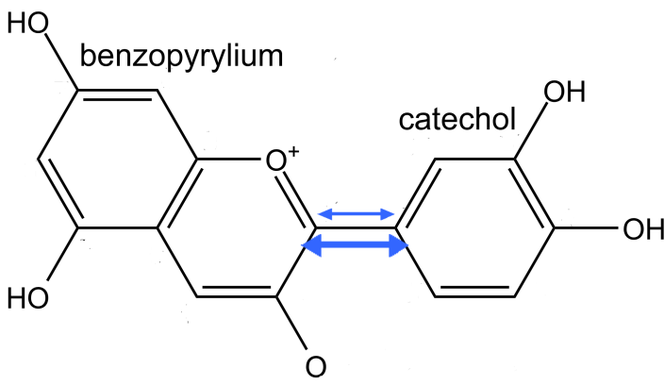


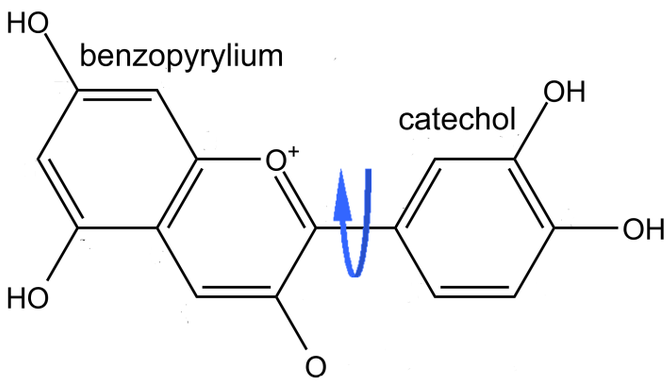


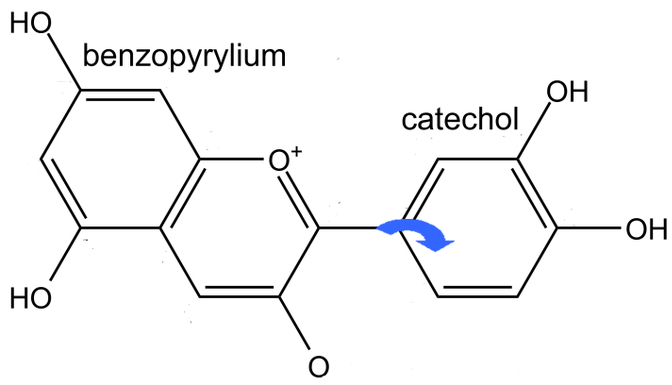


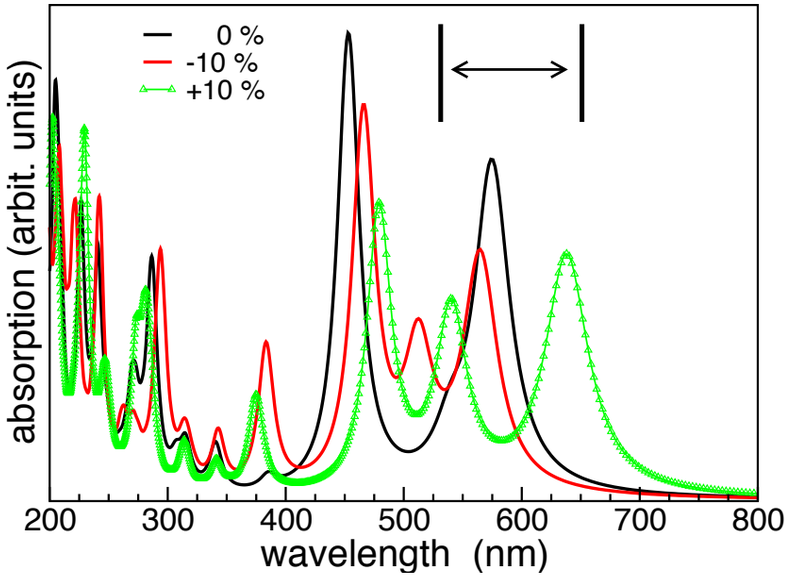


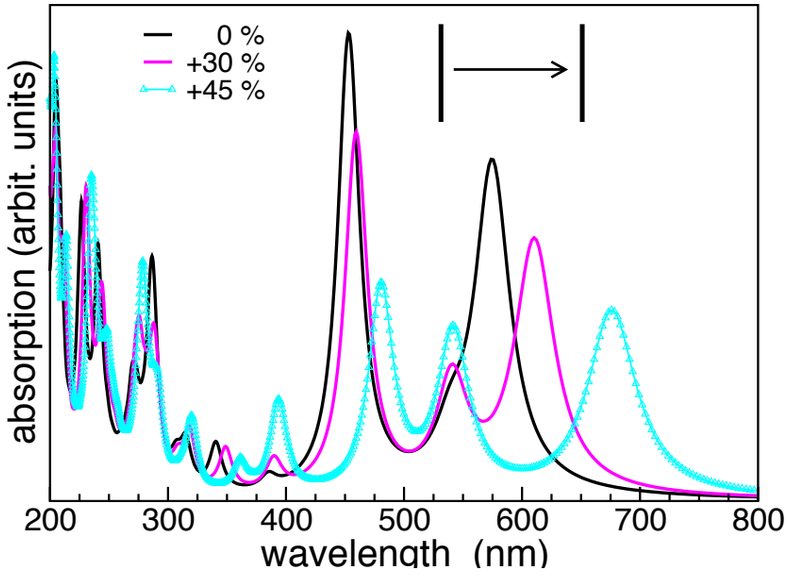
optical effects of intramolecular motion

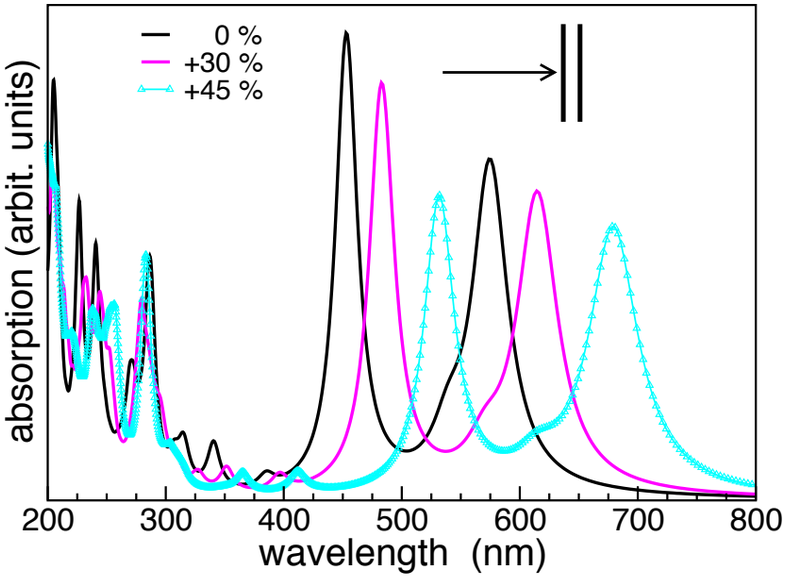












