Polarizable Continuum Model Implementation in the Octopus code

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Outline

1- The basics of the Polarizable Continuum Model (PCM).

2- PCM terms entering the Kohn-Sham Hamiltonian.

2.1 – Atomic basis and real-space representations.
2.2 – Regularization of the Coulomb singularity in real-space.

3- Numerical results.

3.1 – Solvation free energies of neutral solutes.
3.2 – Optical absorption spectra of selected molecules.

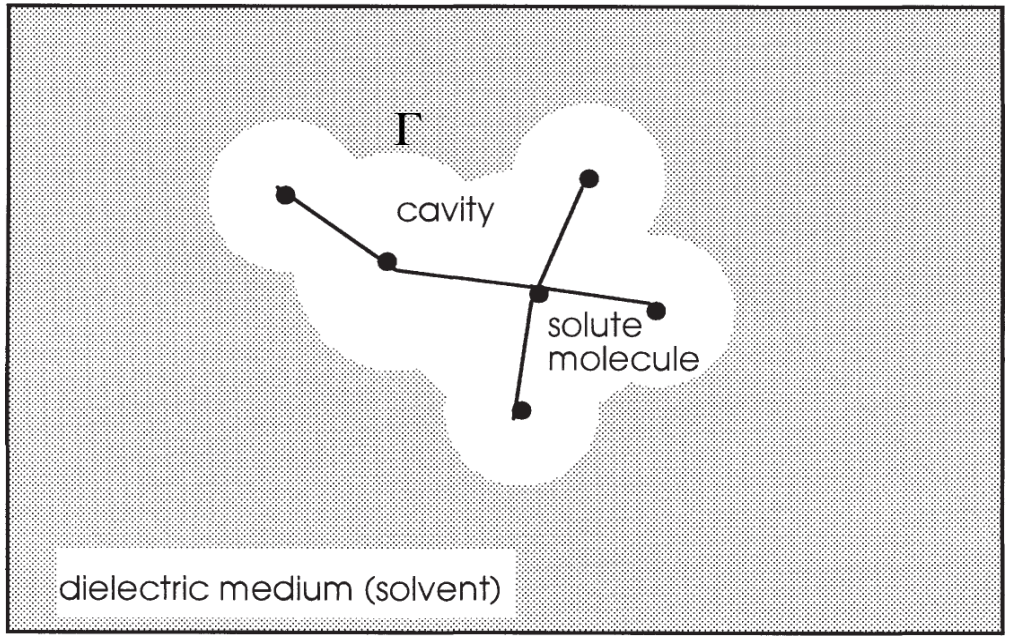
4- What has been coded about PCM in Octopus ?

4.1 – PCM module: main types and subroutines.

5- Conclusions.

The basics of PCM model

S. Miertuš et al. Chem. Phys. ***55****, 117 (1981).*



- The solvent is a ***continuous dielectric medium*** polarized by the solute molecule.
- Solute molecule is hosted by the ***cavity*** within the surface Γ.
- The ***shape of*** Γ should reproduced the ***molecular shape***.
- The molecule is treated **quantum mechanically**.

Effective Hamiltonian

$$\hat{H}^{\text{eff}} = \hat{H}^0_{\text{M}} - \sum_{i=1}^{N_e} [v^e_{\text{PCM}}(\mathbf{r}_i) + v^n_{\text{PCM}}(\mathbf{r}_i)] + \frac{1}{2}\int n^n(\mathbf{r})\; v^n_{\text{PCM}}(\mathbf{r})\; d\mathbf{r}$$

Poisson equation + boundary conditions at Γ

$$-\epsilon\nabla^2 V(\mathbf{r}) = [n(\mathbf{r}) + n^n(\mathbf{r})]$$

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

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

$$V(\mathbf{r}) = V_{\text{M}}(\mathbf{r}) + v^e_{\text{PCM}}(\mathbf{r}) + v^n_{\text{PCM}}(\mathbf{r}) \longrightarrow \text{Solvent Reaction potentials.}$$

Apparent surface charges (ASC)

- The latter Poisson Eq. can be rewritten as: $-\nabla^2 V(\mathbf{r}) = [n(\mathbf{r}) + n^n(\mathbf{r})] + \sigma(\mathbf{s})$

  with $\sigma(\mathbf{s})$ being a apparent charge density distributed on the cavity surface.

- The PCM potential is expressed in terms of $\sigma(\mathbf{s})$: $v_{\mathrm{PCM}}(\mathbf{r}) = \int_\Gamma \frac{\sigma(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d\mathbf{s}$

- $\sigma(\mathbf{s})$ is the unique solution of the equation: *Cances et al.* *J. Math. Chem. 23, 309 (1998)*

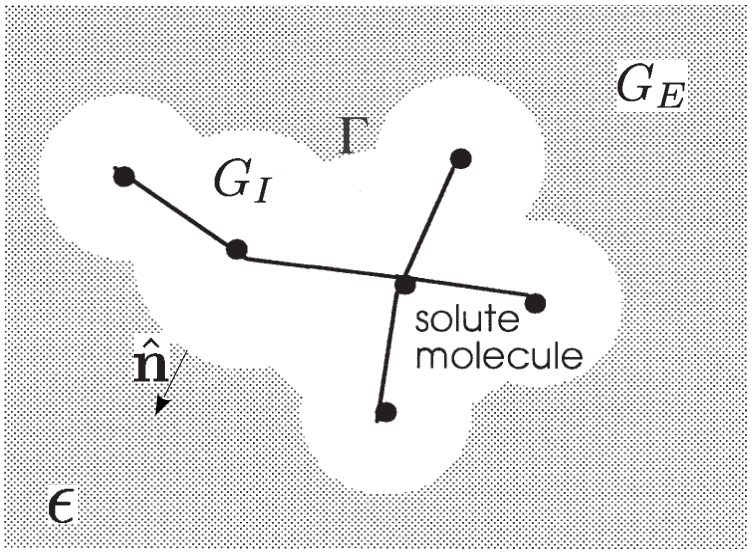
$$[S_E(2\pi + D_I^*) + (2\pi - D_E)S_I]\,\sigma = \left[S_E S_I^{-1}(2\pi - D_I) - (2\pi - D_E)\right] V_{\mathrm{M}}$$

Integral operators

$$(\hat{S}_{I(E)} \cdot \sigma)(\mathbf{r}) = \int_\Gamma G_{I(E)}(\mathbf{r}, \mathbf{r}')\sigma(\mathbf{r}')d\mathbf{r}'$$

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

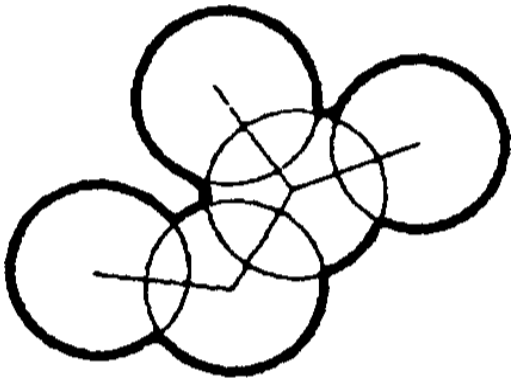
PCM-IEF



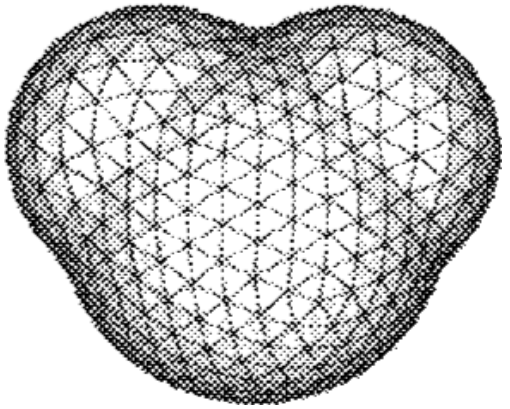
Apparent surface charge method (ASC): *in practice*

- Definition of the cavity and its subdivision in *tesserae* (GEPOL procedure)

Pascual et al. J. Comp. Chem. 11, 1047 (1990)



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



2- Cavity surface *tessellation:* projecting the 60 faces of a pentakis dodecahedron inscribed in each sphere.

