Ab-initio modeling of opto-electronic properties of molecules in solvents and in proximity to a semiconductor nanoparticle

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Outline

1) Brief Introduction.

2) Modeling solvation effects in real-space and real-time within DFT.

2.1) The basics of the Polarizable Continuum Model (PCM).

2.2) Regularization of the solvent potential in a real-space representation.

2.3) Ground and excited states: DFT & TDDFT + PCM.

2.4) Benchmark: Solvation energies and optical response of simple molecules in water.

3) Extended PCM to model a dye molecule in proximity to a semiconductor NP.

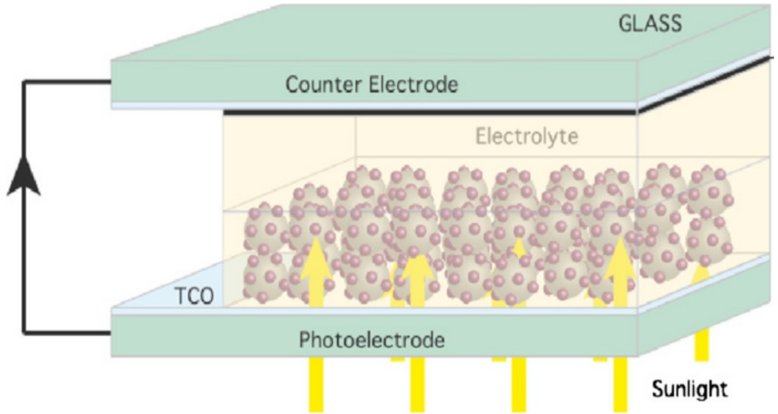
3.1) The generalized PCM response matrix.

3.2) Excited state oxidation potential (ESOP) of the dye L0 in proximity to a TiO2 NP.

4) Conclusions and Perspectives.

Dye-sensitized solar cells (DSSCs)

Typical architecture

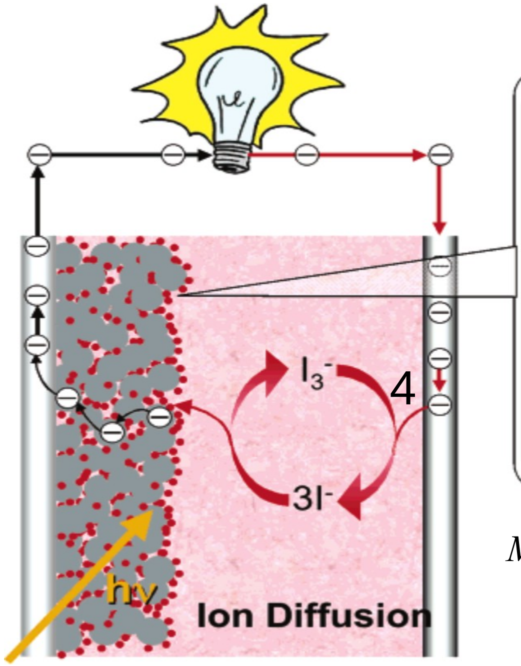


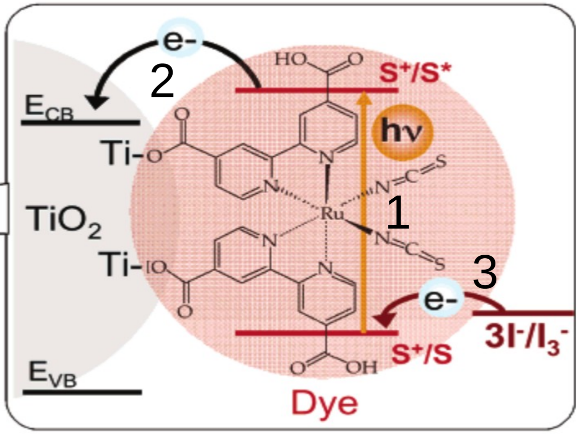
Nazeeruddin et al. Sol. Energy 85, 1172 (2011)

Multi-scale system composed by:

- TiO_2 mesoporous semiconductor film.
- Sensitizer adsorbed onto the surface.
- Electrolyte solution with a redox couple.
- Counter electrode like platinum.

Working principle





M. Gratzel, Inor. Chem., 44, 6841 (2005)

1. Photon absorption in the dye.
2. Electron injection into the NP.
3. Dye regeneration.
4. Reduction of redox mediator.

Solvent polarization may influence all these processes

Ultrafast charge separation dynamics

ARTICLE

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OPEN

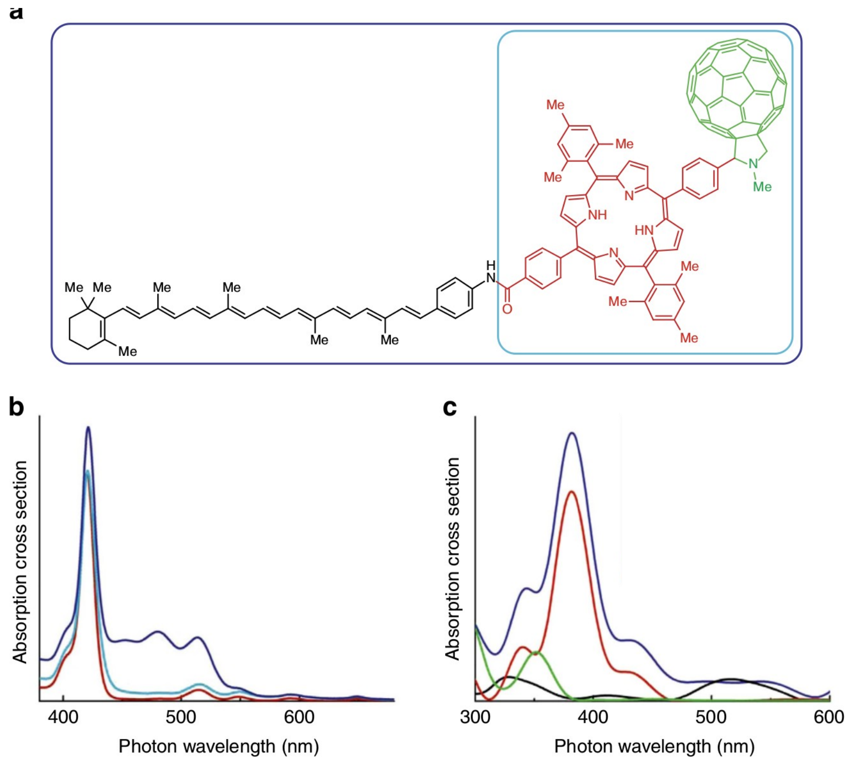
Quantum coherence controls the charge separation in a prototypical artificial light-harvesting system

Carlo Andrea Rozzi[1,*], Sarah Maria Falke[2,*], Nicola Spallanzani[1,3], Angel Rubio[4,5], Elisa Molinari[1,3], Daniele Brida[6], Margherita Maiuri[6], Giulio Cerullo[6], Heiko Schramm[7], Jens Christoffers[7] & Christoph Lienau[2]

Solvent effects unexplored in the dynamics

- *Science 344, 1001 (2014)*
- *Adv. Funct. Mater. 25, 2047 (2015)*

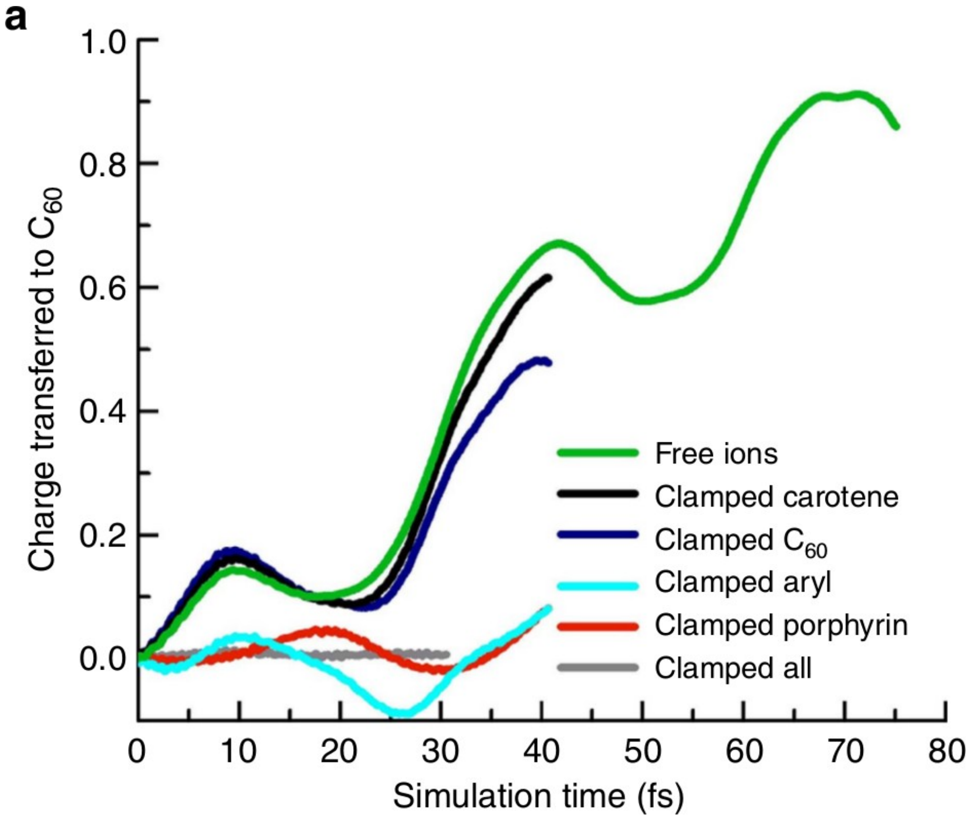
Absorption spectrum of the carotene-porphyrin-fullerene triad
Nat. Commun. 4:1602 (2013)



Experimental
(in toluene)

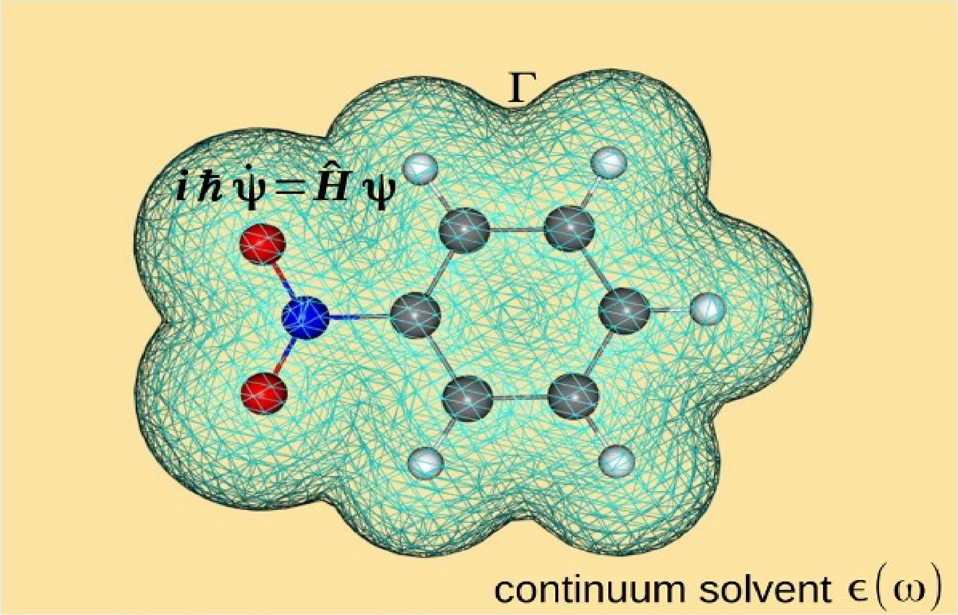
Theory (TDDFT)
in vacuo

RT-TDDFT + Ehrenfest
nuclear dynamics



The basics of PCM model

J. Tomasi et al. Chem. Rev. ***105****, 2999 (2005)*



- The solvent is a *continuous dielectric medium* polarized by the solute molecule.
- Solute molecule is hosted by the *cavity* within the surface $\boldsymbol{\Gamma}$.

  $\rho_{\mathrm{M}}(\mathbf{r}) = 0$ for **r** out of the cavity (C)
- The shape of $\boldsymbol{\Gamma}$ should reproduced the *molecular shape*.
- The molecule is treated *quantum mechanically*.

Poisson equation + boundary conditions at $\boldsymbol{\Gamma}$

$$-\nabla^2 V(\mathbf{r}) = 4\pi\rho_{\mathrm{M}}(\mathbf{r}) \text{ within C}$$

$$-\epsilon\nabla^2 V(\mathbf{r}) = 0 \text{ outside C}$$

$$V_{\mathrm{in}} - V_{\mathrm{out}} = 0$$

$$(\partial V/\partial\vec{n})_{\mathrm{in}} - \epsilon\,(\partial V/\partial\vec{n})_{\mathrm{out}} = 0$$

$$V(\mathbf{r}) = V_{\mathrm{M}}(\mathbf{r}) + v_{\mathrm{R}}(\mathbf{r})$$

$v_{\mathrm{R}}(\mathbf{r})$:solvent reaction potential

$$-\nabla^2 v_{\mathrm{R}}(\mathbf{r}) = 0 \text{ in and outside C}$$

$$[v_{\mathrm{R}}] = 0 \text{ in } \Gamma$$

$$v_{\mathrm{R}}(\mathbf{r}) \to 0 \text{ at infinity}$$

Apparent surface charge method (ASC)

- $v_{\mathrm{R}}(\mathbf{r})$ can be expressed in terms of an apparent surface charges:

$$v_{\mathrm{R}}(\mathbf{r}) = \int_{\Gamma} \frac{\sigma(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d\mathbf{s}$$

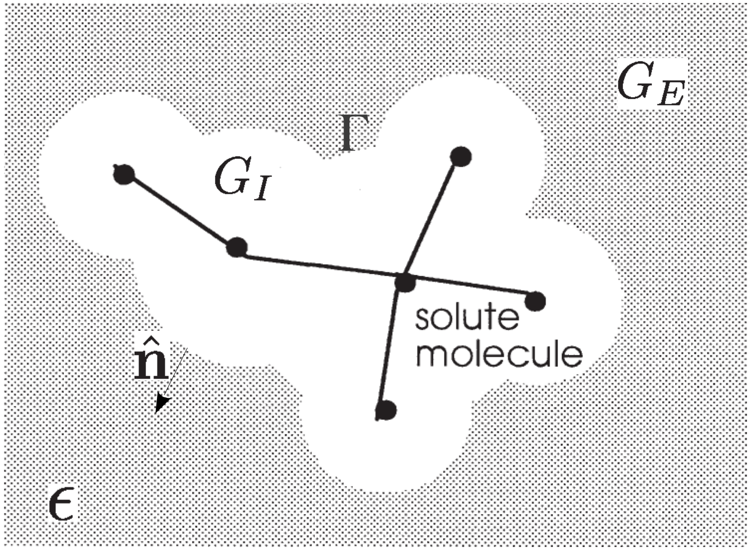
- $\sigma(\mathbf{s})$ is the unique solution of the equation:

Cances et al. J. Math. Chem. 23, 309 (1998)

$$\left[S_E(2\pi + D_I^*) + (2\pi - D_E)S_I\right]\sigma = \left[S_E S_I^{-1}(2\pi - D_I) - (2\pi - D_E)\right] V_{\mathrm{M}}$$

$$(\hat{S}_{I(E)}\ \sigma)(\mathbf{x}) = \int_{\Gamma} G_{I(E)}(\mathbf{x},\mathbf{y})\sigma(\mathbf{y})d\mathbf{y}$$

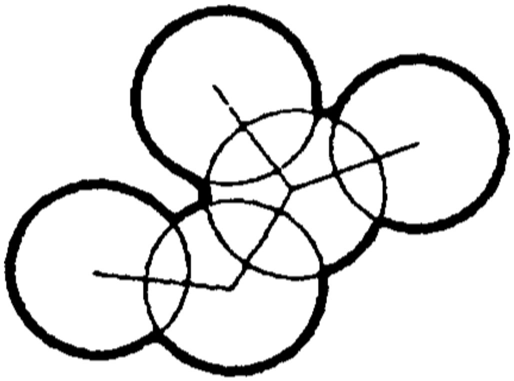
$$(\hat{D}_{I(E)}\ \sigma)(\mathbf{x}) = \int_{\Gamma} \left[\epsilon_{I(E)}\nabla_{\mathbf{y}} G_{I(E)}(\mathbf{x},\mathbf{y})\cdot\hat{\mathbf{n}}(\mathbf{y})\right]\sigma(\mathbf{y})d\mathbf{y}$$



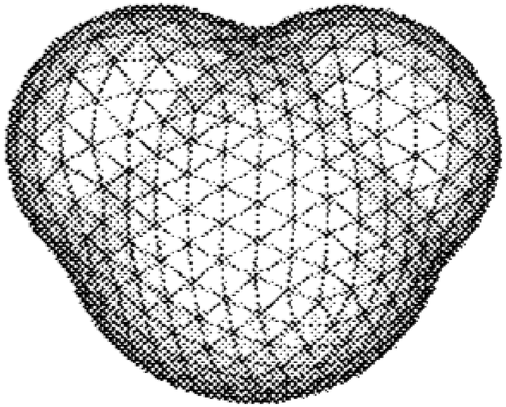
Apparent surface charge method (ASC): *in practice*

1- The cavity is defined by the union of interlocking van der Waals spheres .

2- Cavity surface *tessellation:* projecting the faces of polyhedra inscribed in each sphere.



Pascual et al. J. Comp. Chem. 11, 1047 (1990)
There are many other algorithms.



discretized equations

$$v_{\mathrm{R}}(\mathbf{r}) = \int_{\Gamma} \frac{\sigma(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d\mathbf{s} \approx \sum_{k=1}^{T} \frac{\sigma(\mathbf{s}_k) A_k}{|\mathbf{r}-\mathbf{s}_k|} = \sum_{k=1}^{T} \frac{q_k}{|\mathbf{r}-\mathbf{s}_k|}$$

$$\left[\mathbf{S}_E(2\pi\mathbf{I}+\mathbf{D}_I^*) + (2\pi\mathbf{I}-\mathbf{D}_E)\mathbf{S}_I\right]\mathbf{A}^{-1}\mathbf{q} = \left[\mathbf{S}_E\mathbf{S}_I^{-1}(2\pi\mathbf{I}-\mathbf{D}_I) - (2\pi\mathbf{I}-\mathbf{D}_E)\right]\mathbf{V}_{\mathrm{M}}$$

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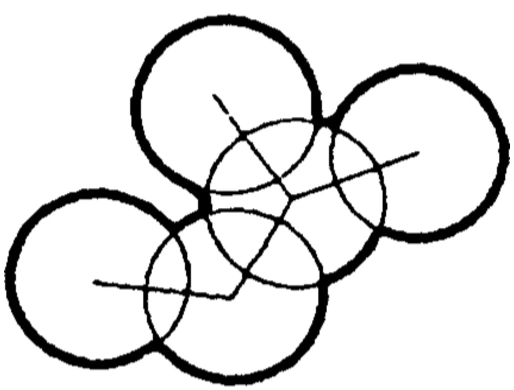

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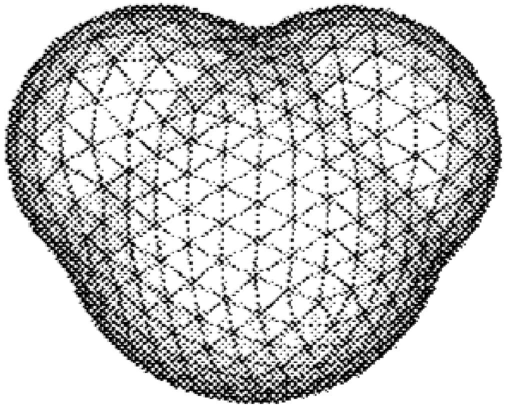

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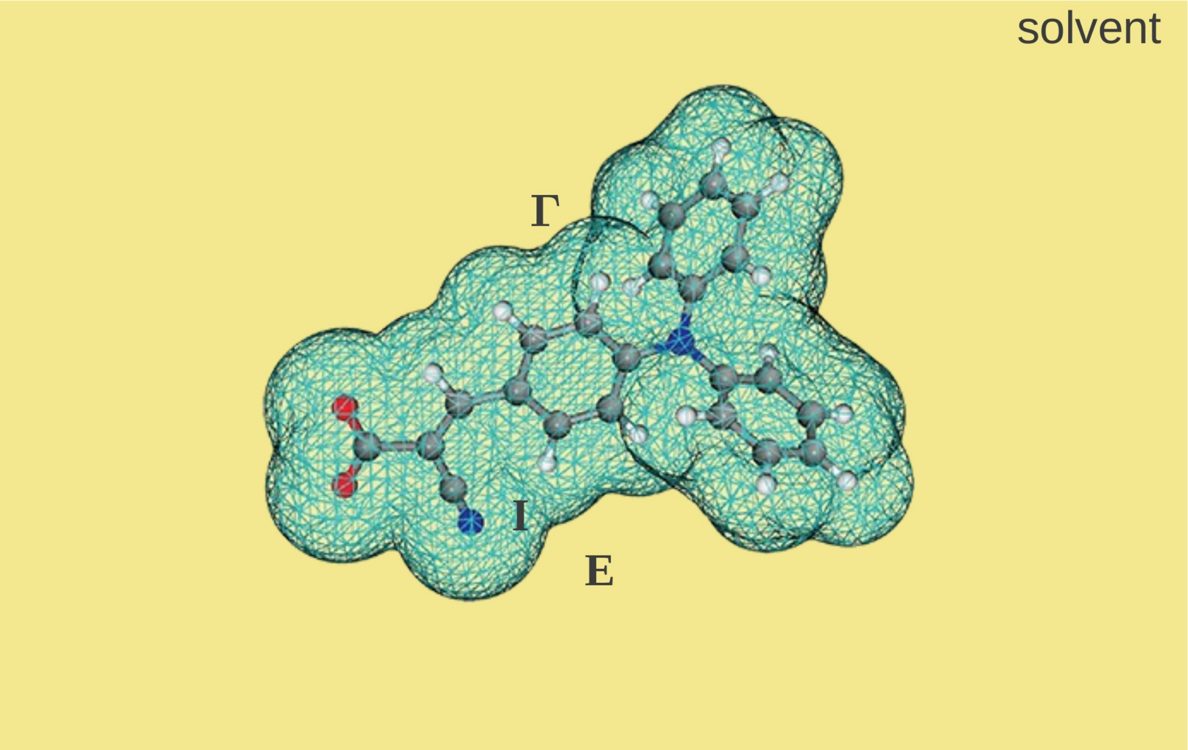
$$\mathbf{q} = \underbrace{\left\{\left[\mathbf{S}_E(2\pi\mathbf{I}+\mathbf{D}_I^*) + (2\pi\mathbf{I}-\mathbf{D}_E)\mathbf{S}_I\right]\mathbf{A}^{-1}\right\}^{-1}\left[\mathbf{S}_E\mathbf{S}_I^{-1}(2\pi\mathbf{I}-\mathbf{D}_I) - (2\pi\mathbf{I}-\mathbf{D}_E)\right]}\mathbf{V}_\mathrm{M}$$

$$\mathbf{q} = \mathbf{Q}(\epsilon)\mathbf{V}_\mathrm{M}$$

- $\mathbf{Q}$ → PCM response matrix.
- $\mathbf{V}_\mathrm{M}[\rho^e, \rho^n] = \mathbf{V}_\mathrm{Hartree}[\rho^e] + \mathbf{V}_\mathrm{Z}[\rho^n]$

IEF-PCM equations: **Molecule + solvent**



Green functions

$$G_I(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

$$G_E(\mathbf{r},\mathbf{r}') = \frac{1}{\epsilon^{\mathrm{solv}}}\frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

$$\xrightarrow{G,\,[\epsilon\nabla G\cdot\hat{n}]}$$

S and D matrix elements

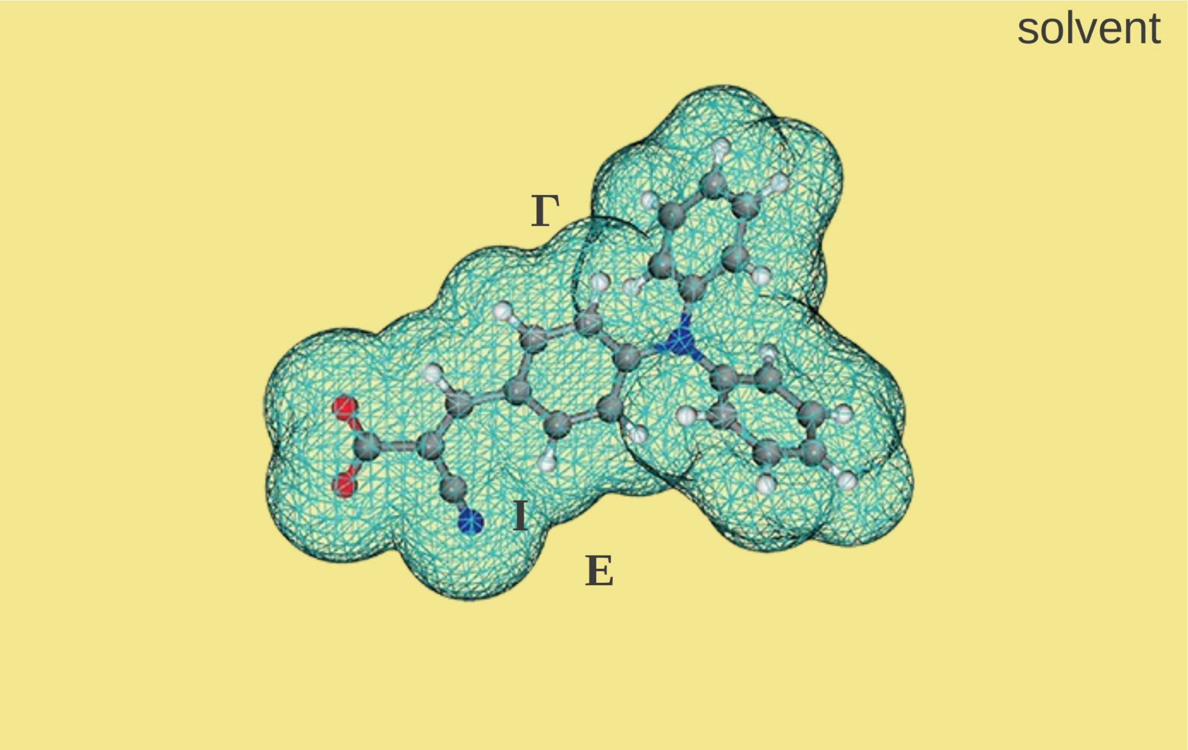
$$S_{ij}^I = k\sqrt{\frac{4\pi}{A_i}}\delta_{ij} + (1-\delta_{ij})\frac{1}{|\mathbf{s}_i-\mathbf{s}_j|}$$

$$S_{ij}^E = S_{ij}^I/\epsilon^{\mathrm{solv}}$$

$$D_{ij}^I = -k\frac{\sqrt{4\pi A_i}}{2R_i}\delta_{ij} + (1-\delta_{ij})\frac{(\mathbf{s}_i-\mathbf{s}_j)\cdot\hat{n}(\mathbf{s}_j)}{|\mathbf{s}_i-\mathbf{s}_j|^3}A_j$$

$$D_{ij}^E = D_{ij}^I$$

IEF-PCM equations: **Molecule + solvent**



Green functions

PCM response matrix

$$\left.\begin{aligned} G_I(\mathbf{r},\mathbf{r}') &= \frac{1}{|\mathbf{r}-\mathbf{r}'|}\\ G_E(\mathbf{r},\mathbf{r}') &= \frac{1}{\epsilon^{\text{solv}}}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\end{aligned}\right\} \xrightarrow{G,\,[\epsilon\nabla G\cdot\hat{n}]} \boxed{\mathbf{q} = \mathbf{Q}(\{\mathbf{s}\},\,\epsilon^{\text{solv}})\mathbf{V}_{\text{M}}}$$

PCM + DFT

- The starting point is the free energy functional:

$$G[\rho^e,\rho^n] = E^{\mathrm{vac}}[\rho^e] \quad + \quad \frac{1}{2}\int d\mathbf{r}\ \rho^e(\mathbf{r})\,\{v_{\mathrm{R}}[\rho^e](\mathbf{r}) + v_{\mathrm{R}}[\rho^n](\mathbf{r})\}$$
$$+ \quad \frac{1}{2}\int d\mathbf{r}\ \rho^n(\mathbf{r})\,\{v_{\mathrm{R}}[\rho^e](\mathbf{r}) + v_{\mathrm{R}}[\rho^n](\mathbf{r})\}$$

- By taking the functional derivative $\dfrac{\delta G[\rho^e,\rho^n]}{\delta\rho^e(\mathbf{r})}$

$$v_{\mathrm{S}}[\rho^e,\rho^n](\mathbf{r}) = v_{\mathrm{S}}^0[\rho^e](\mathbf{r}) + v_{\mathrm{R}}[\rho^e](\mathbf{r}) + v_{\mathrm{R}}[\rho^n](\mathbf{r})$$

Kohn-Sham Eqs.

