ab initio colors

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what color is all about
what color is all about
what color is all about
what color is all about

\[ \text{anycolor}(\lambda) = r(\lambda) + g(\lambda) + b(\lambda) \]
what makes things glitter the way they do

stimulus = illuminant \times trasmission \times sensitivity
what makes things glitter the way they do

stimulus = illuminant × trasmission × sensitivity
what makes things glitter the way they do

stimulus = illuminant × transmission × sensitivity

S(λ)
what makes things glitter the way they do

stimulus = illuminant × trasmission × sensitivity

\[ S(\lambda) \times e^{-\kappa(\lambda) x} \]
what makes things glitter the way they do

stimulus =
illuminant \times \text{transmission} \times \text{sensitivity}

S(\lambda) \times e^{-\kappa(\lambda)x} \times \operatorname{rgb}(\lambda)
what makes things glitter the way they do

\[ \text{RGB}(x) = \int S(\lambda)e^{-\kappa(\lambda)x} \text{rgb}(\lambda) \, d\lambda \]
a puzzle for you
a puzzle for you

hint: the solution is contained in one of the previous slides
spectroscopy

\[ \kappa(\omega) \propto \omega \text{Im}\alpha(\omega) \]

\[ d(\omega) = \alpha(\omega)E(\omega) \]
\[ \kappa(\omega) \propto \omega \text{Im}\alpha(\omega) \]

\[ d(\omega) = \alpha(\omega)E(\omega) \]

\[ \alpha(\omega) = \sum_{n \neq 0} \left[ \frac{X_{0n}X_{n0}}{\omega - E_{n0} + i\delta} - \frac{X_{0n}X_{n0}}{\omega + E_{n0} + i\delta} \right] \]

\[ \text{Im}\alpha(\omega) \]

\[ |X_{n0}|^2 \]

\[ \Gamma_n \]

\[ E_{n0} \]
spectroscopy

\[ \kappa(\omega) \propto \omega \text{Im} \alpha(\omega) \]

\[ \mathbf{d}(\omega) = \alpha(\omega) \mathbf{E}(\omega) \]

\[ \alpha(\omega) = \sum_{n \neq 0} \left[ \frac{X_{0n}X_{n0}}{\omega - E_{n0} + i\delta} - \frac{X_{0n}X_{n0}}{\omega + E_{n0} + i\delta} \right] \]

probe \rightarrow system \rightarrow response
optical spectra from TDDF (perturbation) T

\[ d(t) = \text{Tr}(d\rho(t)) \]
optical spectra from TDDF (perturbation) T

\[ d(t) = \text{Tr}(d\rho(t)) \]

\[ \rho(t) = \sum_v |\phi_v(t)\rangle \langle \phi_v(t)| \]
optical spectra from TDDF (perturbation) T

\[ d(t) = \text{Tr}(d\rho(t)) \]

\[ \rho(t) = \sum_v |\phi_v(t)\rangle \langle \phi_v(t)| \]

\[ i \frac{\partial \phi_v(\mathbf{r}, t)}{\partial t} = (-\Delta + v_{KS}(\mathbf{r}, t)) \phi_v(\mathbf{r}, t) \]
optical spectra from TDDF (perturbation) T

\[ d(t) = \text{Tr}(d\rho(t)) \]

\[ \rho(t) = \sum_v |\phi_v(t)\rangle\langle\phi_v(t)| \]

\[ i \frac{\partial \phi_v(r, t)}{\partial t} = (-\Delta + v_{KS}(r, t)) \phi_v(r, t) \]

\[ i \dot{\rho}(t) = [H_{KS}(t), \rho(t)] \]
optical spectra from TDDF (perturbation) T

\[ i \dot{\rho}(t) = [H_{KS}(t), \rho(t)] \]
optical spectra from TDDF (perturbation) $T$

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

\[
\rho(t) = \rho^\circ + \rho^\prime(t)
\]

\[
H_{KS}(t) = H^\circ + V^\prime_{ext}(t) + V^\prime_{HXC}(t)
\]

\[
i \rho^\prime = [H^\circ, \rho^\prime] + [V^\prime_{HXC}, \rho^\circ] + [V^\prime_{ext}, \rho^\circ] + \mathcal{O}(V^{'2})
\]
optical spectra from TDDF (perturbation) T