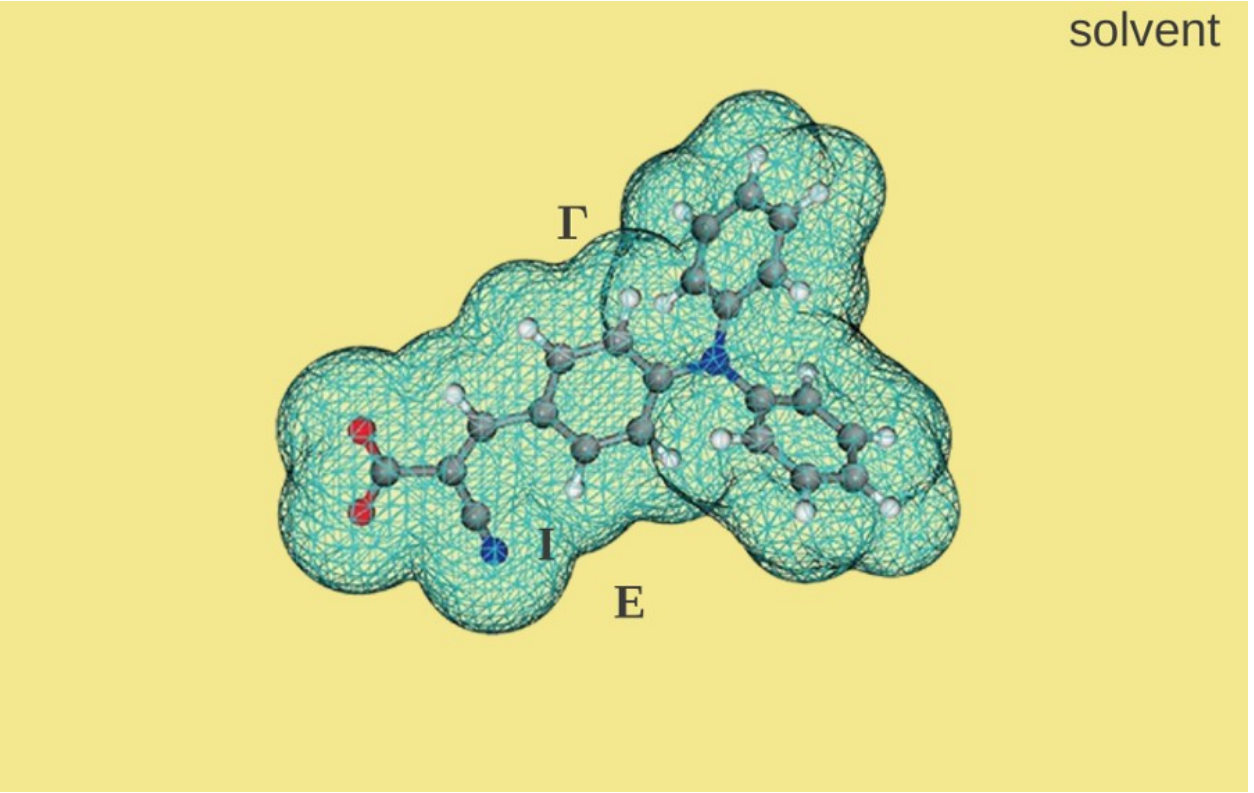
$$v_{\mathrm{PCM}}(\mathbf{r}) = \int_{\Gamma} \frac{\sigma(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d\mathbf{s} \approx \sum_{k=1}^{T} \frac{\sigma(\mathbf{s}_k) A_k}{|\mathbf{r}-\mathbf{s}_k|} = \sum_{k=1}^{T} \frac{q_k}{|\mathbf{r}-\mathbf{s}_k|}$$

- Polarization charges are computed by using the PCM matrix (*JCP 139, 024105 (2013))*

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

- $\mathbf{Q} = \mathbf{Q}(\epsilon, \mathbf{s}_k, ..)$ $T \times T$ response matrix.
- $\mathbf{V}_{\mathrm{M}}[n, n^n] = \mathbf{V}_{\mathrm{Hartree}}[n] + \mathbf{V}_{\mathrm{Z}}[n^n]$ Molecule electrostatic potential.

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

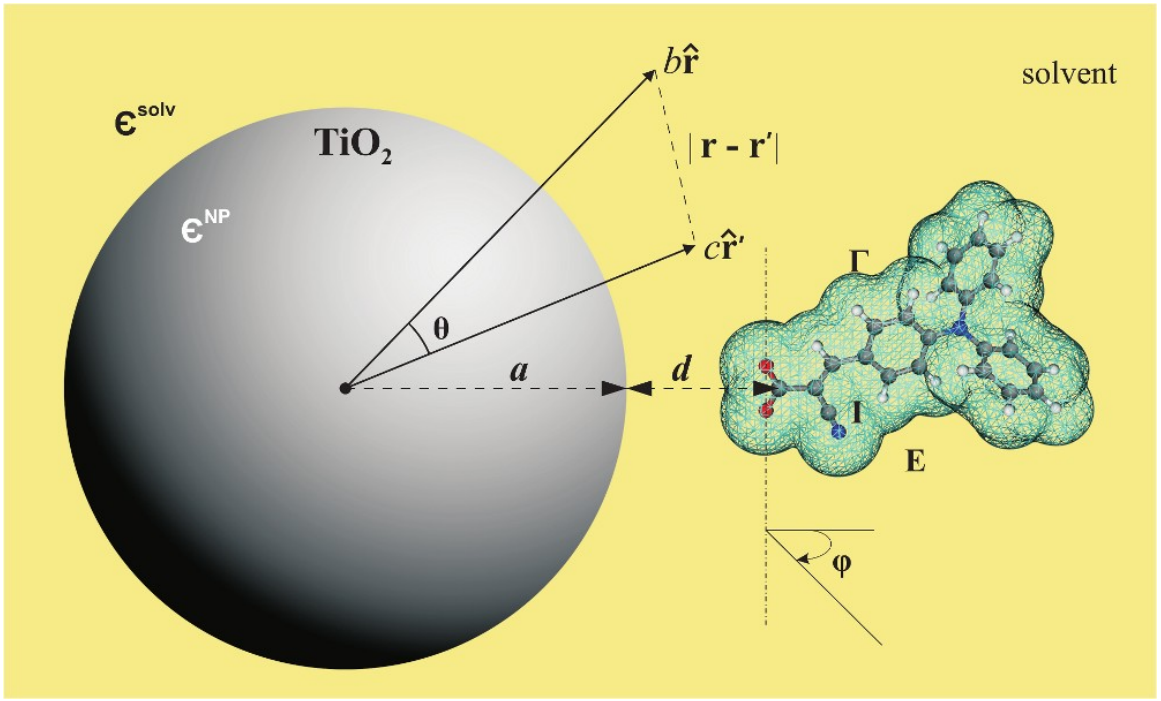


$$G_I(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|}$$ Green function in vacuo.

$$G_E(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi\epsilon^{\mathrm{solv}}}\frac{1}{|\mathbf{r}-\mathbf{r}'|}$$ Typical solvation condition.

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

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



$$G_I(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|}$$

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

$$G_{\mathrm{E}}(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi\epsilon^{\mathrm{solv}}}\left\{G_I(\mathbf{r},\mathbf{r}') - \sum_{n=1}^{\infty}\frac{a^{2n+1}}{(bc)^{n+1}}C_n P_n(cos\theta) - \left[\frac{\epsilon^{\mathrm{NP}}-\epsilon^{\mathrm{solv}}}{\epsilon^{\mathrm{NP}}+\epsilon^{\mathrm{solv}}}\right]\left[\frac{a}{c|\mathbf{r}-(a^2/c)\hat{\mathbf{r}}'|} - \frac{a}{cb}\right]\right\}$$

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

PCM terms in the Kohn-Sham Eqs.