$$\left(-\frac{\nabla^2}{2} + v_{\mathrm{s}}^0[\rho^e](\mathbf{r}) + \sum_{i=1}^{T}\left[\frac{q^e(\mathbf{s}_i) + q^n(\mathbf{s}_i)}{|\mathbf{r}-\mathbf{s}_i|}\right]\right)\varphi_j(\mathbf{r}) = \varepsilon_j\varphi_j(\mathbf{r})$$

$$q^{e/n}(\mathbf{s}_k) = \sum_{l=1}^{T} Q(\mathbf{s}_k,\mathbf{s}_l;\epsilon)V_{\mathrm{M}}[\rho^{e/n}](\mathbf{s}_l)$$

PCM + DFT: real-space (RS) representation

- Finite-differences methods are robust and accurate.
- Potentials and orbitals are directly evaluated in RS.
- Well suited for massive parallel computing.
- Center for Theor. and Comput. Chemistry, Norway.
  Real-space numerical grid methods in quantum chemistry
  Phys. Chem. Chem. Phys. **17**, 31357 (2015).

$$v_{\mathrm{R}}(\mathbf{r}) = \sum_{i=1}^{T} \left[\frac{q^e(\mathbf{s}_i) + q^n(\mathbf{s}_i)}{|\mathbf{r} - \mathbf{s}_i|} \right]$$

Coulomb singularity: $\mathbf{r} \rightarrow \mathbf{s}_i$

We used Gaussians to regularize the reaction field

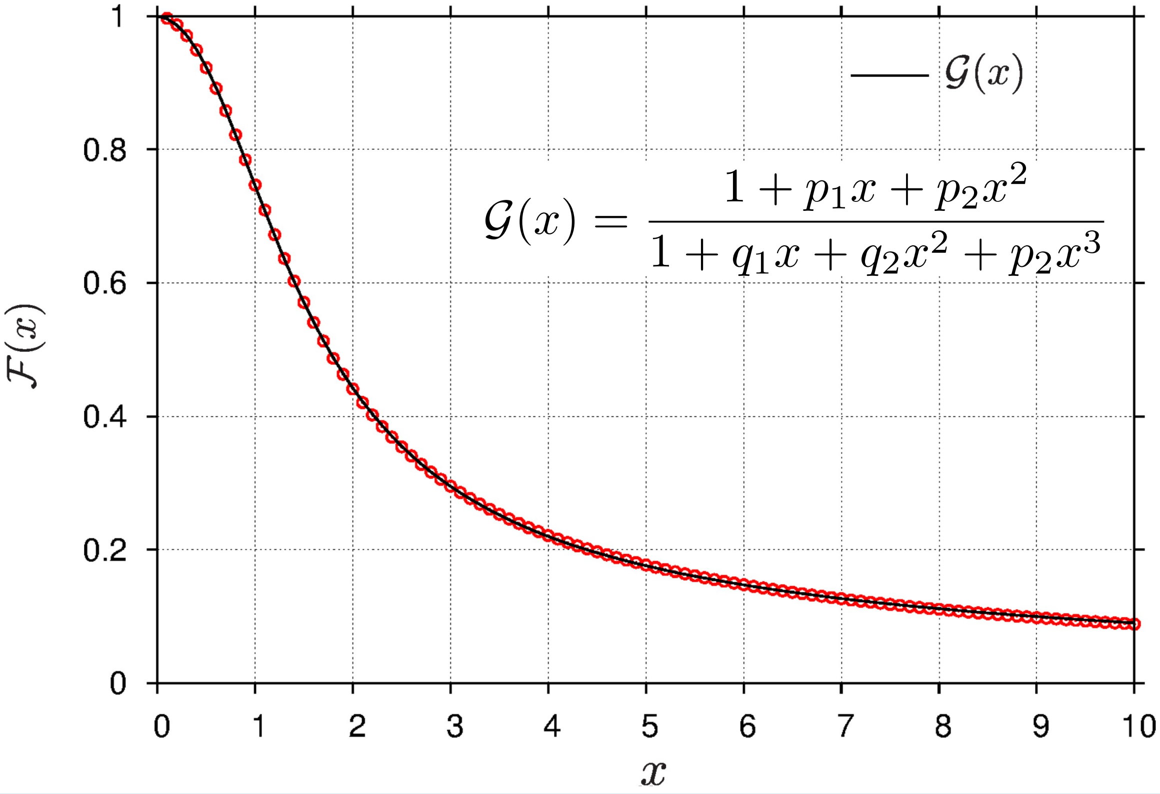
A. Delgado et al. J. Chem. Phys. 143, 144111 (2015)

$$q(\mathbf{s}_i)$$

$$\rho(\mathbf{r}, \mathbf{s}_i) = \frac{q(\mathbf{s}_i)}{(\alpha \pi A_i)^{3/2}} e^{-|\mathbf{r}-\mathbf{s}_i|^2/\alpha A_i}$$

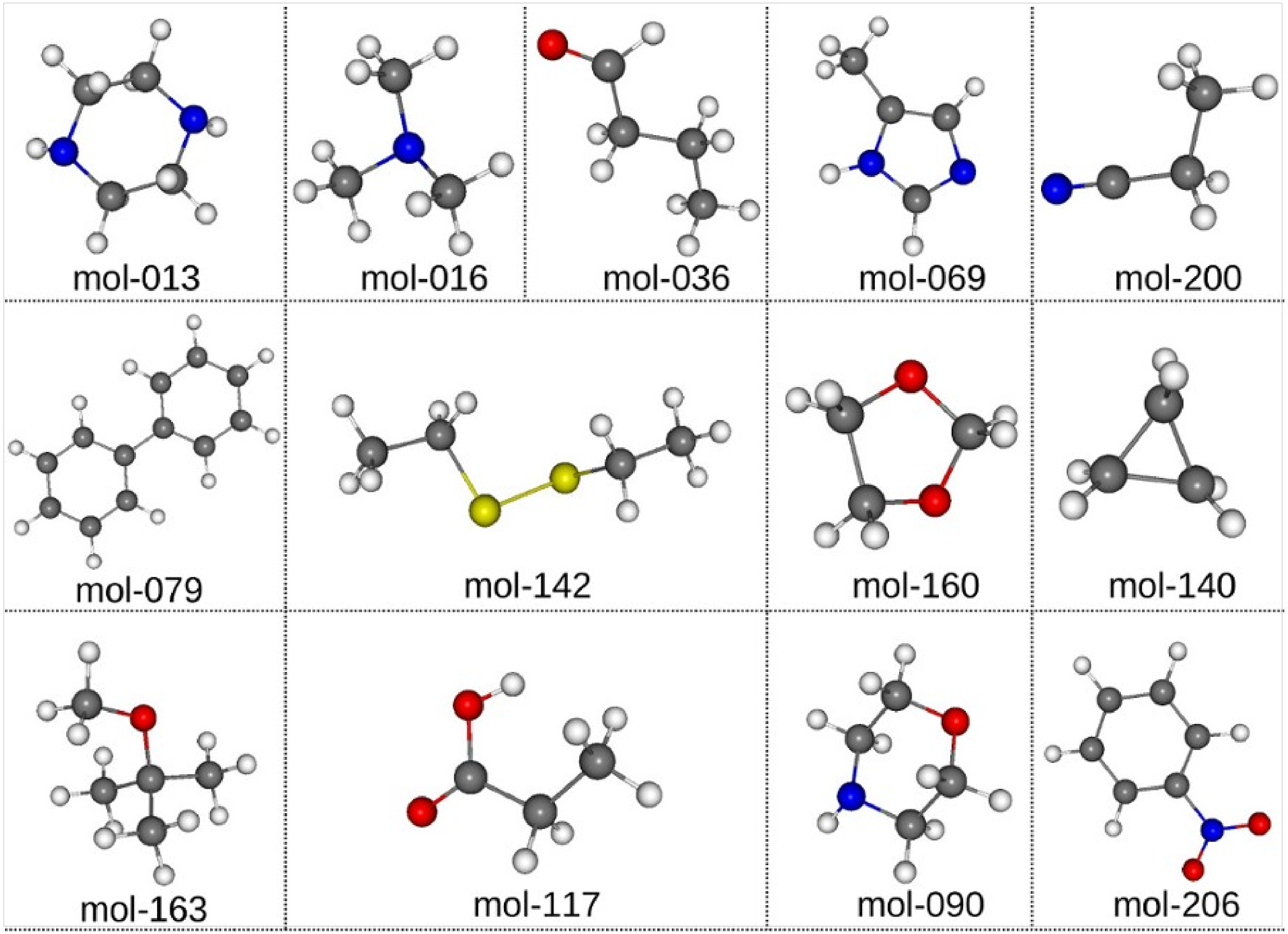
$$v_{\mathrm{R}}(\mathbf{r}, \mathbf{s}_i) = \frac{2q(\mathbf{s}_i)}{\sqrt{\pi \alpha A_i}} \mathcal{F}(|\mathbf{r} - \mathbf{s}_i|/\sqrt{\alpha A_k})$$

$$\mathcal{F}(x) = \int_x^{\infty} dx' \left\{ \frac{\Gamma(3/2) - \Gamma(3/2, x'^2)}{x'^2} \right\}$$



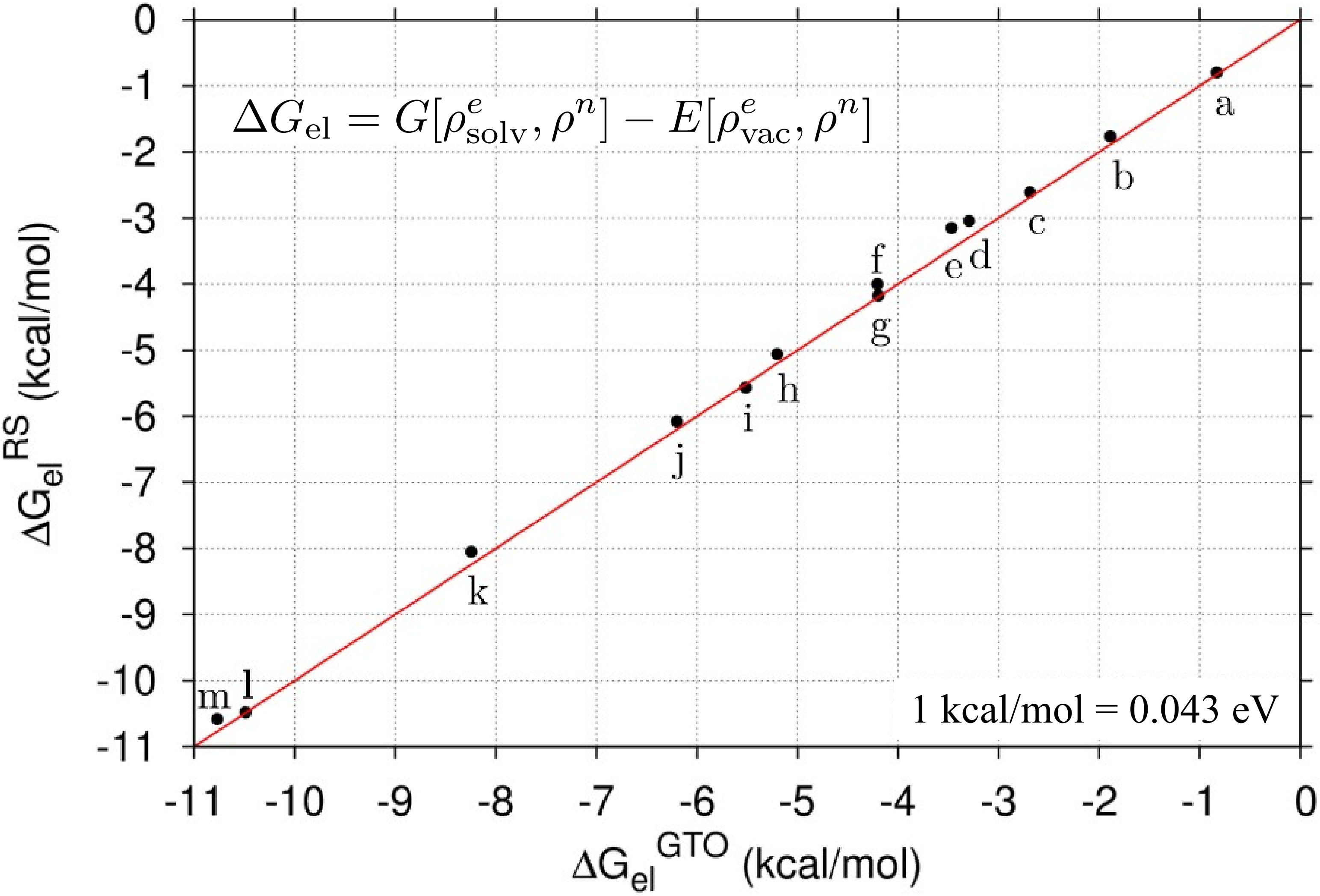
Results: set of molecules for testing PCM implementation

- Real-space calculations performed with **Octopus** (www.tddft.org)
- Solvent = water
- Benchmark with similar calculations obtained with **GAMESS**