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

\[
\rho(t) = \rho^o + \rho'(t)
\]

\[
H_{KS}(t) = H^o + V'_{ext}(t) + V'_{HXC}(t)
\]

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

\[
i \dot{\rho}' = \mathcal{L} \rho' + [V'_{ext}, \rho^o]
\]
optical spectra from TDDF (perturbation) T

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

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

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

\[
(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \rho^\circ]
\]
optical spectra from TDDF (perturbation) T

\[(\omega - \mathcal{L})\tilde{\rho}'(\omega) = [\tilde{V}_{ext}'(\omega), \rho^\circ]\]
optical spectra from TDDF (perturbation) $T$

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

$$\alpha(\omega) = \text{Tr}(d\tilde{\rho}'(\omega))$$
optical spectra from TDDF (perturbation) T

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

\[\alpha(\omega) = \text{Tr}(d\tilde{\rho}'(\omega))\]

\[= (d, (\omega - \mathcal{L})^{-1} \cdot [\tilde{V}'_{ext}(\omega), \rho^\circ])\]
optical spectra from TDDF (perturbation) T

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

\[ \alpha(\omega) = \text{Tr}(d\tilde{\rho}'(\omega)) \]

\[ = (d, (\omega - \mathcal{L})^{-1} \cdot [\tilde{V}'_{ext}(\omega), \rho^\circ]) \]

\[ \equiv (u, (\omega - \mathcal{L})^{-1} \cdot v) \]
the Lanczos connection

\[ g(\omega) = \langle \phi_0 | (\omega - \mathcal{H})^{-1} | \phi_0 \rangle \]
the Lanczos connection

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


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

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

\[ \phi_{-1} = 0 \]

\[ b_{n+1} \phi_{n+1} = (\mathcal{H} - a_n) \phi_n - b_n \phi_{n-1} \]

\[ \langle \phi_{n+1} | \phi_{n+1} \rangle = 1 \]

\[ a_n = \langle \phi_n | \mathcal{H} | \phi_n \rangle \]
the Lanczos connection

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

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

\[ \mathcal{H} = \begin{pmatrix}
  a_0 & b_1 & 0 & \cdots & 0 \\
  b_1 & a_1 & b_2 & 0 & \cdots \\
  0 & b_2 & a_2 & \ddots & 0 \\
  \vdots & 0 & \ddots & \ddots & b_n \\
  0 & \cdots & 0 & b_n & a_n
\end{pmatrix} \]
the Lanczos connection

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

\[ \mathcal{H} = \begin{pmatrix} a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & 0 & \vdots \\ 0 & b_2 & a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & b_n \\ 0 & \cdots & 0 & b_n & a_n \end{pmatrix} \]
the Lanczos connection

\[ g(\omega) = \langle \phi_0 | (\omega - \mathcal{H})^{-1} | \phi_0 \rangle \]
the DFPT representation

\[ \tilde{\rho}'(\omega) = \left( \begin{array}{cc} 0 & Y^\dagger \\ X & 0 \end{array} \right) \]
\[ \tilde{\rho}'(\omega) = \sum_{cv} \left( X_{cv}(\omega) \left| \varphi_c^\circ \right\rangle \left\langle \varphi_v^\circ \right| + Y_{cv}(\omega) \left| \varphi_v^\circ \right\rangle \left\langle \varphi_c^\circ \right| \right) \]
the DFPT representation

\[ \tilde{\rho}'(\omega) = \sum_{cv} \left( X_{cv}(\omega) |\phi_c^o\rangle \langle \phi_v^o| + Y_{cv}(\omega) |\phi_v^o\rangle \langle \phi_c^o| \right) \]

\[ = \sum_v \left( |\phi_v'(\omega)\rangle \langle \phi_v^o| + |\phi_v^o\rangle \langle \phi_v'(-\omega)| \right) \]
\[ \tilde{\rho}'(\omega) = \sum_{cv} \left( X_{cv}(\omega) |\varphi_c^o\rangle \langle \varphi_v^o| + Y_{cv}(\omega) |\varphi_v^o\rangle \langle \varphi_c^o| \right) \]