- The starting point is the free energy functional:

$$G[n, n^n] = E^{\text{vac}}[n] + \frac{1}{2}\int d\mathbf{r}\; n(\mathbf{r})\left\{v^e_{\text{PCM}}[n](\mathbf{r}) + v^n_{\text{PCM}}[n^n](\mathbf{r})\right\} + \frac{1}{2}\int d\mathbf{r}\; n^n(\mathbf{r})\left\{v^e_{\text{PCM}}[n](\mathbf{r}) + v^n_{\text{PCM}}[n^n](\mathbf{r})\right\}$$

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

$$v_{\text{KS}}[n, n^n](\mathbf{r}) = v^{\text{vac}}_{\text{KS}}[n](\mathbf{r}) + \underbrace{v^e_{\text{PCM}}[n](\mathbf{r}) + v^n_{\text{PCM}}[n^n](\mathbf{r})}$$

$$= \sum_{i=1}^{T}\left[\frac{q^e_i + q^n_i}{|\mathbf{r} - \mathbf{s}_i|}\right]$$

atomic basis set representation: *Gaussian, Gamess, NWChem . . . .*

$$v_{\rm KS}[n,n^n](\mathbf{r}) = v_{\rm KS}^{\rm vac}[n](\mathbf{r}) + \sum_{i=1}^{T}\left[\frac{q_i^e + q_i^n}{|\mathbf{r}-\mathbf{s}_i|}\right]$$

$$\varphi^{\rm mo}(\mathbf{r}) = \sum_\mu C_\mu \chi_\mu^{\rm ao}(\mathbf{r})$$

$$(v_{\rm KS})_{\mu\nu} = (v_{\rm KS}^{\rm vac})_{\mu\nu} + \frac{1}{2}\sum_i [V_{\rm Z}(\mathbf{s}_i) q^e_{\mu\nu}(\mathbf{s}_i) + \phi^e_{\mu\nu}(\mathbf{s}_i) q^n(\mathbf{s}_i)] + \sum_i \phi^e_{\mu\nu}(\mathbf{s}_i) q^e(\mathbf{s}_i)$$

$$\mathbf{q}^{\mathbf{e}}_{\mu\nu} = \mathbf{Q}\mathbf{\Phi}_{\mu\nu}$$

$$\int d\mathbf{r} \frac{\chi^*_\mu(\mathbf{r})\chi_\nu(\mathbf{r})}{|\mathbf{r}-\mathbf{s}_i|}$$

$$q^e(\mathbf{s}_i) = \sum_{\mu\nu} p_{\mu\nu} q^e_{\mu\nu}(\mathbf{s}_i)$$

self-consistent term

$$v_{\rm KS}[n,n^n](\mathbf{r}) = v_{\rm KS}^{\rm vac}[n](\mathbf{r}) + \sum_{i=1}^{T}\left[\frac{q_i^e + q_i^n}{|\mathbf{r}-\mathbf{s}_i|}\right]$$

The solvent reaction potential becomes singular in the limit $\mathbf{r} \to \mathbf{s}_i$

- How does the PCM field is regularized?

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

- A_i is the area of the i-th tessera and α is a parameter to fit the gaussian width.

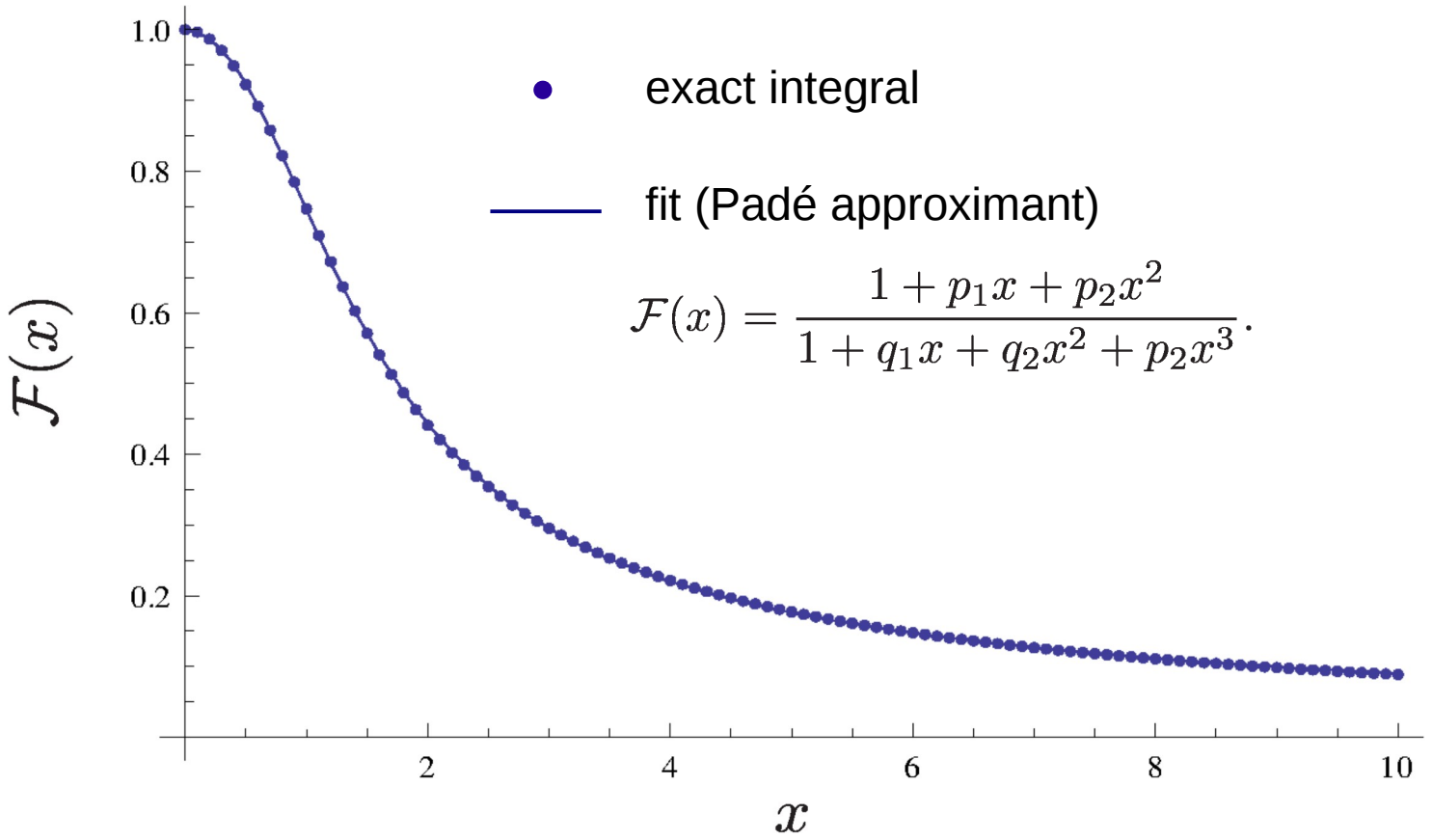
$$\frac{q_i}{|\mathbf{r}-\mathbf{s}_i|} \dashrightarrow \Phi_i(\mathbf{r}) = \frac{2q_i}{\sqrt{\pi\alpha A_i}} \int_{|\mathbf{r}-\mathbf{s}_i|/\sqrt{\alpha A_i}}^{\infty} dx \left\{\frac{\Gamma(3/2) - \Gamma(3/2,x^2)}{x^2}\right\}$$