Solvation free energies in water

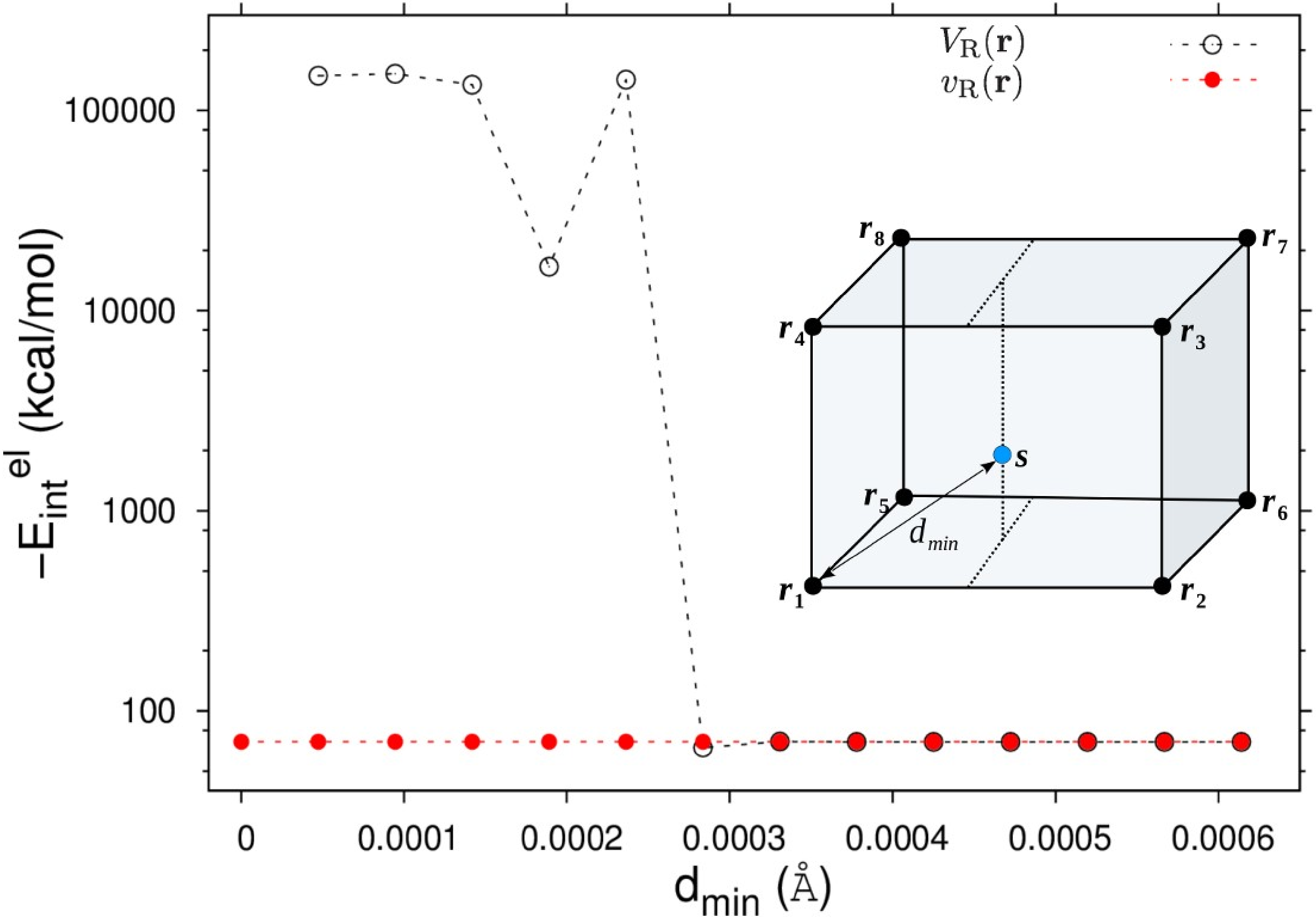
- Density functional
  GGA - PBE
- RS grid: R= 5 Å Δ = 0.15 Å
  Octopus
- GTO: 6-311+G(d,p)
  GAMESS



A. Delgado et al. J. Chem. Phys. 143, 144111 (2015)

Showing the singularity effects: calculations in Cl^-

- Density functional
  GGA - PBE
- RS grid: R= 5 Å Δ = 0.15 Å
  Octopus

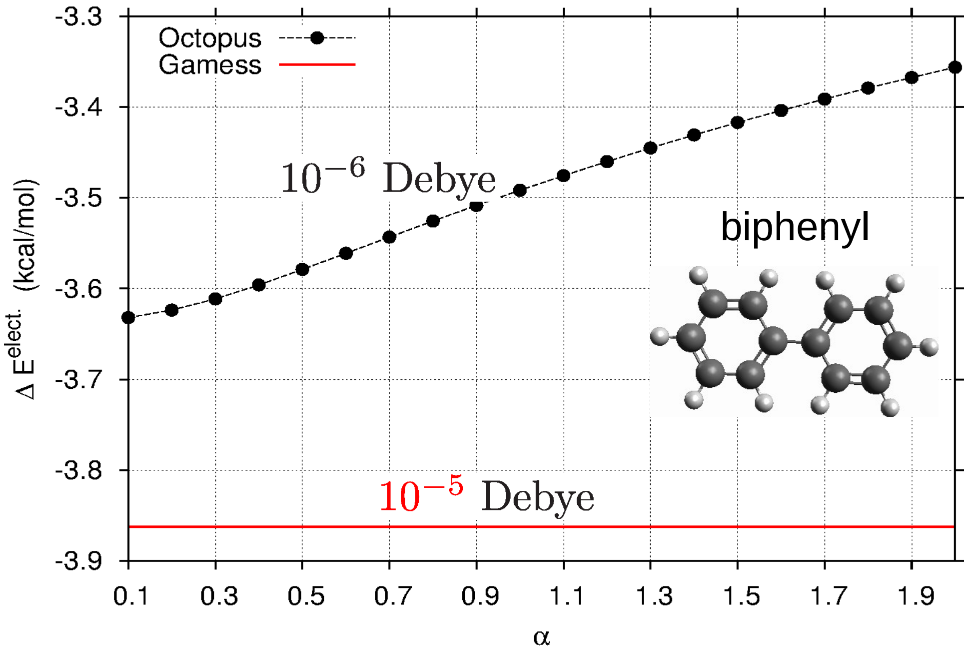


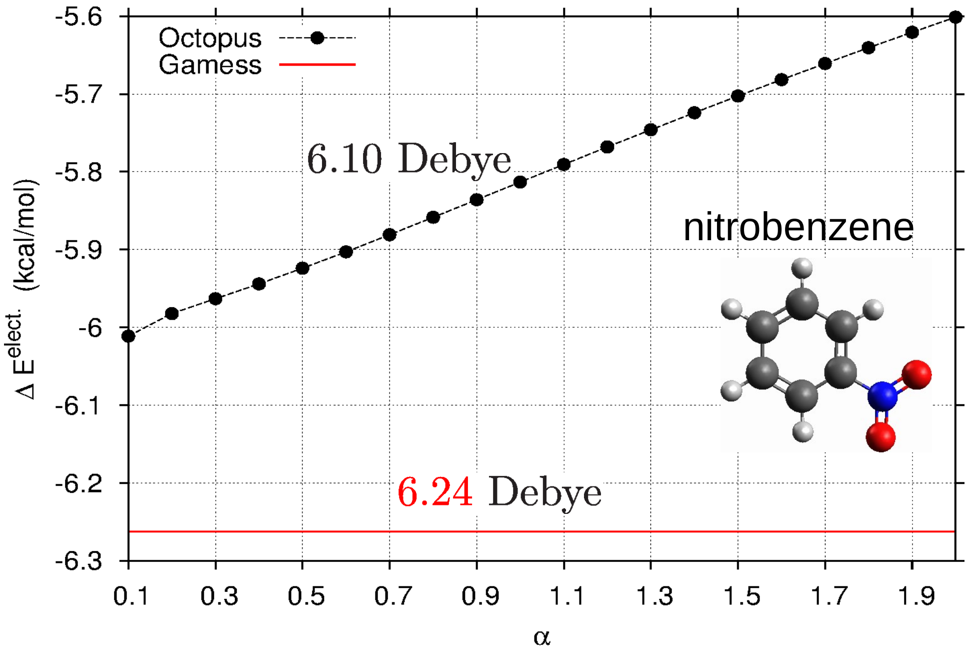
A. Delgado et al. J. Chem. Phys. 143, 144111 (2015)

Dependence on the parameter α

- Density functional
  GGA - PBE
- RS grid: R= 5 Å Δ = 0.15 Å
  Octopus
- GTO: 6-311+G(d,p)
  GAMESS

$$\rho(\mathbf{r}, \mathbf{s}_i) = \frac{q(\mathbf{s}_i)}{(\alpha\pi A_i)^{3/2}} e^{-|\mathbf{r}-\mathbf{s}_i|^2/\alpha A_i}$$





A. Delgado et al. J. Chem. Phys. 143, 144111 (2015)

Optical properties: TDDFT + PCM

Real-time propagation of KS orbitals (time domain)

$$i\hbar\frac{\partial}{\partial t}\varphi_j(\mathbf{r},t) = H_{\mathrm{KS}}[\rho^e](\mathbf{r},t)\varphi_j(\mathbf{r},t)$$

Perturbation at t = 0: $v_{\mathrm{ext}}(\mathbf{r},t) = -e\mathbf{r}\cdot\mathbf{K}\delta(t)$

↓

$$\begin{aligned}\varphi_j(\mathbf{r},0^+) &= \exp\left\{-\frac{i}{\hbar}\int_{0^-}^{0^+} dt[H^0_{\mathrm{KS}} - e\mathbf{r}\cdot\mathbf{K}\delta(t)]\right\}\varphi_j(\mathbf{r},0^-)\\ &= \exp(ie\mathbf{r}\cdot\mathbf{K}/\hbar)\varphi_j(\mathbf{r},0^-)\end{aligned}$$

propagate in time ↓ $\mathbf{D}(t) = -e\int d^3r\ \mathbf{r}\rho^e(\mathbf{r},t)$

$$\alpha_{\gamma\delta}(\omega) = \frac{1}{K_\delta}\int_0^\infty dt\ [D_\gamma(t) - D_\gamma(0^-)]e^{-i\omega t}$$

$$\sigma(\omega) \sim \mathrm{Im}\{\alpha(\omega)\}$$

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propagate in time ↓

Solvent response in real-time

S. Corni et al. J. Phys. Chem. A, 119, 5405 (2015)

$$\mathbf{q}(t) = \int_{-\infty}^{\infty} dt' f(t-t')\tilde{\mathbf{Q}}\mathbf{V}_{\mathrm{M}}(t') \qquad f(t-t') = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega(t-t')}f(\omega)$$

$$\epsilon(\omega) = \epsilon_d + \frac{\epsilon_0-\epsilon_d}{1-i\omega\tau}$$ (Debye solvent)

$\tilde{\mathbf{Q}}$: is frequency independent. Singling out the frequency in IEF-PCM is possible but not trivial. Take a look at the reference above.

Optical properties: TDDFT + PCM

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By considering $\epsilon_d = \epsilon_0$

$$\mathbf{q}(t) = \mathbf{Q}\mathbf{V}_{\mathrm{M}}(t)$$

- solvent polarization equilibrates $\rho^e(t)$
- Good approximation for weakly polar solvents

Optical properties: TDDFT + PCM

RT propagation of KS orbitals (time domain)

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Perturbation at t = 0: $v_{\mathrm{ext}}(\mathbf{r},t) = -e\mathbf{r}\cdot\mathbf{K}\delta(t)$

propagate in time

Solvent response in real-time

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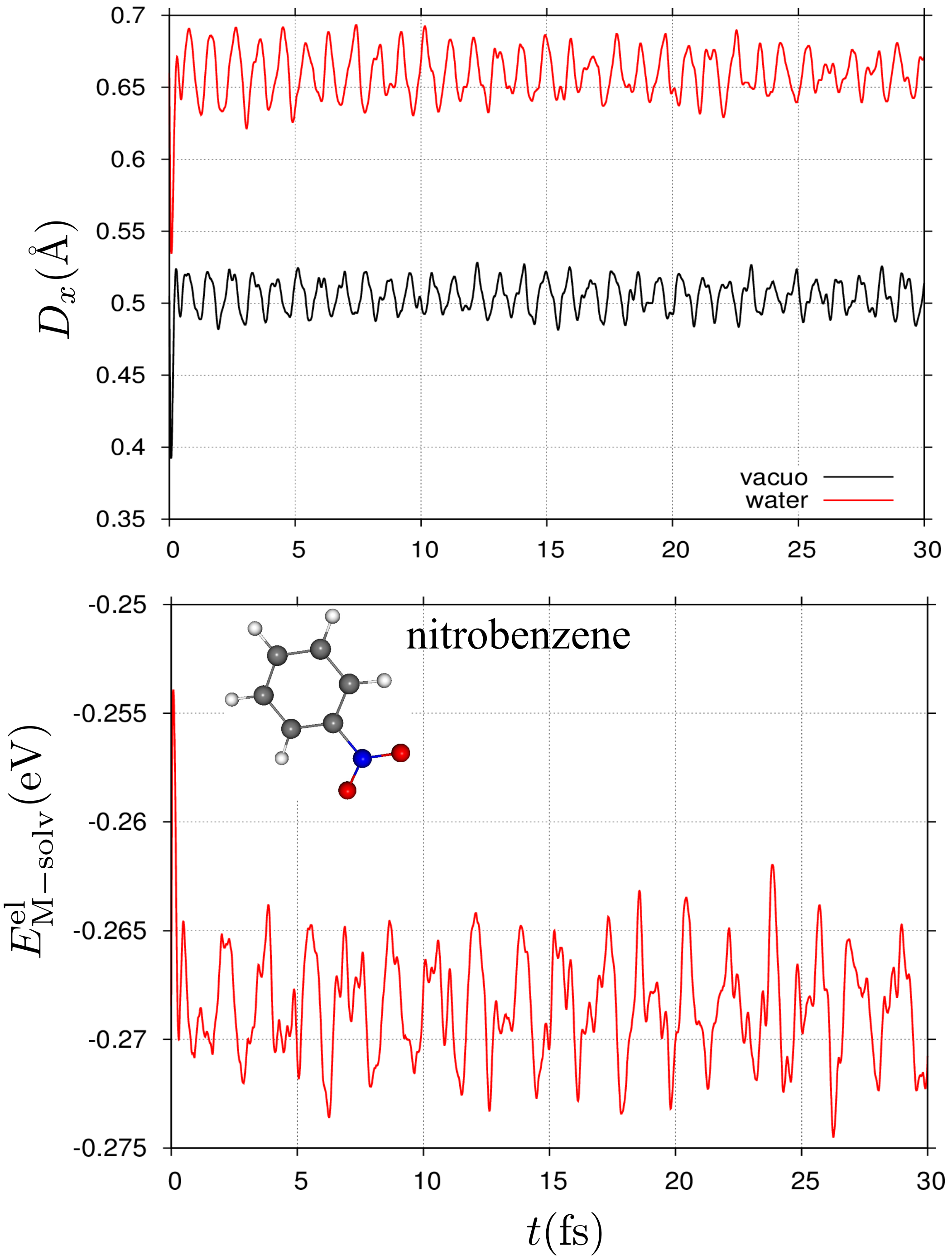
Optical properties: TDDFT + PCM



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propagate in time

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propagate in time

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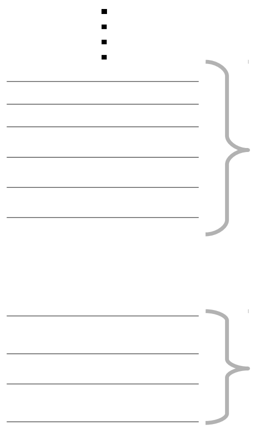
$$\sigma(\omega) \sim \mathrm{Im}\{\alpha(\omega)\}$$

Linear response approx. (frequency domain)

$$\begin{bmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{bmatrix}\begin{bmatrix}\mathbf{X}\\ \mathbf{Y}\end{bmatrix} = \omega\begin{bmatrix}-\mathbf{1} & 0\\ 0 & \mathbf{1}\end{bmatrix}\begin{bmatrix}\mathbf{X}\\ \mathbf{Y}\end{bmatrix}$$

$$A_{ai,bj} = \delta_{ab,ij}(\varepsilon_a - \varepsilon_i) + K_{ai,bj}$$

$$B_{ai,bj} = K_{ai,jb}$$



a, b (unoccupied)

i, j (occupied)