O.B. Malcioğlu, A. Calzolari, R. Gebauer, D. Varsano, and S.B., JACS **133**, 15425 (2011)

QUANTUMESPRESSO

13 July 2010 A bugfix release, v.4.2.1, of the Quantum ESPRESSO distribution is available for download.

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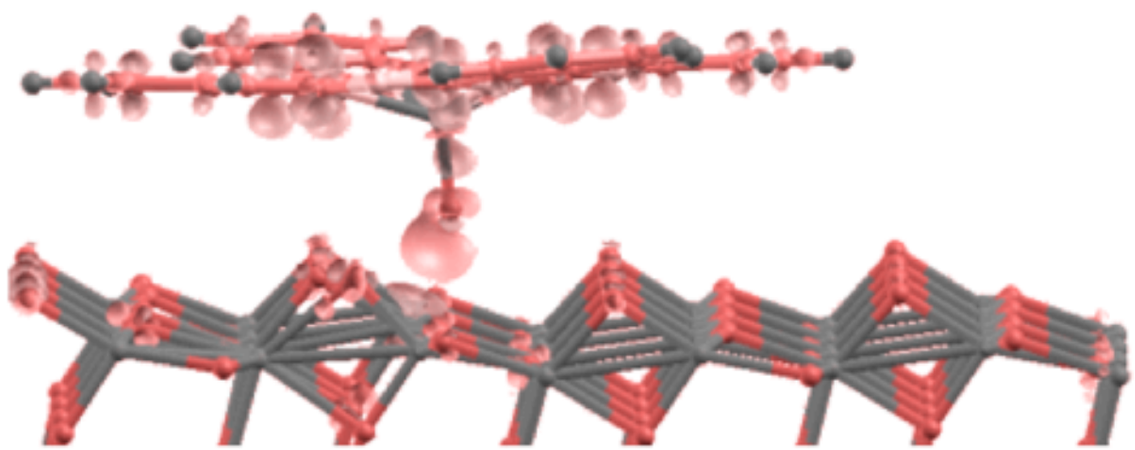