Regularized PCM potential

$$v_{\rm KS}[n,n^n](\mathbf{r}) = v_{\rm KS}^{\rm vac}[n](\mathbf{r}) + \sum_{i=1}^{T} [\Phi_i^e(\mathbf{r}) + \Phi_i^n(\mathbf{r})]$$

with:

$$\Phi_i(\mathbf{r}) = \frac{2q_i}{\sqrt{\pi\alpha A_i}} \int_{|\mathbf{r}-\mathbf{s}_i|/\sqrt{\alpha A_i}}^{\infty} dx \left\{ \frac{\Gamma(3/2) - \Gamma(3/2, x^2)}{x^2} \right\} = \frac{2q_i}{\sqrt{\pi\alpha A_i}} \mathcal{F}(|\mathbf{r}-\mathbf{s}_i|/\sqrt{\alpha A_i})$$



PCM terms in the ground state energy

$$G[n] = \sum_{j=1}^{N_{occ}} \varepsilon_j - \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \int d\mathbf{r}\; n(\mathbf{r})v_{xc}[n](\mathbf{r}) + E_{xc}[n]$$

$$- \int d\mathbf{r}\; n(\mathbf{r})\left\{v^e_{\mathrm{PCM}}(\mathbf{r}) + v^n_{\mathrm{PCM}}(\mathbf{r})\right\}$$

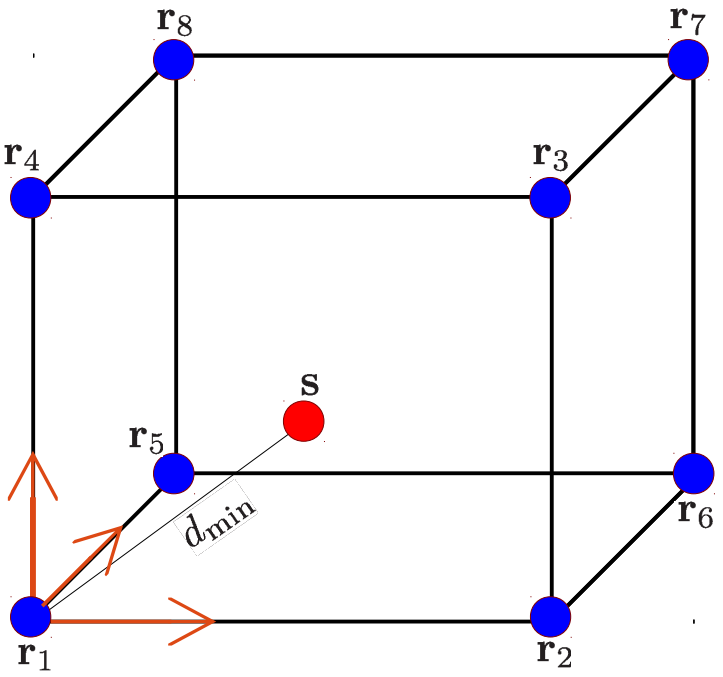
$$+ \frac{1}{2}\sum_{i=1}^{T}\left[V_{\mathrm{Hartree}}(\mathbf{s}_i) + V_{\mathrm{Z_{val}}}(\mathbf{s}_i)\right]\left[q^e(\mathbf{s}_i) + q^n(\mathbf{s}_i)\right]$$

$\mathbf{s_i} \notin$ simulation domain

- Finding the closest grid point for each tessera.

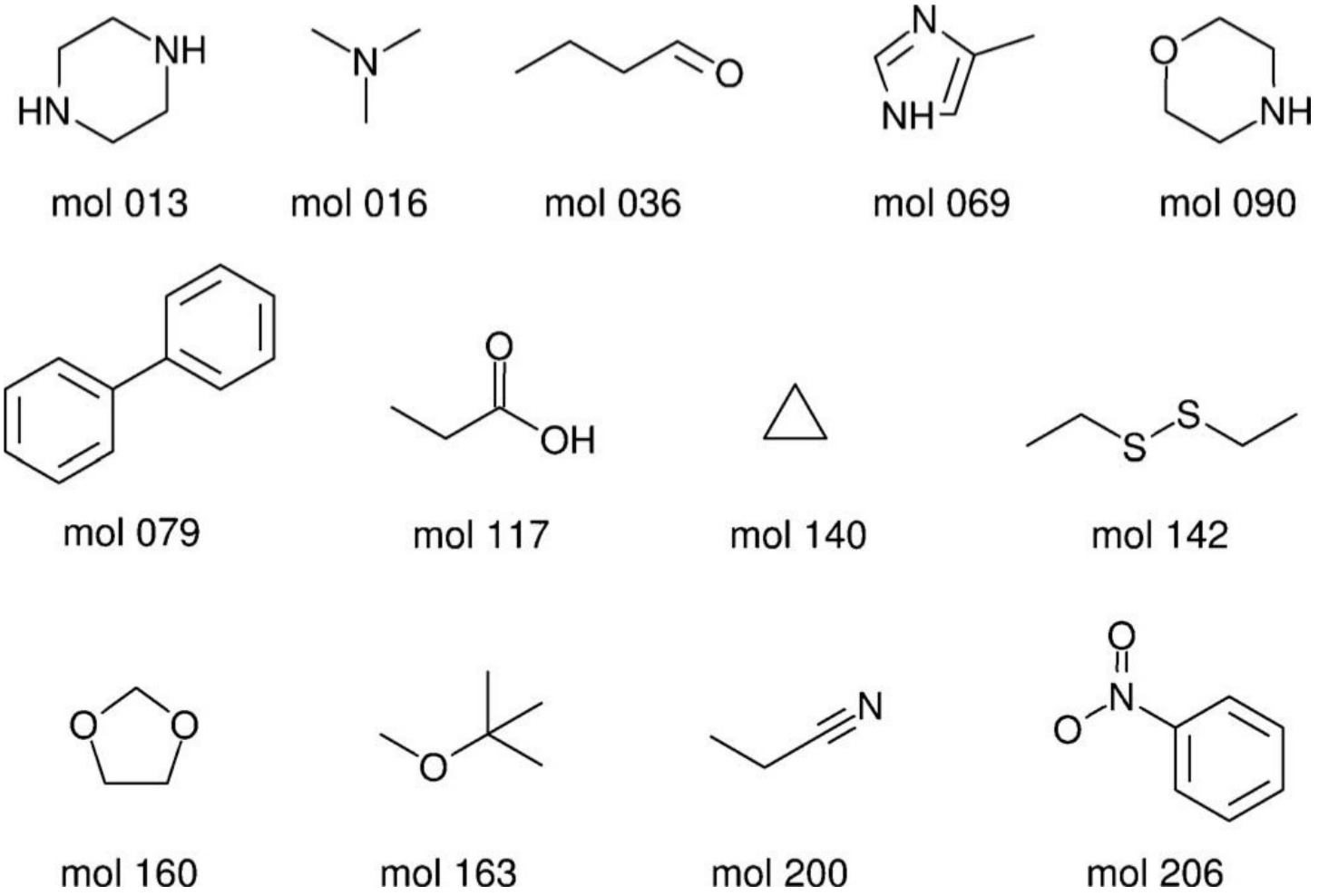
- Building the eight cube's vertices.