KS orbitals

$$K_{ai,bj} = K^0_{ai,bj} + \int_\Gamma d\mathbf{s}'d\mathbf{s}\ \Phi_{ai}(\mathbf{s}')\mathbf{Q}(\epsilon,\mathbf{s}',\mathbf{s})\Phi_{bj}(\mathbf{s})$$

$$\Phi_{ai}(\mathbf{s}) = \int d\mathbf{r}\ \frac{\varphi_a^*(\mathbf{r})\varphi_i^*(\mathbf{r})}{|\mathbf{s}-\mathbf{r}|}$$

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propagate in time

Solvent response in real-time

$$\mathbf{q}(t) = \mathbf{Q}\mathbf{V}_{\mathrm{M}}(t)$$

$$\alpha_{\gamma\delta}(\omega) = \frac{1}{K_\delta}\int_0^\infty dt\ [D_\gamma(t) - D_\gamma(0^-)]e^{-i\omega t}$$

$$\sigma(\omega) \sim \mathrm{Im}\{\alpha(\omega)\}$$

Linear response approx. (frequency domain)

$$\begin{bmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{bmatrix}\begin{bmatrix}\mathbf{X}\\ \mathbf{Y}\end{bmatrix} = \omega\begin{bmatrix}-\mathbf{1} & 0\\ 0 & \mathbf{1}\end{bmatrix}\begin{bmatrix}\mathbf{X}\\ \mathbf{Y}\end{bmatrix}$$

$$A_{ai,bj} = \delta_{ab,ij}(\varepsilon_a - \varepsilon_i) + K_{ai,bj}$$

$$B_{ai,bj} = K_{ai,jb}$$

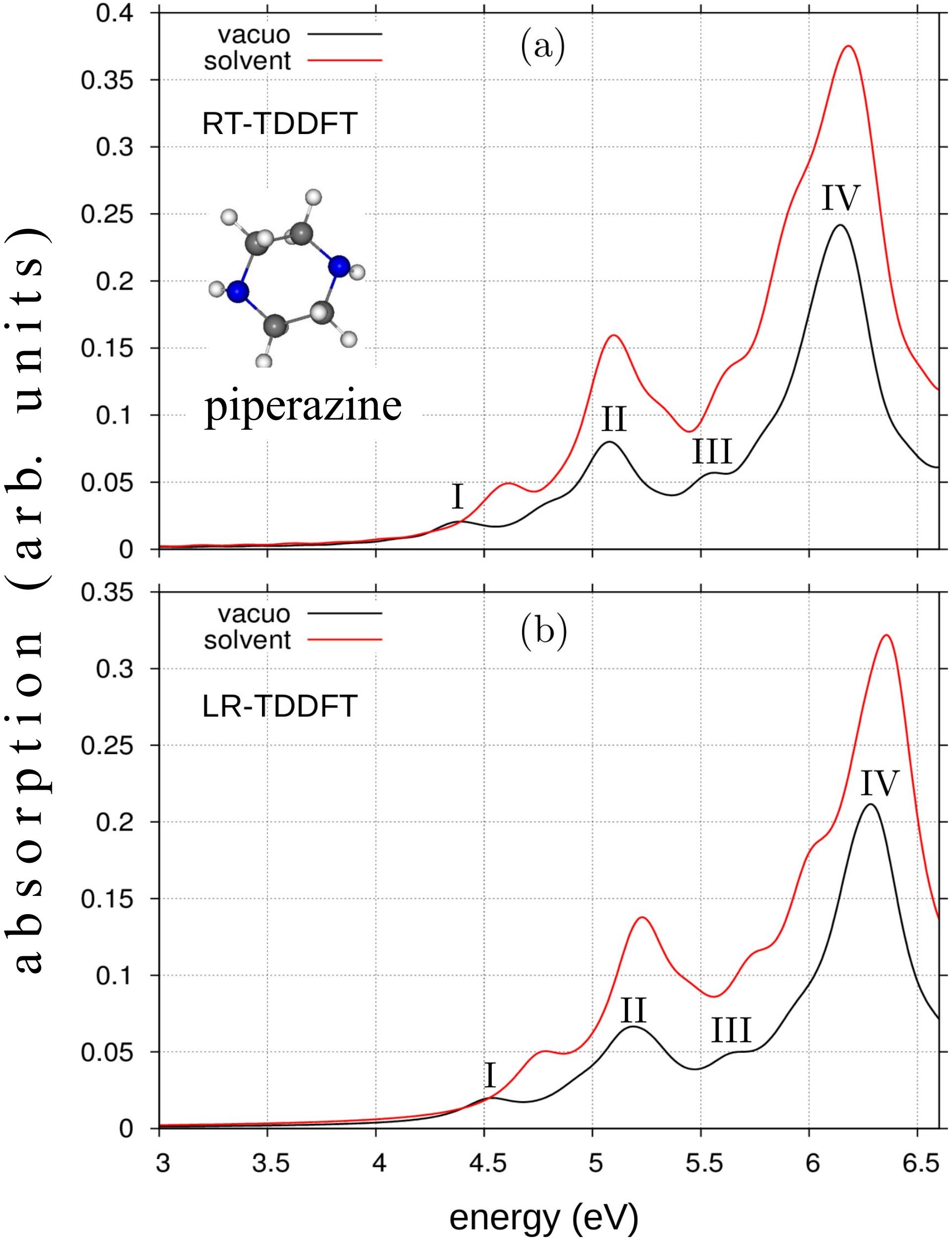
$$K_{ai,bj} = K^0_{ai,bj} + \int_\Gamma ds'ds\ \Phi_{ai}(\mathbf{s}')\mathbf{Q}(\epsilon,\mathbf{s}',\mathbf{s})\Phi_{bj}(\mathbf{s})$$

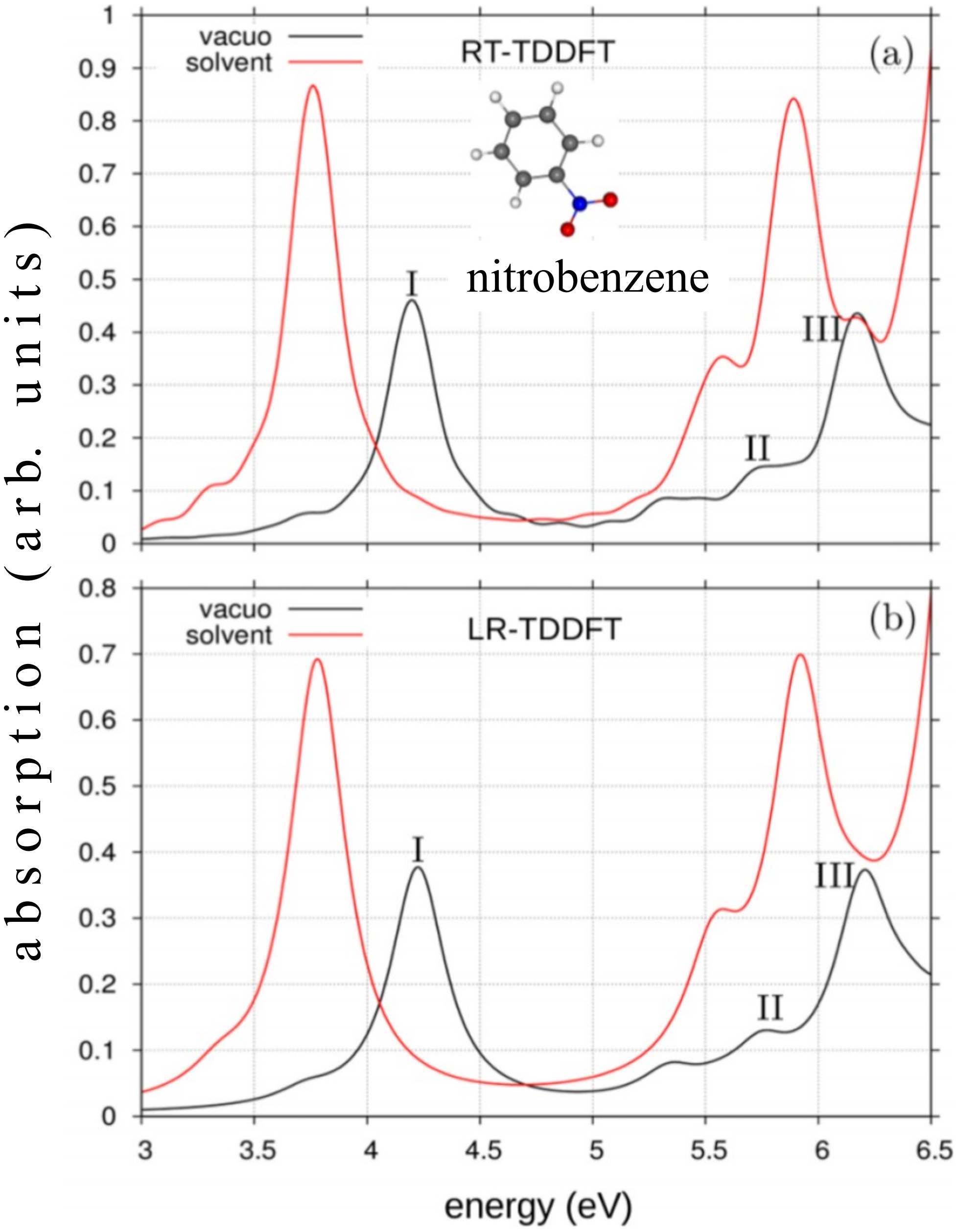
$\omega, \rho^e_1(\mathbf{r},\omega)$

$$\sigma(\omega) \sim \sum_{ia}[\langle a|\mathbf{r}|i\rangle X_{ia}(\omega) + \langle i|\mathbf{r}|a\rangle Y_{ia}(\omega)]$$

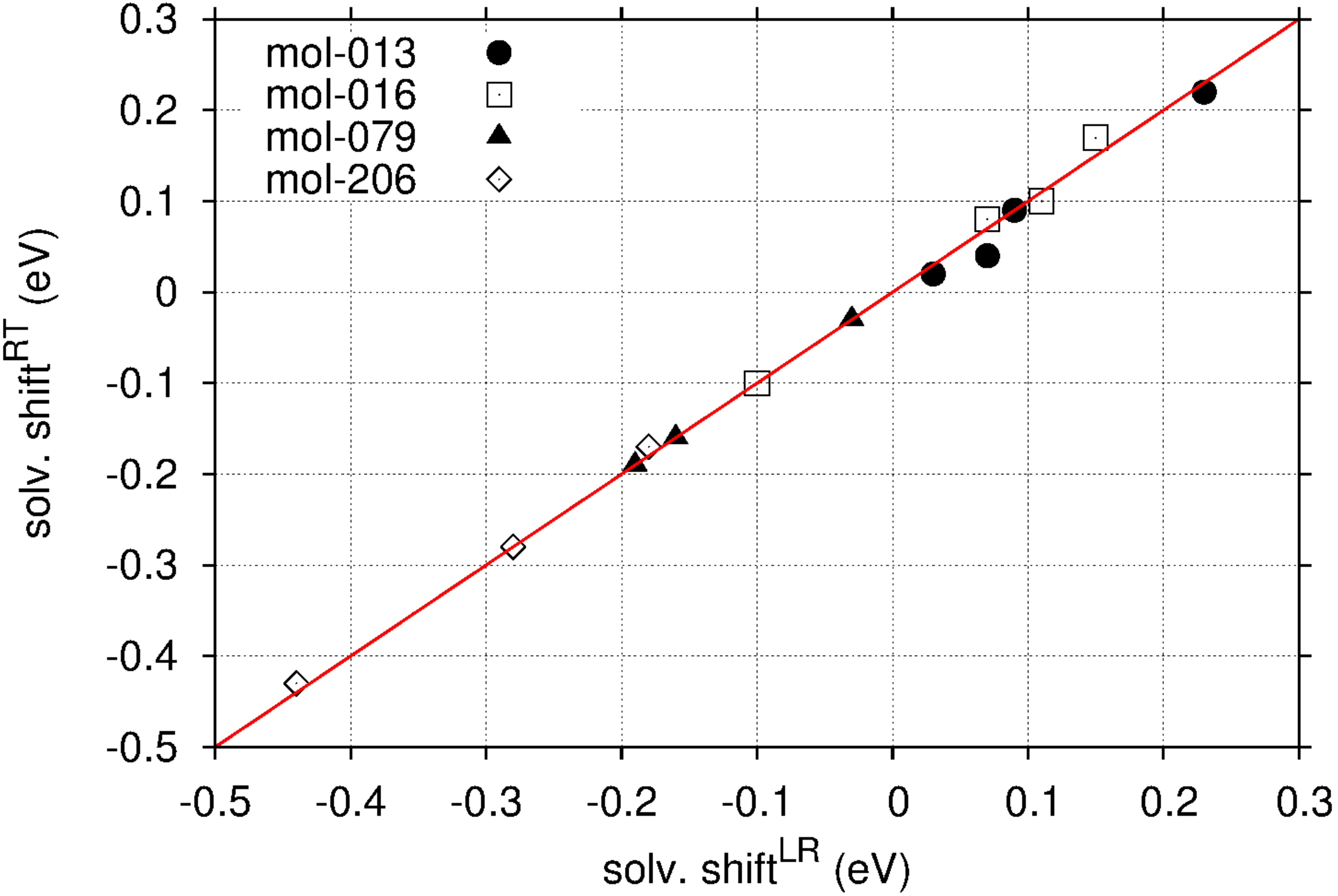
Absorption spectra

- XC = PBE
- RS-DFT: R= 5 Å Δ = 0.19 Å
  RT-TDDFT: Tmax=30 fs Δt=1.7 as
- LR-TDDFT: 6-311+G(d,p)



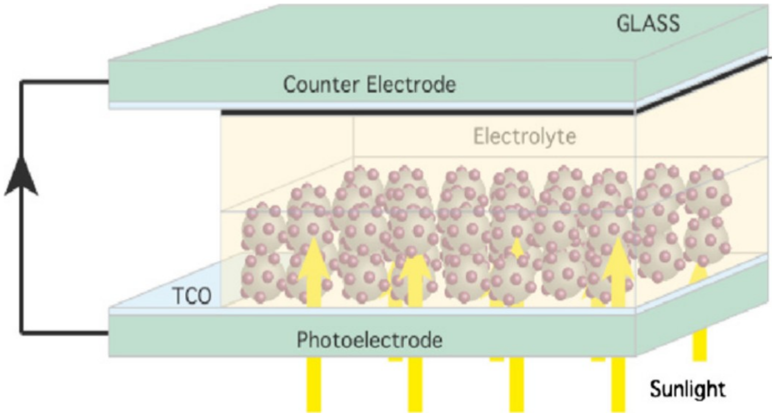


Solvatochromic shifts: RT-TDDFT .vs. LR-TDDFT



Back to dye-sensitized solar cells (DSSCs)