What I cannot compute, I do not understand [adapted from Richard P. Feynman]

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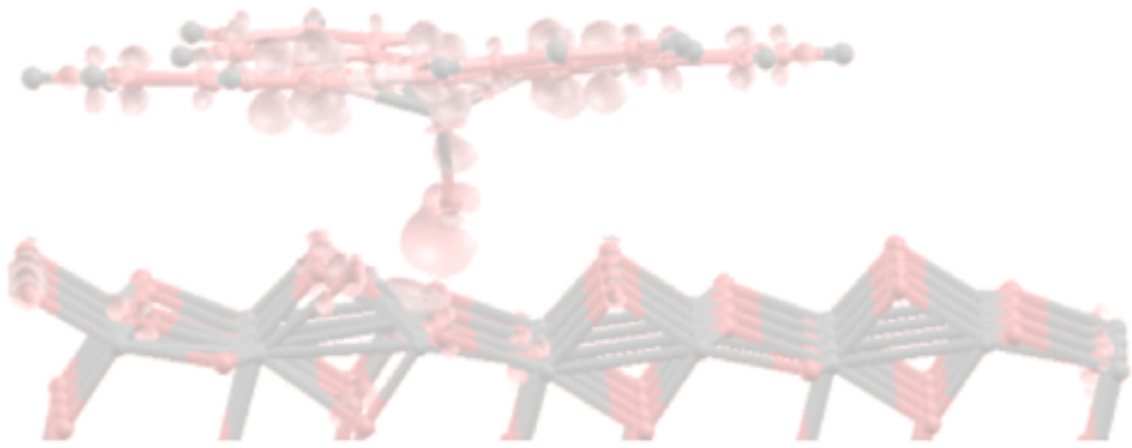

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QUANTUM ESPRESSO

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **21** (2009) 395502 (19pp) doi:10.1088/0953-8984/21/39/395502

QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials

Paolo Giannozzi[1,2], Stefano Baroni[1,3], Nicola Bonini[4], Matteo Calandra[5], Roberto Car[6], Carlo Cavazzoni[7,8], Davide Ceresoli[4], Guido L Chiarotti[9], Matteo Cococcioni[10], Ismaila Dabo[11], Andrea Dal Corso[1,3], Stefano de Gironcoli[1,3], Stefano Fabris[1,3], Guido Fratesi[12], Ralph Gebauer[1,13], Uwe Gerstmann[14], Christos Gougoussis[5], Anton Kokalj[1,15], Michele Lazzeri[5], Layla Martin-Samos[1], Nicola Marzari[4], Francesco Mauri[5], Riccardo Mazzarello[16], Stefano Paolini[3,9], Alfredo Pasquarello[17,18], Lorenzo Paulatto[1,3], Carlo Sbraccia[1,†], Sandro Scandolo[1,13], Gabriele Sclauzero[1,3], Ari P Seitsonen[5], Alexander Smogunov[13], Paolo Umari[1] and Renata M Wentzcovitch[10,19]