- Trilinear interpolation to get $V_{\mathrm{Hartree}}(\mathbf{s})$



Numerical results: set of molecules to test PCM

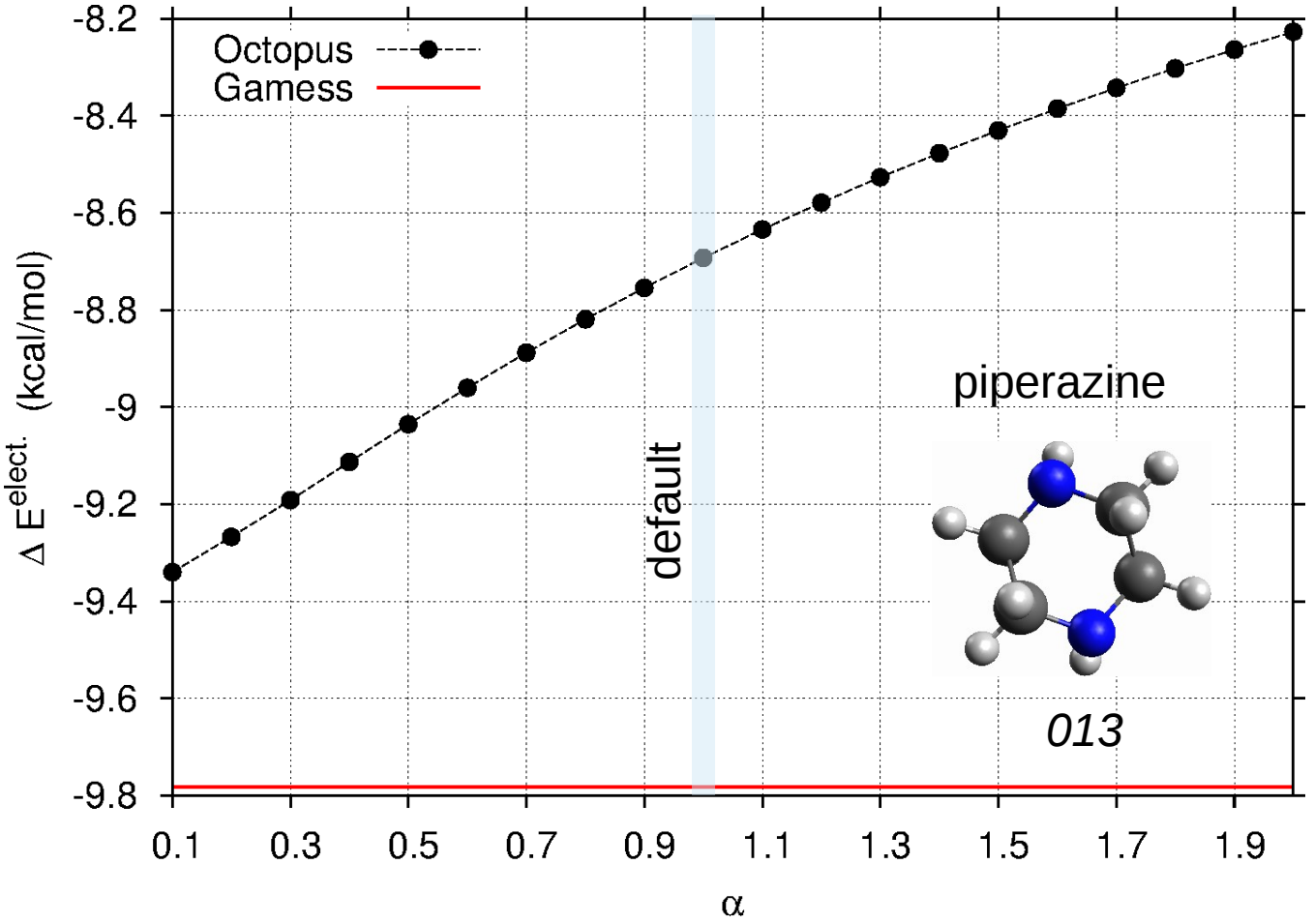
- Neutral organic molecules (*Andreussi et al. JCP 136, 064102 (2012)*).
- Geometries optimized with *GAMESS* at the level of PBE / 6-31(d).



solute - solvent electrostatic interaction energy in water

$$\Delta E^{elect.} = \frac{1}{2}\sum_{i=1}^{T}\left[V_{\mathrm{Hartree}}(\mathbf{s}_i) + V_{\mathrm{Z_{val}}}(\mathbf{s}_i)\right]\left[q^e(\mathbf{s}_i) + q^n(\mathbf{s}_i)\right]$$

- XC = PBE
- Octopus: R= 5 Å Δ = 0.15 Å
- GAMESS: TZ 6311+G(d,p)



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

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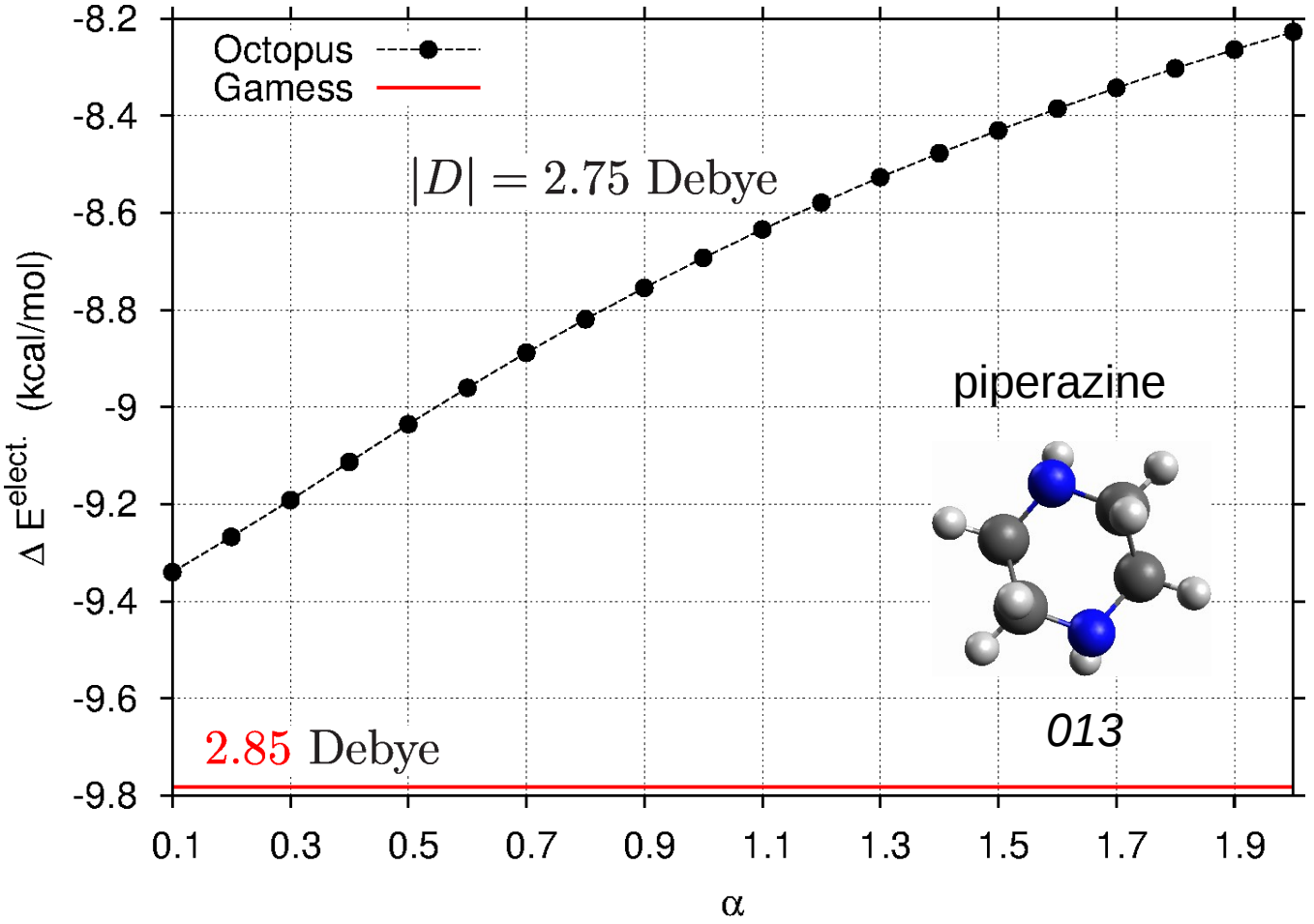