\[ = \sum_v \left( |\varphi'_v(\omega)\rangle \langle \varphi_v^o| + |\varphi_v^o\rangle \langle \varphi'_v(-\omega)| \right) \]

\[ |\{x_v(r)\}, \{y_v(r)\}\rangle \]

\[ P_v x_v = P_v y_v = 0 \]
the DFPT representation

\[ \tilde{\rho}'(\omega) = \sum_{cv} (X_{cv}(\omega)\varphi_\omega^\circ \langle \varphi_v^\circ | + Y_{cv}(\omega)\varphi_v^\circ \langle \varphi_\omega^\circ |) \]

\[ = \sum_v \left( |\varphi'_v(\omega)\rangle \langle \varphi_v^\circ | + |\varphi_v^\circ \rangle \langle \varphi'_v(-\omega)| \right) \]

\[ \{x_v(r)\}, \{y_v(r)\} \]

\[ P_v x_v = P_v y_v = 0 \]

\[ \mathcal{L} \tilde{\rho}' \quad \mathcal{L}^\top \tilde{\rho}' \quad \Rightarrow \quad \{H^\circ x_v(r)\} \quad \& \quad \{V'_ee(r)\varphi_v^\circ(r)\} \]
the DFPT representation

\[ \tilde{\rho}'(\omega) = \sum_{cv} \left( X_{cv}(\omega) | \varphi_v^0 \rangle \langle \varphi_v^0 | + Y_{cv}(\omega) | \varphi_v^0 \rangle \langle \varphi_v^0 | \right) = \sum_{v} \left( | \varphi'_v(\omega) \rangle \langle \varphi_v^0 | + | \varphi_v^0 \rangle \langle \varphi'_v(-\omega) | \right) \]

\[ | \{ x_v(\mathbf{r}) \}, \{ y_v(\mathbf{r}) \} \rangle \]

\[ P_v x_v = P_v y_v = 0 \]

\[ \mathcal{L} \tilde{\rho}' \quad \mathcal{L}^\top \tilde{\rho}' \quad \Rightarrow \quad \{ H^\circ x_v(\mathbf{r}) \} \quad \& \quad \{ V_{ee}(\mathbf{r}) \varphi_v^0(\mathbf{r}) \} \]

\[ n'(\mathbf{r}) = \frac{1}{2} \sum_{v} (x_v(\mathbf{r}) + y_v(\mathbf{r})) \varphi_v^0(\mathbf{r}) \]
benzene, a benchmark

\[ \text{Im}(\omega) \] for benzene with US PP's - $E_{\text{cut}}=30$ Ry

\[ \omega \text{ [eV]} \]
benzene, a benchmark

\[ N = 500 \]
\[ N = 1000 \]

US PP’s - \( E_{\text{cut}} = 30 \) Ry
benzene, a benchmark

N=1000
N=2000

US PP's - $E_{\text{cut}}=30$ Ry

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benzene, a benchmark

\[ \text{US PP's - } E_{\text{cut}}=30 \text{ Ry} \]
benzene, a benchmark

$\omega \Im \chi(\omega)$

$N=2000$

$N=2300$

real time

US PP's - $E_{\text{cut}}=30$ Ry

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benzene, a benchmark

Im(\omega) = \text{experiment, } N=2300

US PP’s - \text{E}_{\text{cut}}=30 \text{ Ry}

\omega \text{ [eV]}

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speeding up the convergence

US PP's - $E_{cut}=30$ Ry
speeding up the convergence

US PP’s - $E_{\text{cut}}=30$ Ry
speeding up the convergence
speeding up the convergence

\[ a_0 \quad b_1 \quad a_1 \quad b_2 \quad a_2 \quad a_{M-1} \quad \bar{a} \quad b_M \quad \bar{b} \]

\[ \text{Im} \chi(\omega) \]

\[ n=1000 \quad n=2000 \quad n=3000 \quad n=4000 \]

no extrapolation

\[ \omega \text{[eV]} \]