the importance of being non local

a few, politically incorrect, thoughts on

Rydberg series, excitons,
functionals, and common sense

Rydberg series in rare-gas atoms

Argon

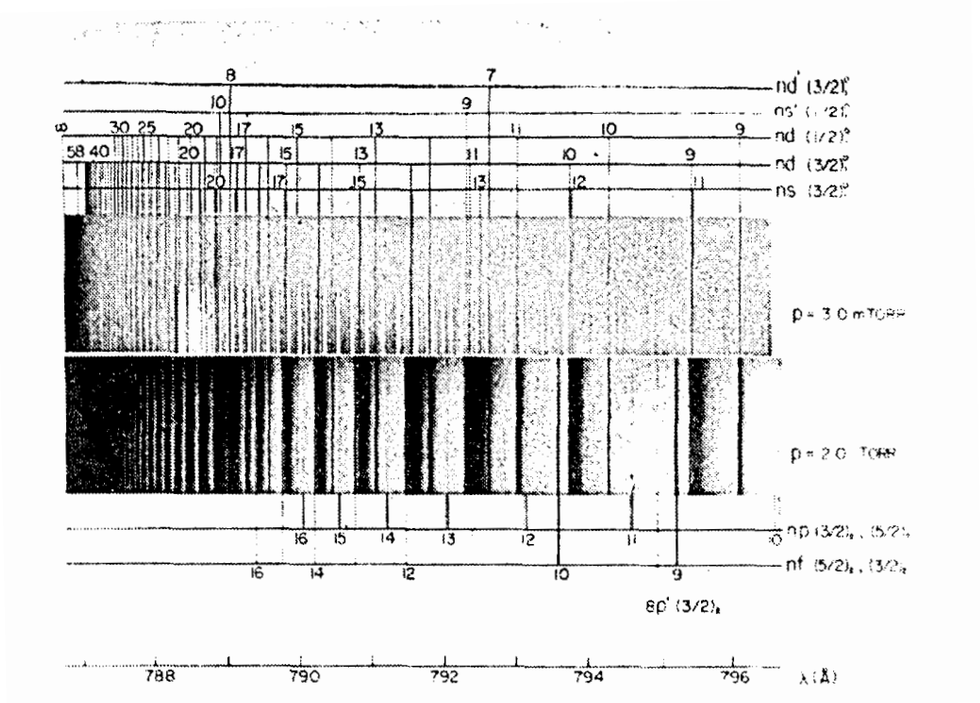


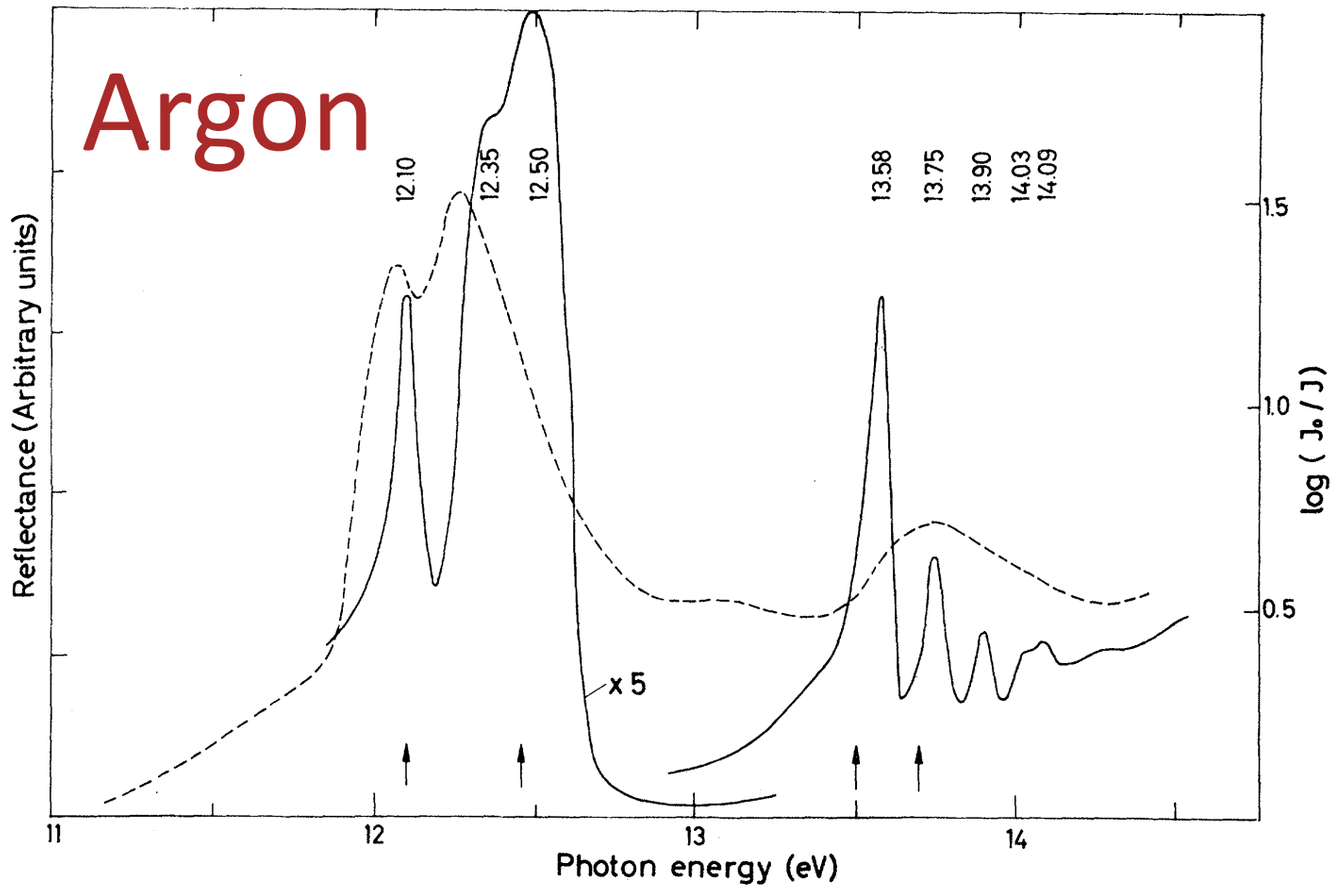
TABLE I. $3p^5ns(\frac{3}{2})_1^\circ \leftarrow 3p^6\ {}^1S_0$ series.