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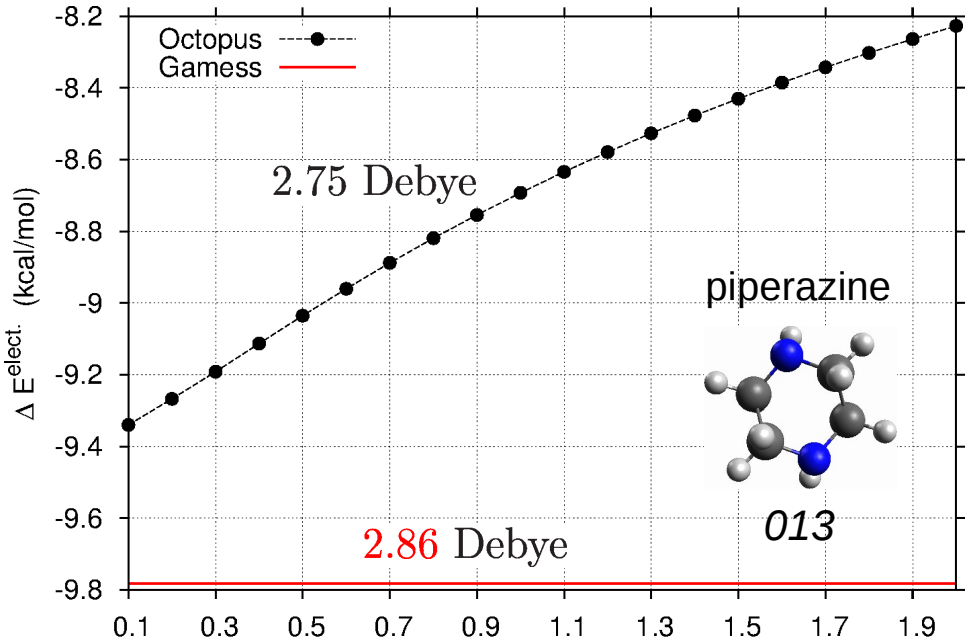
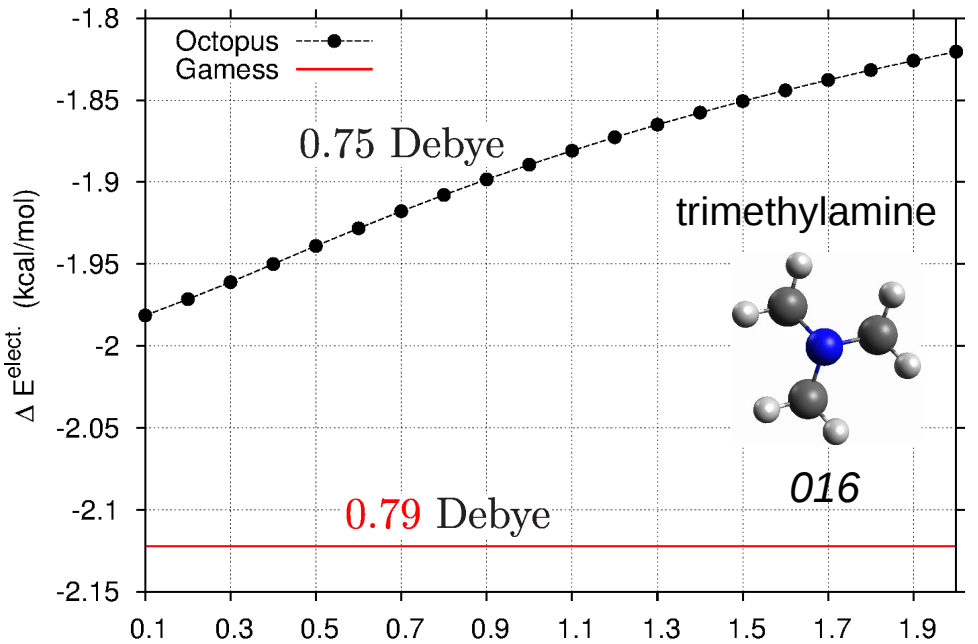
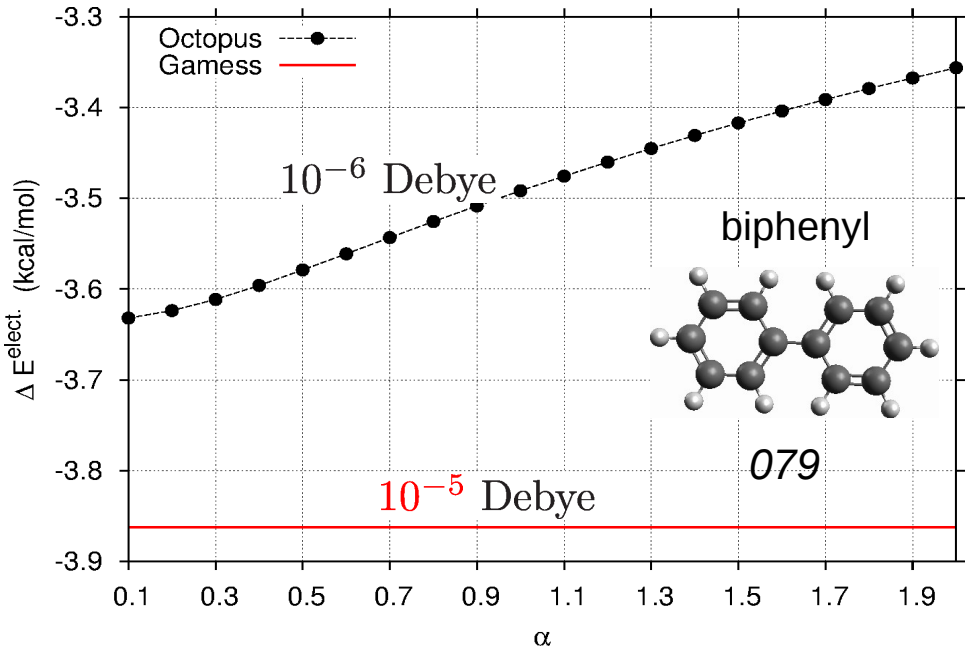
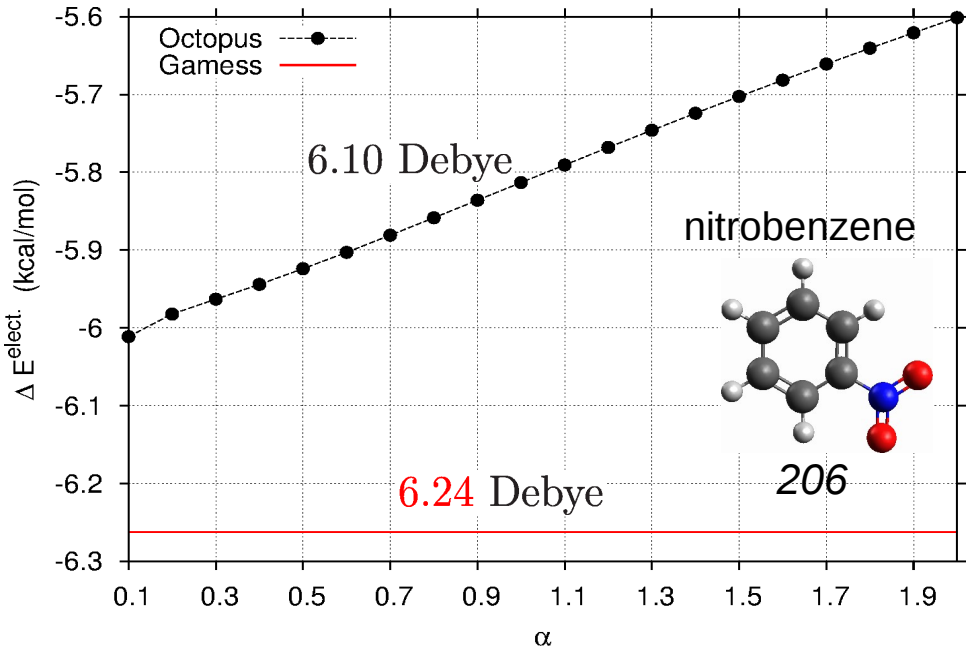