Typical architecture

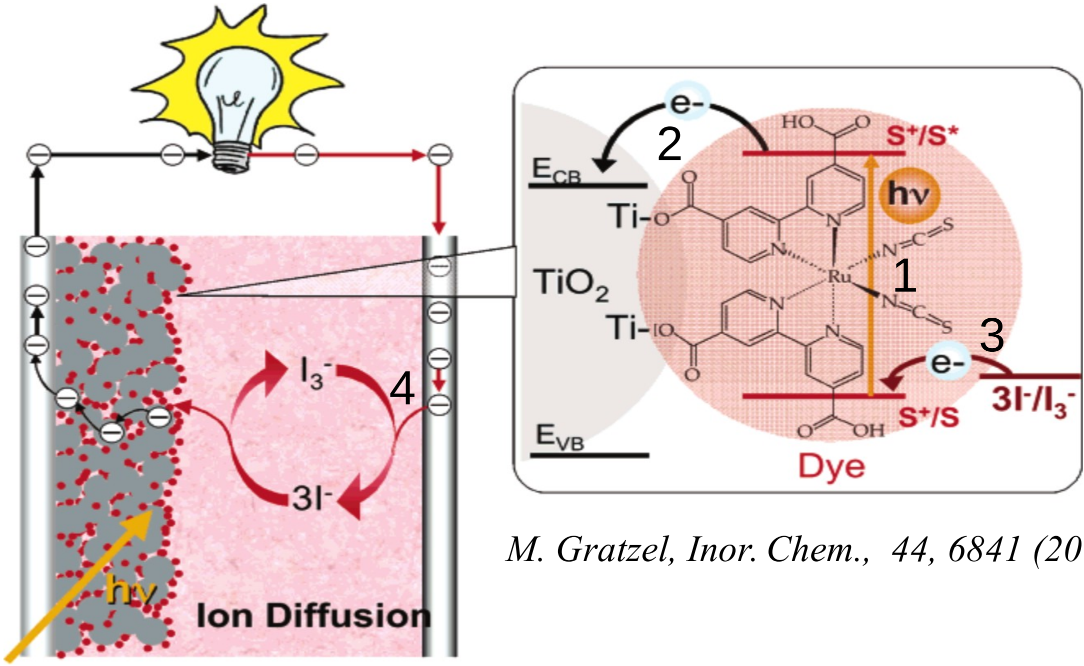


Nazeeruddin et al. Sol. Energy 85, 1172 (2011)

Multi-scale system composed by:

- TiO_2 mesoporous semiconductor film.
- Sensitizer adsorbed onto the surface.
- Electrolyte solution with a redox couple.
- Counter electrode like platinum.

Working principle



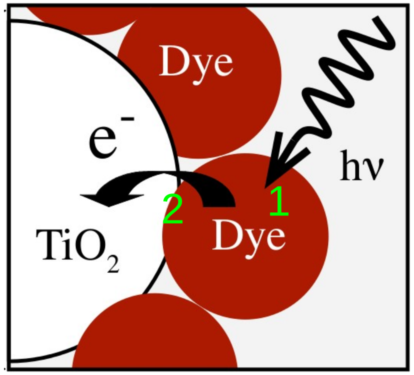
M. Gratzel, Inor. Chem., 44, 6841 (2005)

1. Photon absorption in the dye.
2. Electron injection into the NP.
3. Dye regeneration.
4. Reduction of redox mediator.

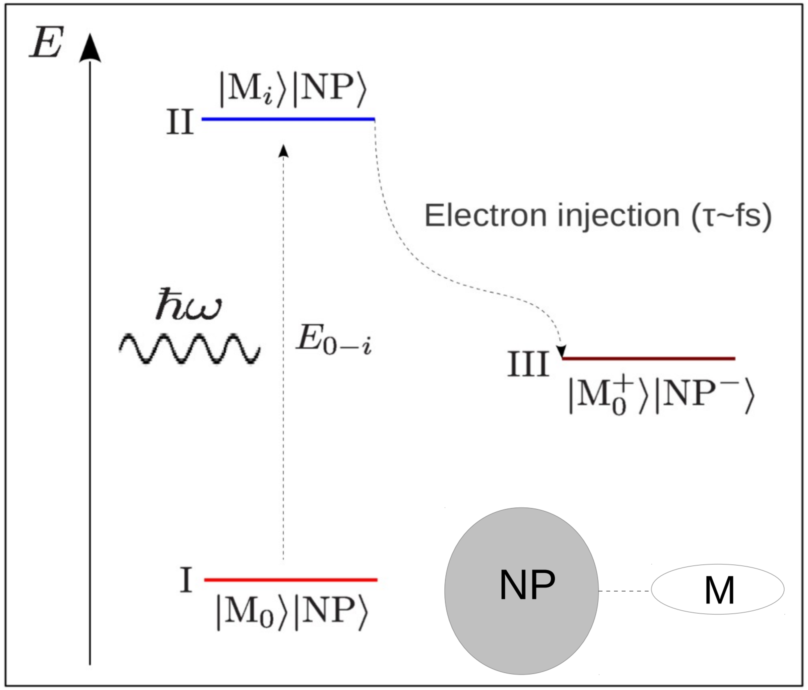
*Solvent **and NP** polarizations may influence all these processes*

ESOP as a key parameter in DSSCs

1. Photon absorption in the dye.
2. Electron injection into the NP.



Energy levels picture



$$\Delta G_{\mathrm{III-II}} < 0$$

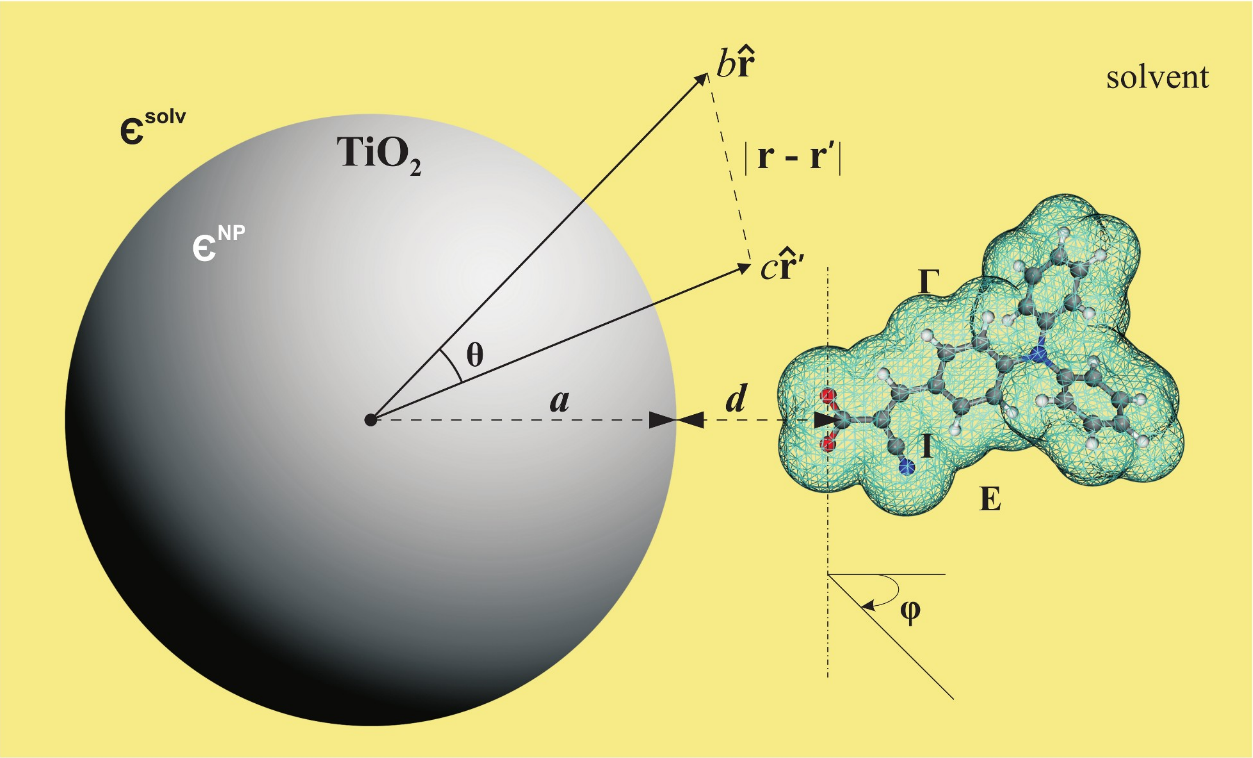
ESOP

$$\Delta G_{\mathrm{III-II}} = -E_{\mathrm{ea}}^{\mathrm{NP}} + [G_0^{\mathrm{M}^+} - G_0^{\mathrm{M}}] - E_{0-i}$$

Our goal:

To compute the **ESOP** of a dye molecule accounting for the *polarization effects* of both, the solvent and the **nanoparticle**.

IEF-PCM equations: **Molecule + solvent + NP**



$$G_I(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

A. Delgado et al. J. Chem. Phys. ***139****, 024105 (2013)*

$$G_{\mathrm{E}}(\mathbf{r},\mathbf{r}') = \frac{1}{\epsilon^{\mathrm{solv}}}\left\{G_I(\mathbf{r},\mathbf{r}') - \sum_{n=1}^{\infty}\frac{a^{2n+1}}{(bc)^{n+1}}C_n P_n(cos\theta) - \left[\frac{\epsilon^{\mathrm{NP}}-\epsilon^{\mathrm{solv}}}{\epsilon^{\mathrm{NP}}+\epsilon^{\mathrm{solv}}}\right]\left[\frac{a}{c|\mathbf{r}-(a^2/c)\hat{\mathbf{r}}'|} - \frac{a}{cb}\right]\right\}$$

$$C_n = \frac{(\epsilon^{\mathrm{NP}}-\epsilon^{\mathrm{solv}})n}{(\epsilon^{\mathrm{NP}}+\epsilon^{\mathrm{solv}})n+\epsilon^{\mathrm{solv}}} - \frac{(\epsilon^{\mathrm{NP}}-\epsilon^{\mathrm{solv}})}{\epsilon^{\mathrm{NP}}+\epsilon^{\mathrm{solv}}},$$

Legendre polynomials

IEF-PCM equations: $\mathbf{S}_E$ and $\mathbf{D}_E$ matrix elements

$$(\hat{S}_E \cdot \sigma) = \int_\Gamma d\mathbf{r} \int_\Gamma G_E(\mathbf{r},\mathbf{r}')\sigma(\mathbf{r}')d\mathbf{r}'$$

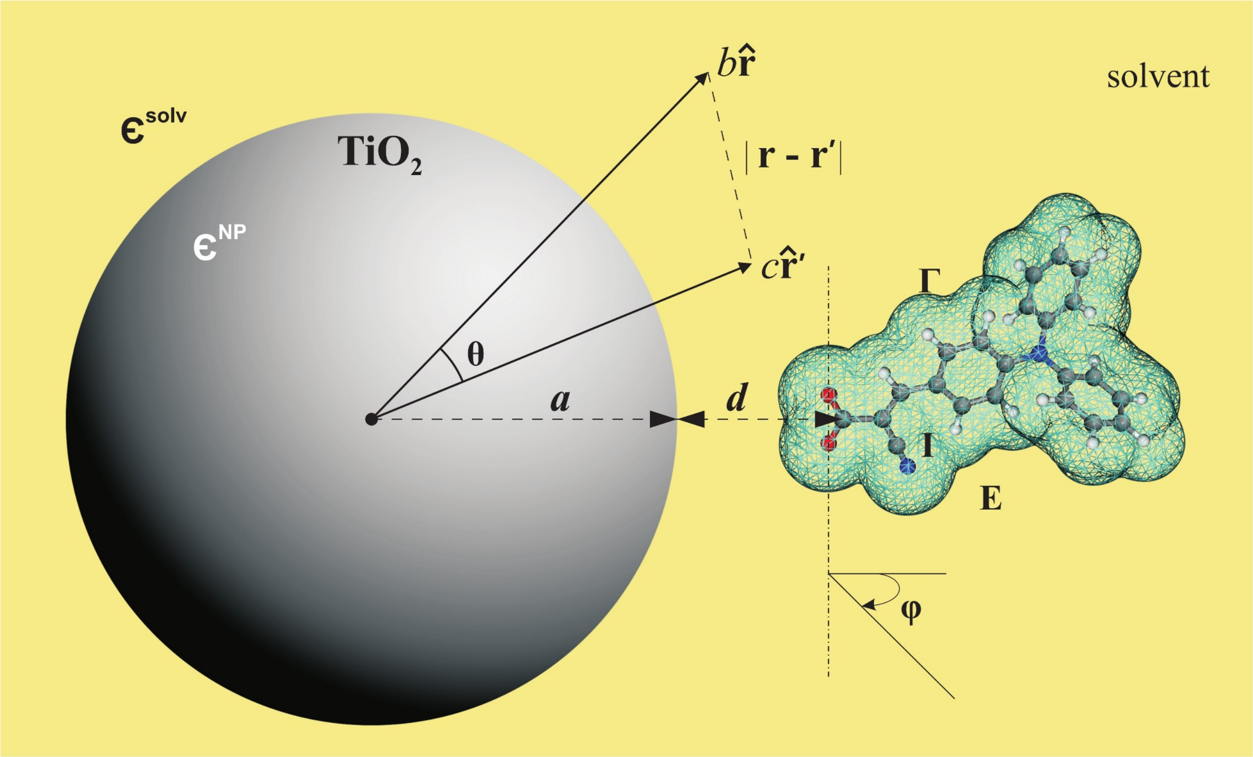
$$S_{ij}^E = \frac{1}{\epsilon^{\text{solv}}}\left\{ S_{ij}^I - \sum_{n=1}^{\infty} \frac{a^{2n+1}}{(b_i c_j)^{n+1}} C_n P_n(cos\theta) - \frac{\epsilon^{\text{NP}} - \epsilon^{\text{solv}}}{\epsilon^{\text{NP}} + \epsilon^{\text{solv}}} \frac{a}{c_j} \left[\frac{1}{|\mathbf{s}_i - (a^2/c_j)\mathbf{s}_j|} - \frac{1}{b_i} \right] \right\}$$

$$(\hat{D}_E \cdot \sigma) = \int_\Gamma d\mathbf{r} \int_\Gamma \left[\epsilon_E \nabla_{\mathbf{r}'} G_E(\mathbf{r},\mathbf{r}') \cdot \hat{\mathbf{n}}(\mathbf{r}')\right] \sigma(\mathbf{r}')d\mathbf{r}'$$

$$\begin{aligned} D_{ij}^E = D_{ij}^I &- \sum_{n=1}^{\infty} \frac{a^{2n+1}C_n}{b_i^{n+1}} \left\{ \frac{-(n+1)[(\mathbf{s}_j - \mathbf{r}_s)\cdot\hat{n}(\mathbf{s}_j)]}{c_j^{n+3}} P_n(cos\theta) \right. \\ &+ \frac{(n+1)(P_{n+1}(cos\theta) - cos\theta P_n(cos\theta))}{c_j^{n+1}(cos^2\theta - 1)} \left[\frac{[(\mathbf{s}_i - \mathbf{r}_s)\cdot\hat{n}(\mathbf{s}_j)]}{b_i c_j} \right. \\ &\left. \left. - \frac{(\mathbf{s}_j - \mathbf{r}_s)\cdot(\mathbf{s}_i - \mathbf{r}_s)}{b_i c_j^3} \left[(\mathbf{s}_j - \mathbf{r}_s)\cdot\hat{n}(\mathbf{s}_j)\right] \right] \right\} A_j \\ &- \left[\frac{\epsilon^{\text{NP}} - \epsilon^{\text{solv}}}{\epsilon^{\text{NP}} + \epsilon^{\text{solv}}}\right] \left(\frac{a}{b_i}\right) \left\{ \frac{[(\mathbf{s}_j - \mathbf{r}_s)\cdot\hat{n}(\mathbf{s}_j)]}{c_j^3} - \frac{[\widehat{(\mathbf{s}_j - \mathbf{r}_s)}\cdot\hat{n}(\mathbf{s}_j)]}{[c_j - a^2/c_j]^2} \right\} A_j \end{aligned}$$