n	λ_{obs} (Å)	I[a]	ν (cm^{-1})	$\nu_{obs}-\nu_{prev}$[b]	n^*
4					
5	879.948	70	113 643.1	0.1	2.8546
6	835.001	56	119 760.3	0.1	3.8640
7	816.463	41	122 479.5	0.1	4.8682
8	806.869	42	123 935.8	−0.1	5.8798[e]
9	801.394	41	124 782.6	−0.1	6.8667
10	797.882	15	125 331.8	−0.1	7.8559[e]
11	795.447	30	125 715.4	−0.1	8.8708
12	793.750	42	125 984.3	0.0	9.874
13	792.513	28	126 180.9	−0.4	10.868[e]
14	791.566	30	126 331.8	−0.2	11.88
15	790.840[e]	60	126 447.9		12.88
16	790.266	36	126 539.6		13.87
17	789.803	36	126 613.9		14.87
18	789.425	33	126 674.4		15.87
19	789.113	30	126 724.5		16.87
20	788.841	36	126 768.3		17.92[e]
21	788.629	34	126 802.3		18.89
22	788.440[d]	59	126 832.8		19.90
∞			127 110.2±0.4		

K. Yoshino, J. Opt. Soc. Am. **60**, 1220 (1970)

$$E\left[3p^6 \rightarrow 3p^5 ns\right] = \mathrm{IP} - \frac{1}{(n+\delta_n)^2}$$