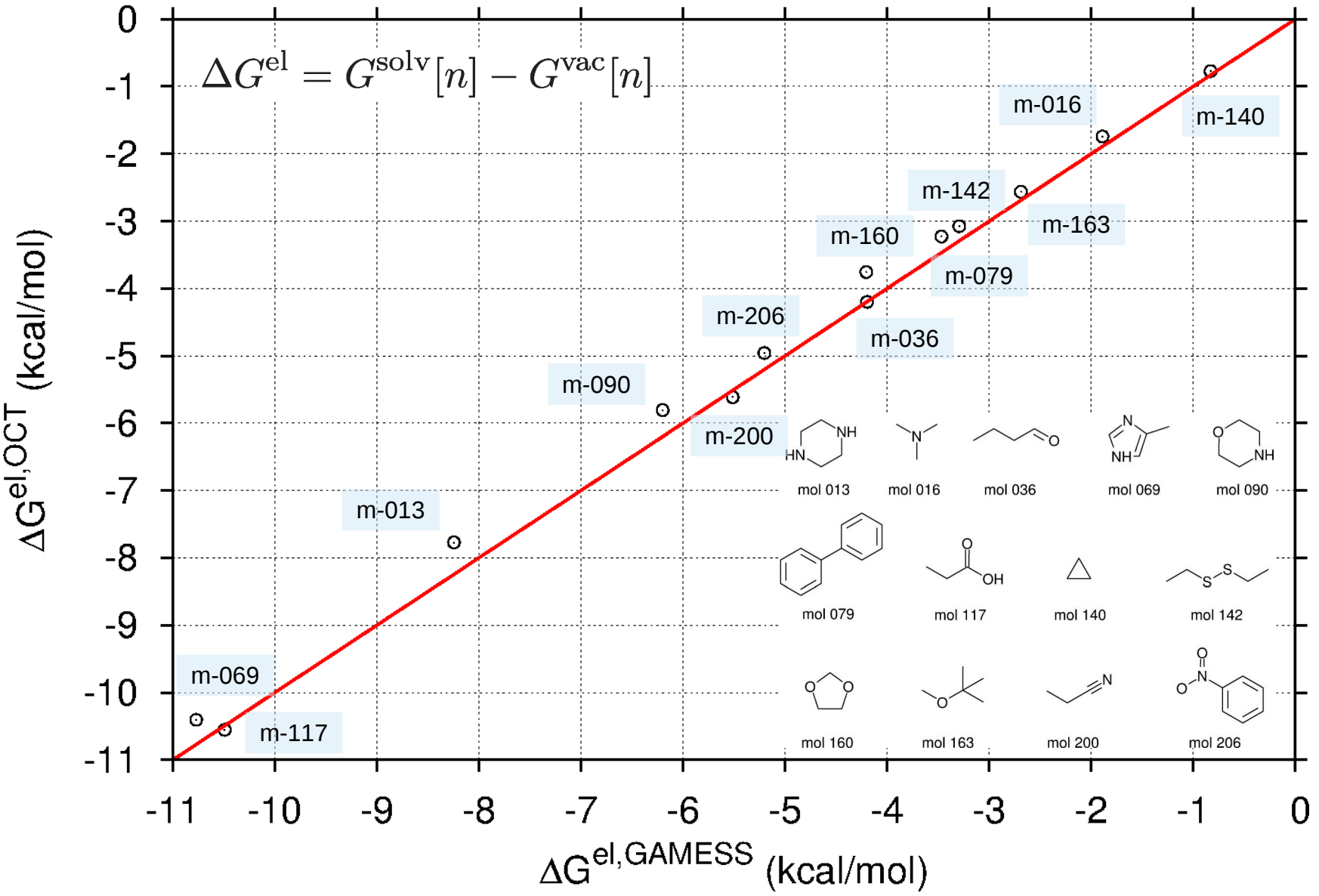






Solvation free energies in water

- XC = PBE
- Octopus: R= 5 Å Δ = 0.15 Å
- GAMESS: TZ 6311+G(d,p)



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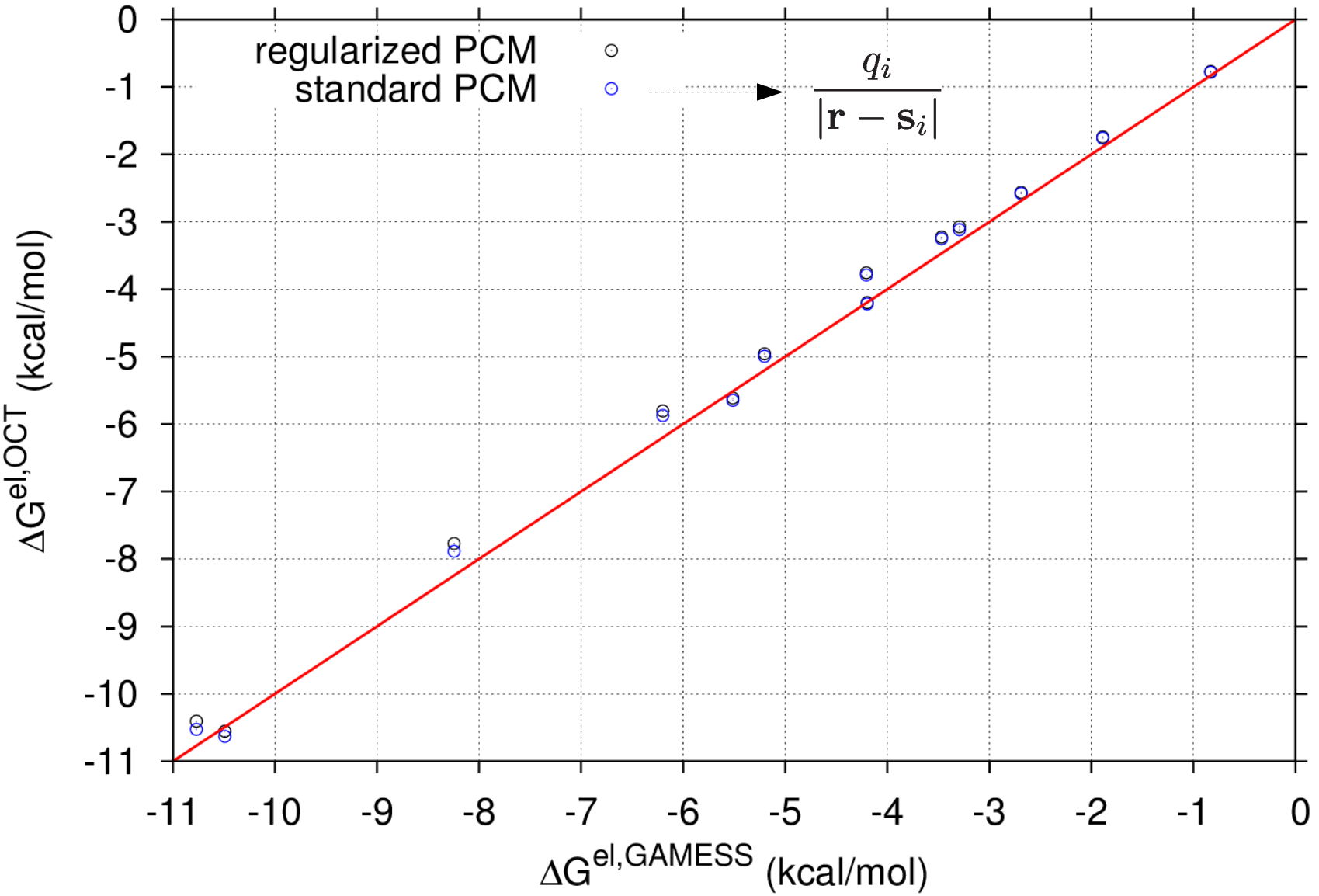