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speeding up the convergence

\[ a_0 \quad b_1 \quad a_1 \quad b_2 \quad a_2 \quad a_{M-1} \quad \bar{a} \quad b_M \quad \bar{b} \]

\[ \text{no extrapolation} \quad \text{extrapolation} \]

\[ \text{Im} \chi(\omega) \]

\[ \omega [\text{eV}] \]

\[ n=1000 \quad n=2000 \quad n=3000 \quad n=4000 \]

\[ n=500 \quad n=1000 \quad n=2000 \quad n=4000 \]

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chlorophyll a

$C_{55}H_{72}MgN_4O$
chlorofyll a

\[ \lambda \text{ [nm]} \]

\[ \alpha \]

**tddft**

**expt**
color and function of anthocyanins

cyanidin-3-glucoside
color and function of anthocyanins

cyanidin-3-glucoside

cyanidin-3-glucoside

TDDFT?
color and function of anthocyanins

cyanidin-3-glucoside

TDDFT:-(

absorbance vs wavelength (nm)

benzopyrylium

TDDFT:

catechol

sugar

cyanidin-3-glucoside

TDDFT:

octopus

gaussian
optical effect of the solvent
optical effect of the solvent
optical effect of the solvent

C$_{21}$H$_{21}$O$_{11}$Cl@(H$_2$O)$_{95}$
339 atoms
938 electrons

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optical effect of the solvent
optical effect of the solvent

![Diagram](image1)

![Diagram](image2)

![Diagram](image3)

![Diagram](image4)
optical effect of the solvent
optical effects of intramolecular motion

everything’s fine?
everything’s fine? nay ...

no Coulombic tail in the eh interaction

- no Rydberg states in molecules
- no excitons in extended systems
- wrong charge-transfer excitations
everything’s fine? nay ...

no Coulombic tail in the eh interaction

- no Rydberg states in molecules
- no excitons in extended systems
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the fix

- exotic frequency-dependent functionals
- non-local (Fock) exchange
  - hybrid functionals
  - BSE equation
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*Ab initio* calculations of optical absorption spectra: Solution of the Bethe–Salpeter equation within density matrix perturbation theory

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more on this line to follow ...
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QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials

Paolo Giannozzi\textsuperscript{1,2}, Stefano Baroni\textsuperscript{1,3}, Nicola Bonini\textsuperscript{4}, Matteo Calandra\textsuperscript{5}, Roberto Car\textsuperscript{6}, Carlo Cavazzoni\textsuperscript{7,8}, Davide Ceresoli\textsuperscript{4}, Guilio L Chiarotti\textsuperscript{9}, Matteo Cococcioni\textsuperscript{10}, Ismaila Dabo\textsuperscript{11}, Andrea Dal Corso\textsuperscript{1}, Stefano de Gironcoli\textsuperscript{1,3}, Stefano Fabris\textsuperscript{1,3}, Guido Fratesi\textsuperscript{12}, Ralph Gebauer\textsuperscript{13}, Uwe Gerstmann\textsuperscript{14}, Christos Gougoussis\textsuperscript{5}, Anton Kokalj\textsuperscript{1,15}, Michele Lazzeri\textsuperscript{5}, Layla Martin-Samos\textsuperscript{1}, Nicola Marzari\textsuperscript{4}, Francesco Mauri\textsuperscript{5}, Riccardo Mazzarello\textsuperscript{16}, Stefano Paolini\textsuperscript{3,9}, Alfredo Pasquarello\textsuperscript{17,18}, Lorenzo Paulatto\textsuperscript{1,3}, Carlo Sbraccia\textsuperscript{1,†}, Sandro Scandolo\textsuperscript{1,13}, Gabriele Sclauzero\textsuperscript{1,3}, Ari P Seitsonen\textsuperscript{5}, Alexander Smogunov\textsuperscript{13}, Paolo Umari\textsuperscript{1} and Renata M Wentzcovitch\textsuperscript{10,19}
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China 9%
other 20%
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