Rydberg series in rare-gas solids



R. Haensel *et al.*, PRL **23**, 1160 (1969)

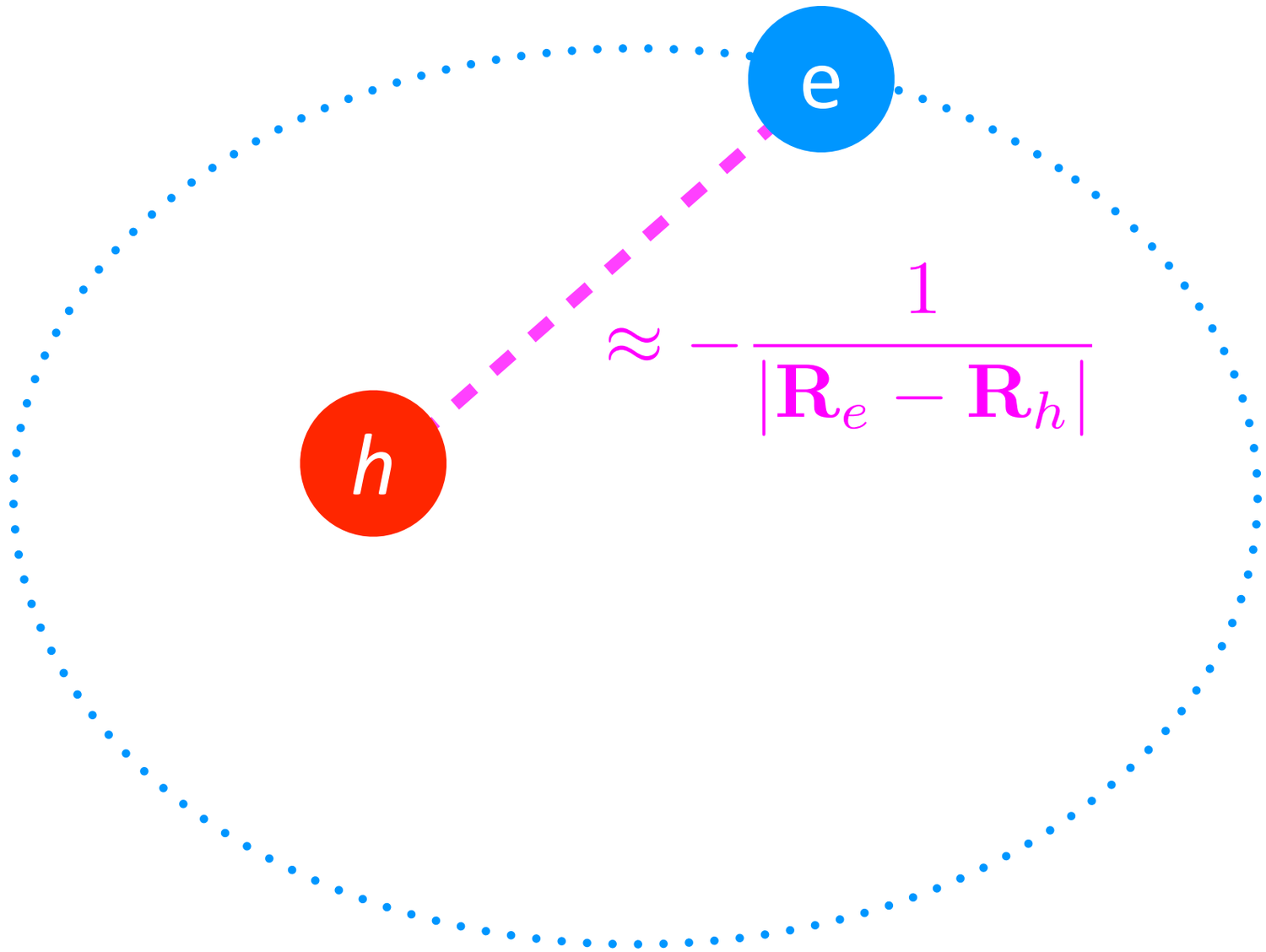
$$E^*(n) = E_G - \frac{\mu^*}{\epsilon_\infty^2 (n + \delta_n)^2}$$

common features of Rydberg and exciton states

- infinite series of hydrogen-like excitations converging to the quasi-particle gap

- finite absorption intensity at the quasi-particle gap

Rydberg and exciton states from common sense



Rydberg series from response calculations

$$(H^\circ - \epsilon_v)x_v(\mathbf{r}) + \sum_{v'} P_c \int K_{vv'}(\mathbf{r},\mathbf{r}')x_{v'}(\mathbf{r}')d\mathbf{r}' = \omega x_v(\mathbf{r})$$

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TDHF	$2\varphi_v^\circ(\mathbf{r})\varphi_{v'}^\circ(\mathbf{r}')\frac{1}{\lvert\mathbf{r}-\mathbf{r}'\rvert} - \delta(\mathbf{r}-\mathbf{r}')\int \varphi_v^\circ(\mathbf{r}'')\varphi_{v'}^\circ(\mathbf{r}'')\frac{1}{\lvert\mathbf{r}-\mathbf{r}''\rvert}d\mathbf{r}''$