J. Chem. Phys. **139**, 024105 (2013)

IEF-PCM equations: **Molecule + solvent + NP**



$$\mathbf{q} = \mathbf{Q}(\epsilon^{\text{solv}}, \epsilon^{\text{NP}}, a, d, \varphi)\mathbf{V}_{\text{M}}$$

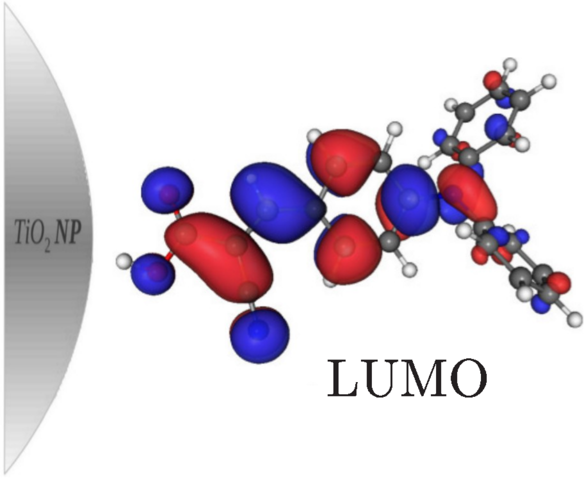
J. Chem. Phys. ***139***, *024105 (2013)*

Lowest excitations of the L0 prot / deprot dyes

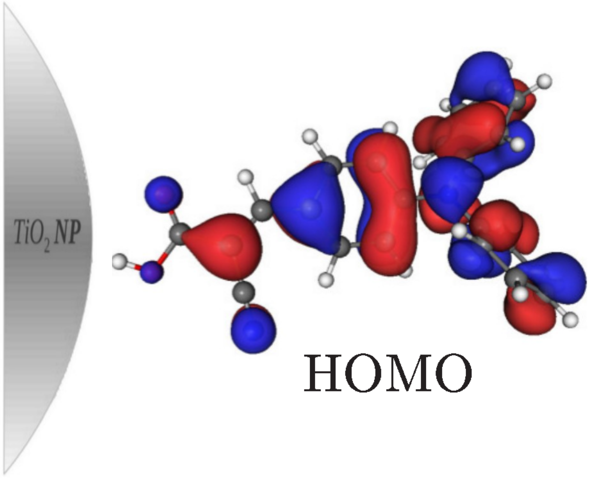
solvent = acetonitrile; $d = 4$ Å, $\varphi = 75°$

(a) protonated, energies in eV.

state	$\omega_i^{(0)}$	E_{0-i}^{TDDFT}	E_{0-i}^{cLR}	f (Coeff.; transition)
1	3.313	3.200	3.280	1.13 (0.96; H → L)
2	4.476	4.473	4.474	0.01 (0.67; H → L+1)
3	4.802	4.778	4.787	0.14 (0.62; H → L+1)
4	4.861	4.810	4.832	0.06 (0.84; H-1 → L)



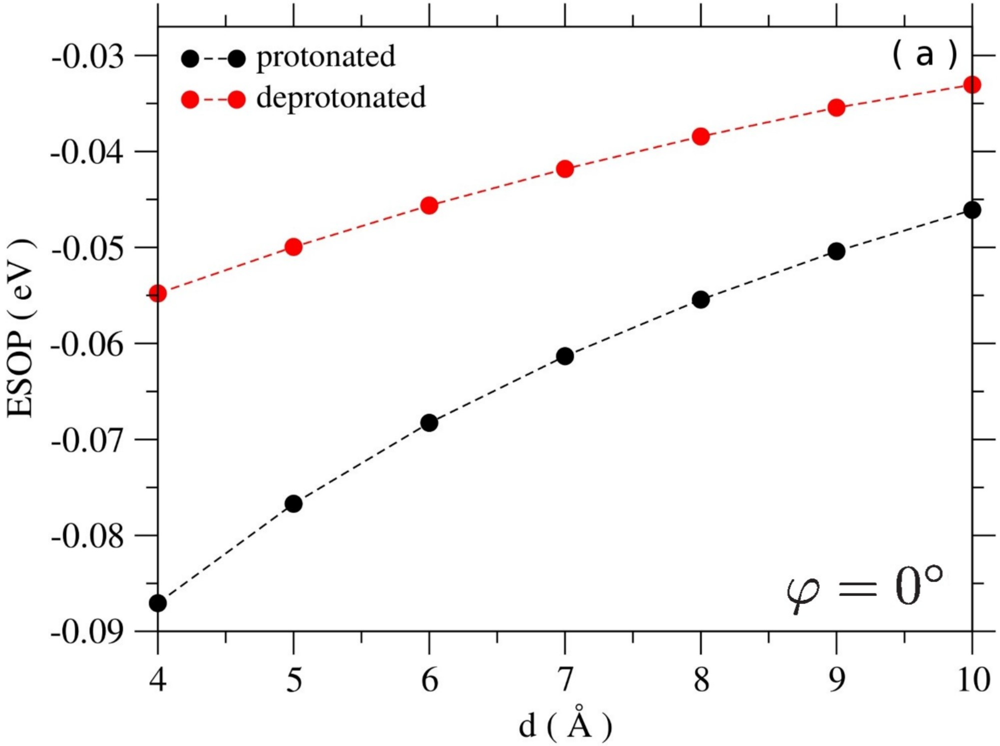
LUMO



HOMO

- LR-TDDFT calculations: XC = CAM-B3LYP / 6-31G(d,p)

ESOP of the L0 prot/deprot dyes

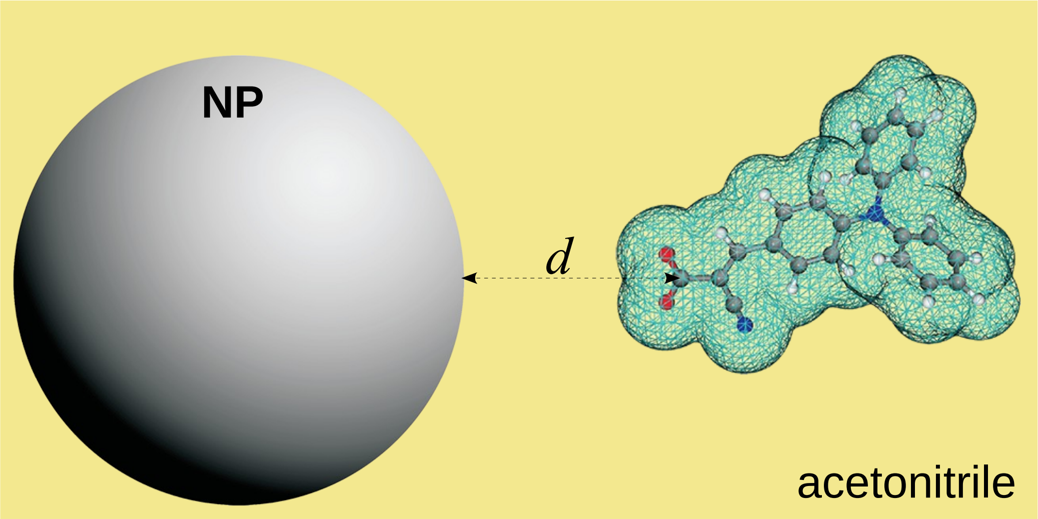


- ESOP referenced to its value in solvent:

ESOP(prot) = 2.95 eV   ESOP(deprot) = 2.33 eV

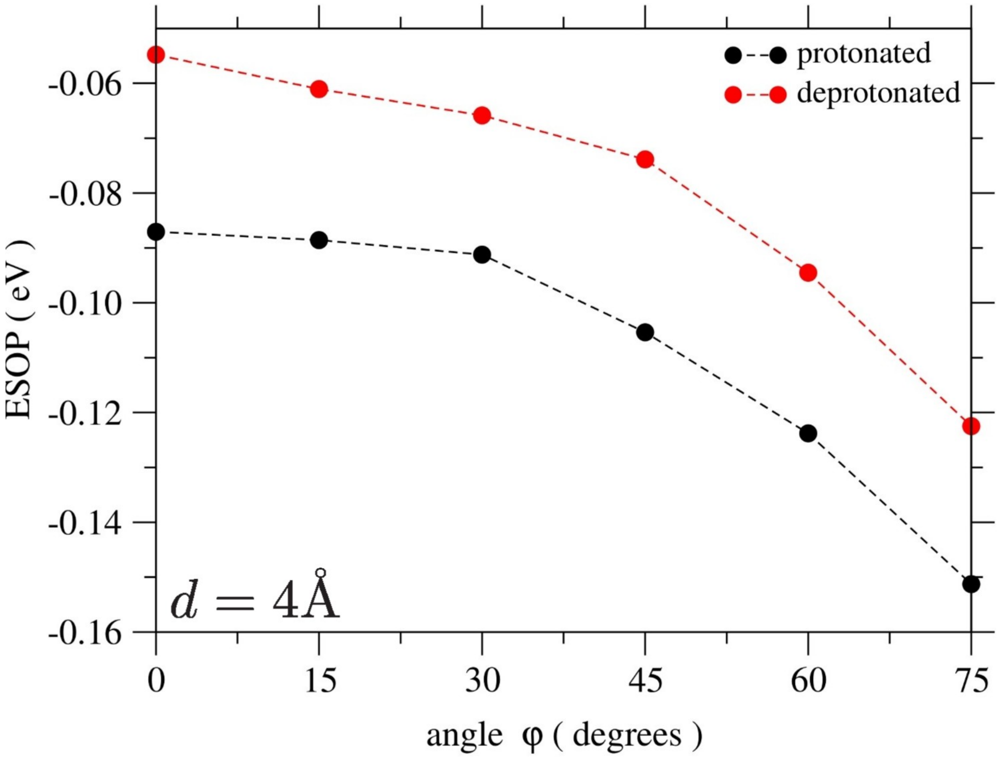
Pastore et al. J. Phys. Chem. C 114, 22742 (2010)

ESOP(exp) = 2.91 eV   ESOP(theo) = 2.86 eV



- The larger ***d***, the smaller the ESOP renormalization (expected).
- For $d \geq 20$ Å: solvation condition.
- Protonated dye renormalizes stronger.
- prot-deprot ESOP gap reduces with ***d***.

ESOP of the L0 prot/deprot dyes



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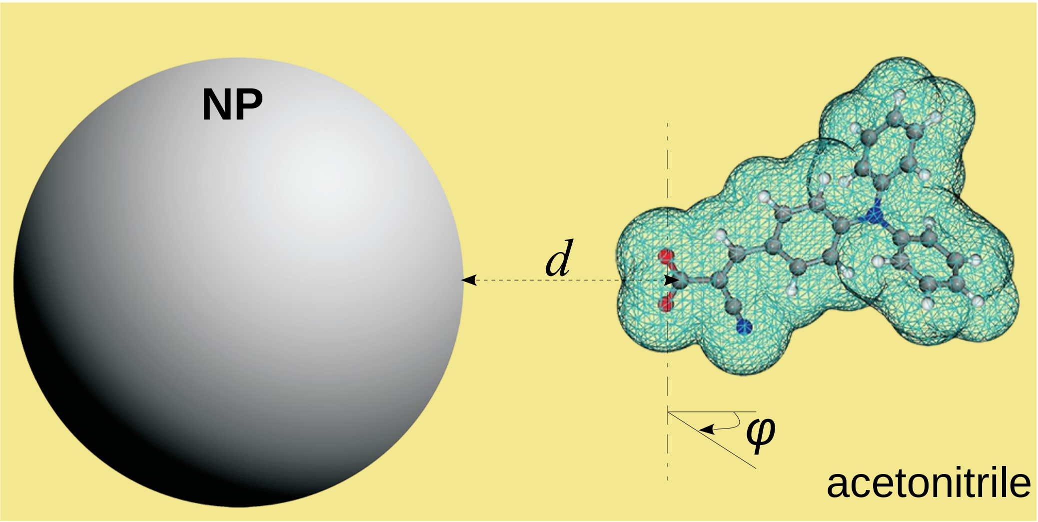
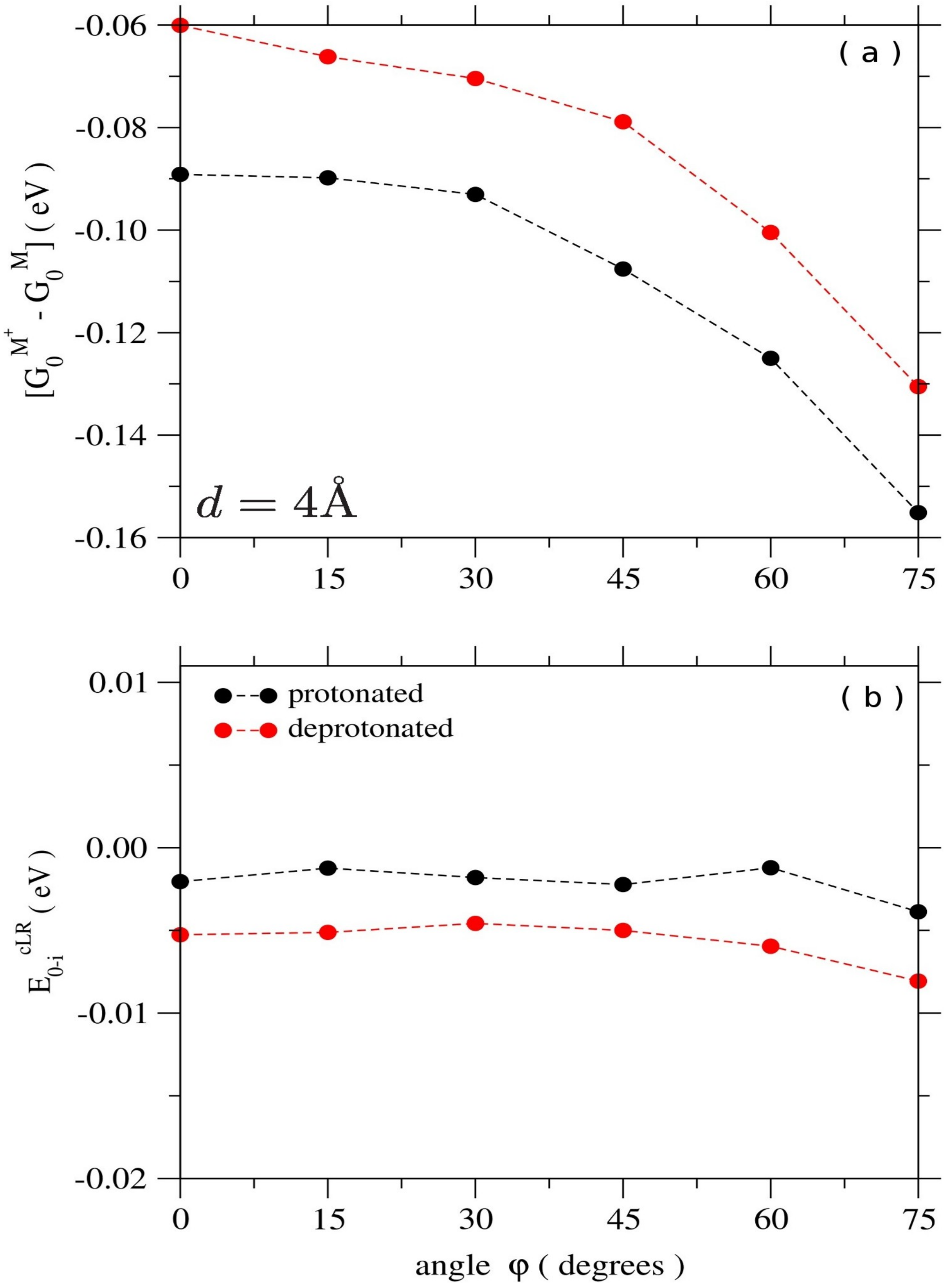