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$$\left(H^\circ + V_{eh}^L + V_{eh}^{NL}\right)x(\mathbf{r}) = \left(\omega - |\epsilon_v|\right)x(\mathbf{r})$$

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local,
long range

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$$V_{eh}^L(\mathbf{r}) = -\int |\varphi_v^\circ(\mathbf{r}')|^2 \frac{1}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$$ local, long range

$$V_{eh}^{NL}x(\mathbf{r}) = 2\varphi_v^\circ(\mathbf{r})\int \kappa(\mathbf{r},\mathbf{r}')\varphi_v^\circ(\mathbf{r}')x(\mathbf{r}')d\mathbf{r}'$$ non local, short range

particle-hole representation

$$(\epsilon_c - \epsilon_v)X_{cv} + \sum_{c'v'} W_{cv}^{c'v'} X_{c'v'} = X_{cv}$$

$$X_{cv} = \int \varphi_c^{\circ *}(\mathbf{r}) x_v(\mathbf{r}) d\mathbf{r} \qquad W_{cv}^{c'v'} = \int \varphi_c^{\circ *}(\mathbf{r}) \varphi_{c'}^{\circ}(\mathbf{r}') K_{vv'}(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

	$W_{cv}^{c'v'}$
TDDFT	$2 \left\langle \varphi_c^{\circ} \varphi_{v'}^{\circ} \left\| \frac{1}{\|\mathbf{r} - \mathbf{r}'\|} + \kappa_{XC}(\mathbf{r}, \mathbf{r}') \right\| \varphi_v^{\circ} \varphi_{c'}^{\circ} \right\rangle$
TDHF	$2 \left\langle \varphi_c^{\circ} \varphi_{v'}^{\circ} \left\| \frac{1}{\|\mathbf{r} - \mathbf{r}'\|} \right\| \varphi_v^{\circ} \varphi_{c'}^{\circ} \right\rangle - \left\langle \varphi_c^{\circ} \varphi_{v'}^{\circ} \left\| \frac{1}{\|\mathbf{r} - \mathbf{r}'\|} \right\| \varphi_{c'}^{\circ} \varphi_v^{\circ} \right\rangle$

exciton series from response calculations

$$\varphi^{\circ}_{c/v}(\mathbf{r}) = \sum_{\mathbf{R}} \mathcal{U}_{c/v}(\mathbf{R}) w_{e/h}(\mathbf{r} - \mathbf{R})$$

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$$\begin{aligned} W(\mathbf{R}_e\mathbf{R}_h, \mathbf{R}'_e\mathbf{R}'_h) = {} & 2\langle w_e(\mathbf{R}_e) w_h(\mathbf{R}'_h) || w_h(\mathbf{R}_h) w_e(\mathbf{R}'_e)\rangle \\ & - \langle w_e(\mathbf{R}_e) w_h(\mathbf{R}'_h) || w_e(\mathbf{R}'_e) w_h(\mathbf{R}_h)\rangle \end{aligned}$$

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short-range, non-local eh interaction:
itinerant Frenkel-like interaction

$$\approx \frac{1}{|\mathbf{R}_e - \mathbf{R}_h|}$$

long-range, local eh interaction:
Wannier-like interaction

atoms vs. insulators, TDDFT vs. TDHF

$$\big(H^{\circ}(1) - H^{\circ}(2)\big)X(12) + \int W(12, 1'2')X(1'2')d1'd2' = \omega X(12)$$

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atoms vs. insulators, TDDFT vs. TDHF

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- a consistent treatment of molecular Rydberg states and of excitons in insulators necessarily requires either hybrid or non-adiabatic functionals

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- a useful ansatz for the reference KS system should lead to an XC functional that we can rationalize and use using physical intuition;
- for spectroscopic applications, a useful XC kernel should reflect the physics of the eh interaction: this can only be obtained giving up a pure-density dependence of the kernel, and singling out a non-local (Fock-like), possibly screened, exchange interaction from the XC potential.

these slides shortly at
http://talks.baroni.me