- ESOP renormalization increases by rotating the dye.
- Maximum renormalization about -0.15 eV.
- prot-deprot ESOP gap reduces by rotating the dye.

Independent contributions to the ESOP



$$\mathrm{ESOP} = [G_0^{M^+} - G_0^{M}] - E_{0-i}$$

Values in solvent

$$G_0^{M^+} - G_0^{M} = (\ 6.23;\ 5.92\ )\ \mathrm{eV}$$

$$E_{0-i}^{\mathrm{cLR}} = (\ 3.28;\ 3.59\ )\ \mathrm{eV}$$

- Optical excitation gap renormalizes weakly due to the NP polarization.
- Main contribution comes from the difference between the ground state energies.

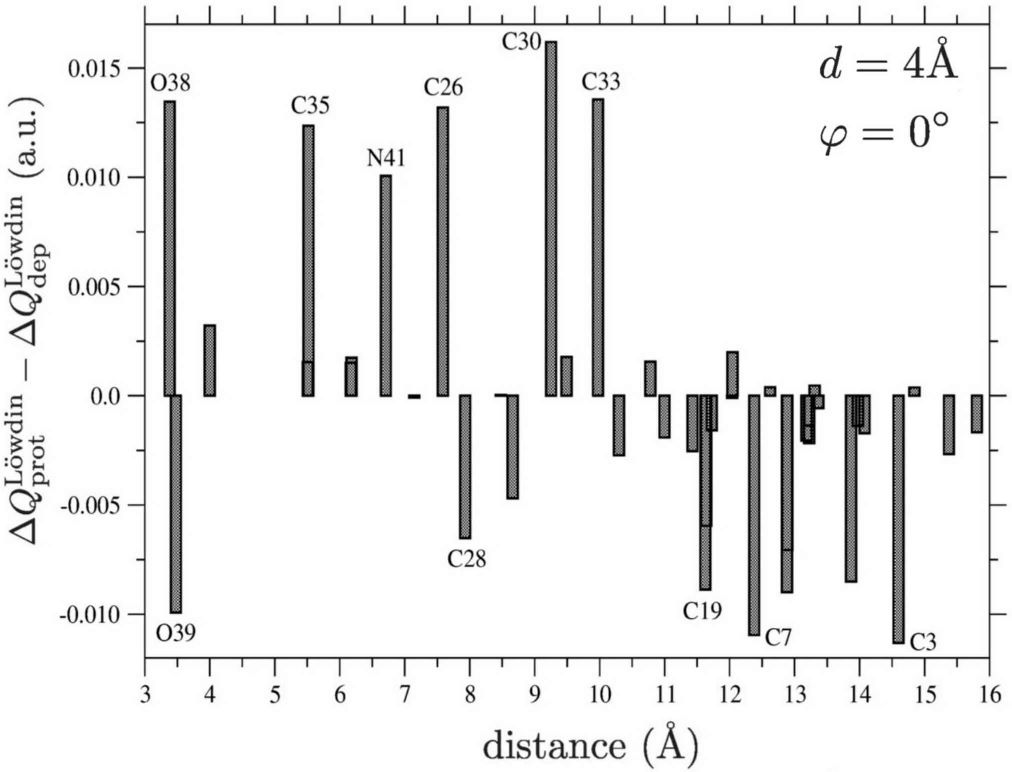
prot/deprot effect on the calculated ESOP

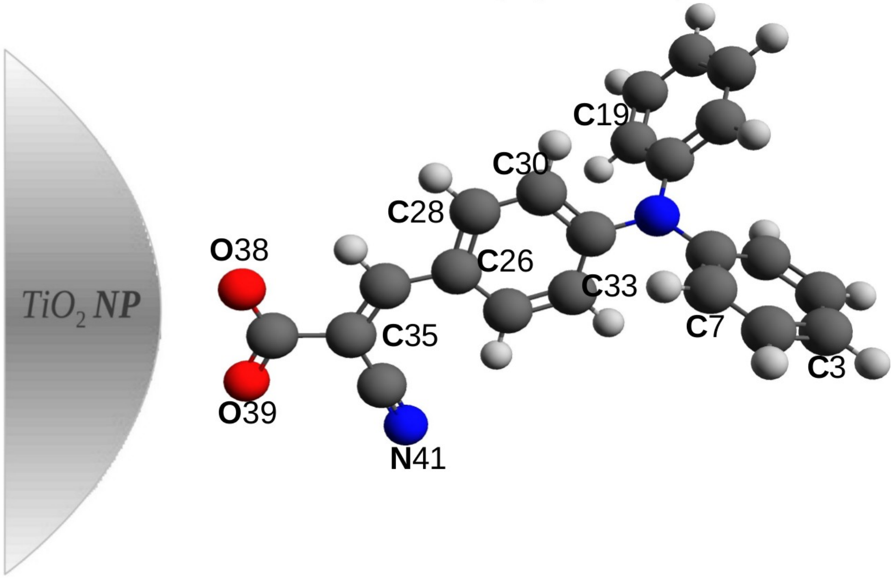
$$\mathrm{ESOP} = [G_0^{\mathrm{M}^+} - G_0^{\mathrm{M}}] - E_{0-i}$$

$$\rho_{\mathrm{M}} \xrightarrow{\text{electron injection}} \rho_{\mathrm{M}+}$$

$$[G_0^{\mathrm{M}^+} - G_0^{\mathrm{M}}] \propto [\rho_{\mathrm{M}+} - \rho_{\mathrm{M}}]$$

$$[\rho_{\mathrm{M}+} - \rho_{\mathrm{M}}] \sim [Q_{\mathrm{M}+}^{\text{Löwding}} - Q_{\mathrm{M}}^{\text{Löwding}}]$$





Conclusions

1) A novel methodology was implemented to account for solvation effects in *real-space* ab-initio electronic structure calculations.

- We used the IEF-PCM model to calculate the solvent polarization response.
- The numerical singularity in the solvent reaction field was regularized by using Gaussian functions to distribute the apparent charges in the van der Waals surface of the solute system.

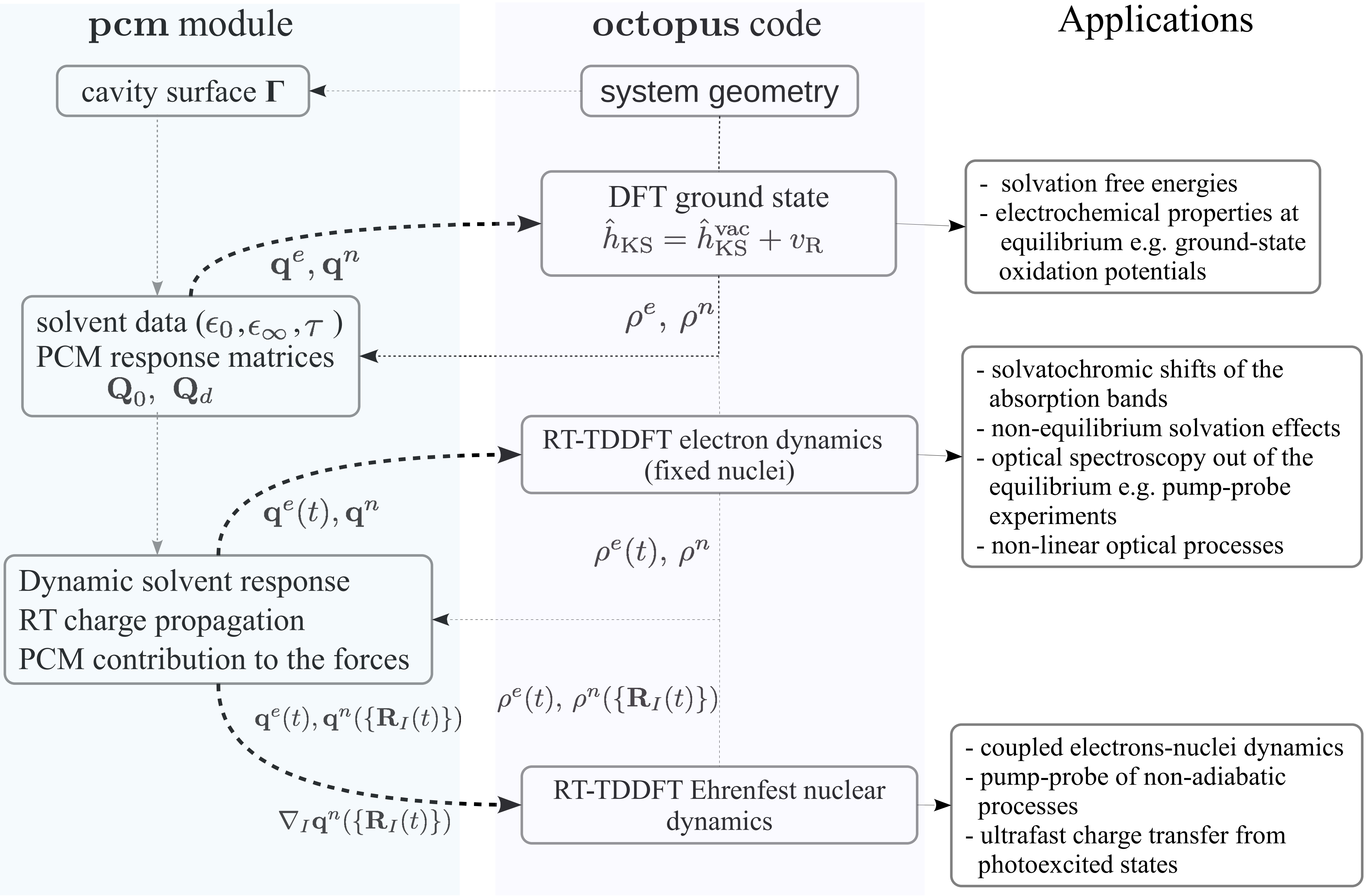
2) The PCM was extended to the real-time domain to address solvent effects in the electron dynamics under the influence of time-dependent fields.

- The real-time solvent polarization was assumed to equilibrate instantaneously the molecular electronic density.
- PCM in the time domain provides a suitable approach to model the optical response, non-linear and ultrafast quantum phenomena in large molecules in a polarizable environment.
- The new methodology is available in the code Octopus (www.tddft.org)

3) The PCM equations were generalized to calculate ground and excited states properties of a molecule close to a semiconductor NP (SNP).

- This methodology was applied to calculate the ESOP of the molecular dye L0 adsorbed to a TiO2 SNP.
- Weak effects due to the NP polarization on the optical absorption excitation. ESOP renormalization dominated by the electrostatic interaction between the oxidized dye and the SNP.
- Implemented in the program GAMESS (www.msg.ameslab.gov/gamess)

Further extensions



pcm module

octopus code

Applications

cavity surface $\boldsymbol{\Gamma}$

system geometry

DFT ground state
$\hat{h}_{\mathrm{KS}} = \hat{h}_{\mathrm{KS}}^{\mathrm{vac}} + v_{\mathrm{R}}$

$\mathbf{q}^e, \mathbf{q}^n$

- solvation free energies
- electrochemical properties at equilibrium e.g. ground-state oxidation potentials

$\rho^e,\ \rho^n$

solvent data ($\epsilon_0, \epsilon_\infty, \tau$)
PCM response matrices
$\mathbf{Q}_0,\ \mathbf{Q}_d$

RT-TDDFT electron dynamics
(fixed nuclei)

- solvatochromic shifts of the absorption bands
- non-equilibrium solvation effects
- optical spectroscopy out of the equilibrium e.g. pump-probe experiments
- non-linear optical processes

$\mathbf{q}^e(t), \mathbf{q}^n$

$\rho^e(t),\ \rho^n$

Dynamic solvent response
RT charge propagation
PCM contribution to the forces

$\mathbf{q}^e(t), \mathbf{q}^n(\{\mathbf{R}_I(t)\})$

$\rho^e(t),\ \rho^n(\{\mathbf{R}_I(t)\})$

$\nabla_I \mathbf{q}^n(\{\mathbf{R}_I(t)\})$

RT-TDDFT Ehrenfest nuclear dynamics

- coupled electrons-nuclei dynamics
- pump-probe of non-adiabatic processes
- ultrafast charge transfer from photoexcited states

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