Looking for the singularity: *calculations in* Cl^-

- XC = PBE
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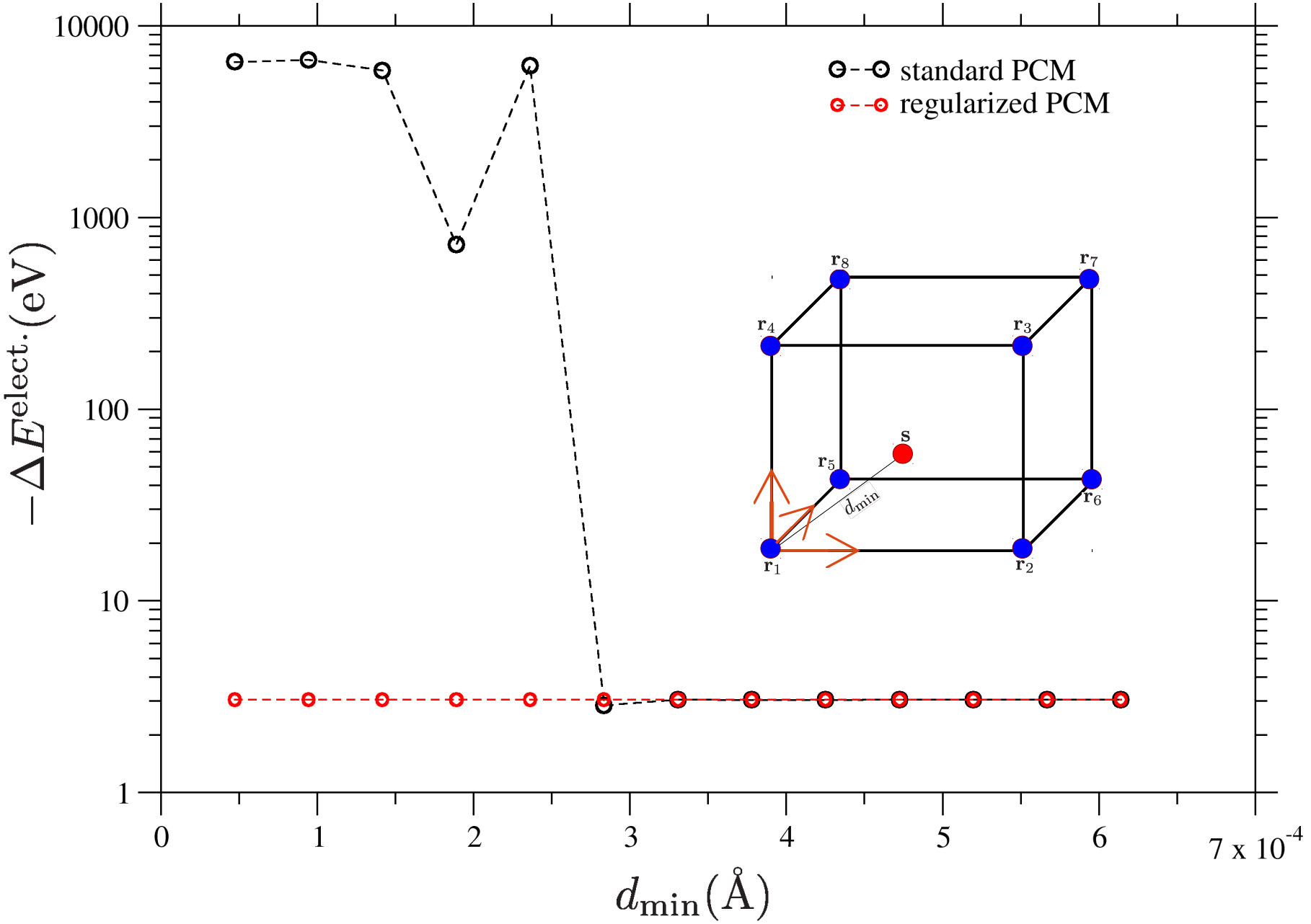

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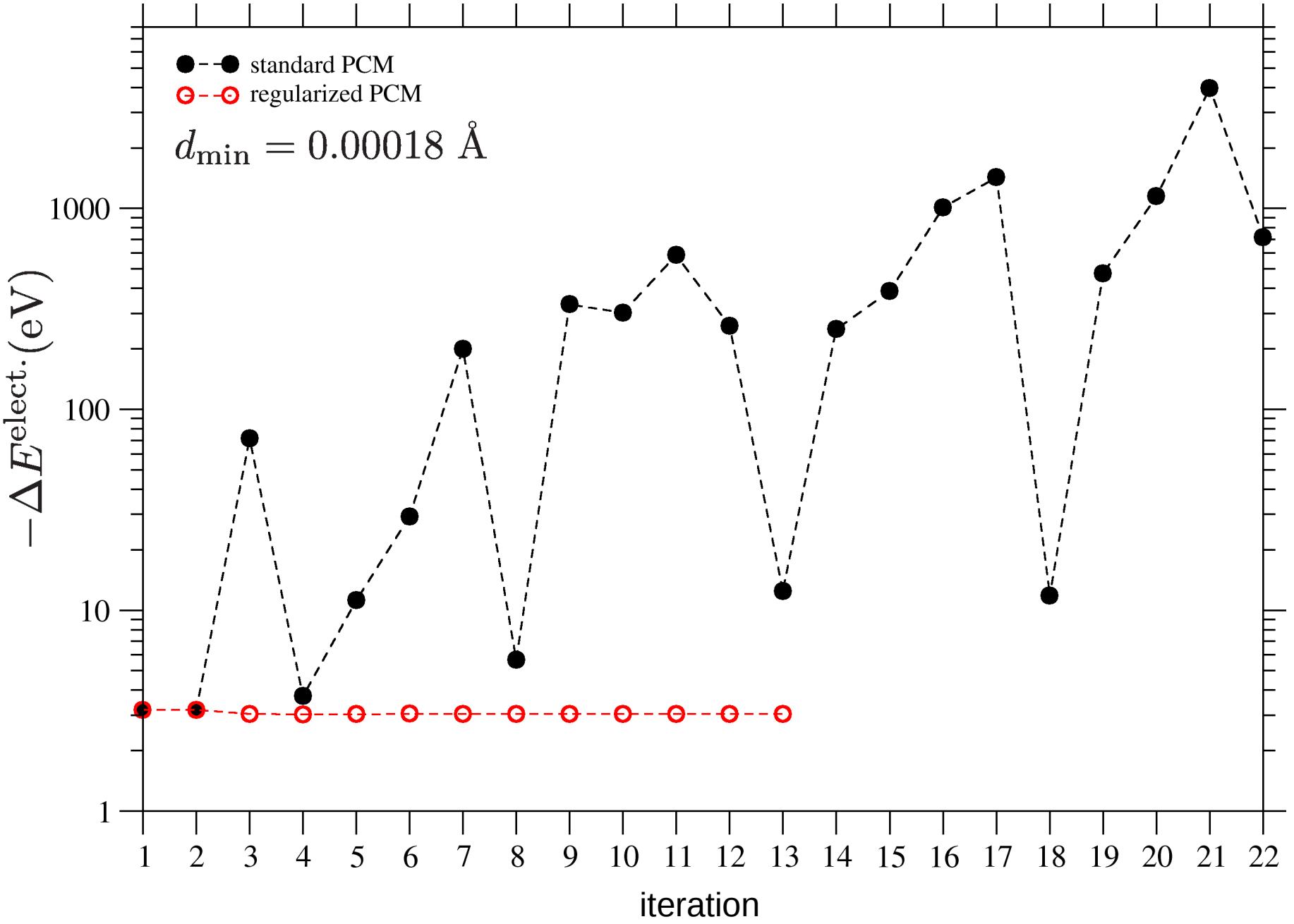
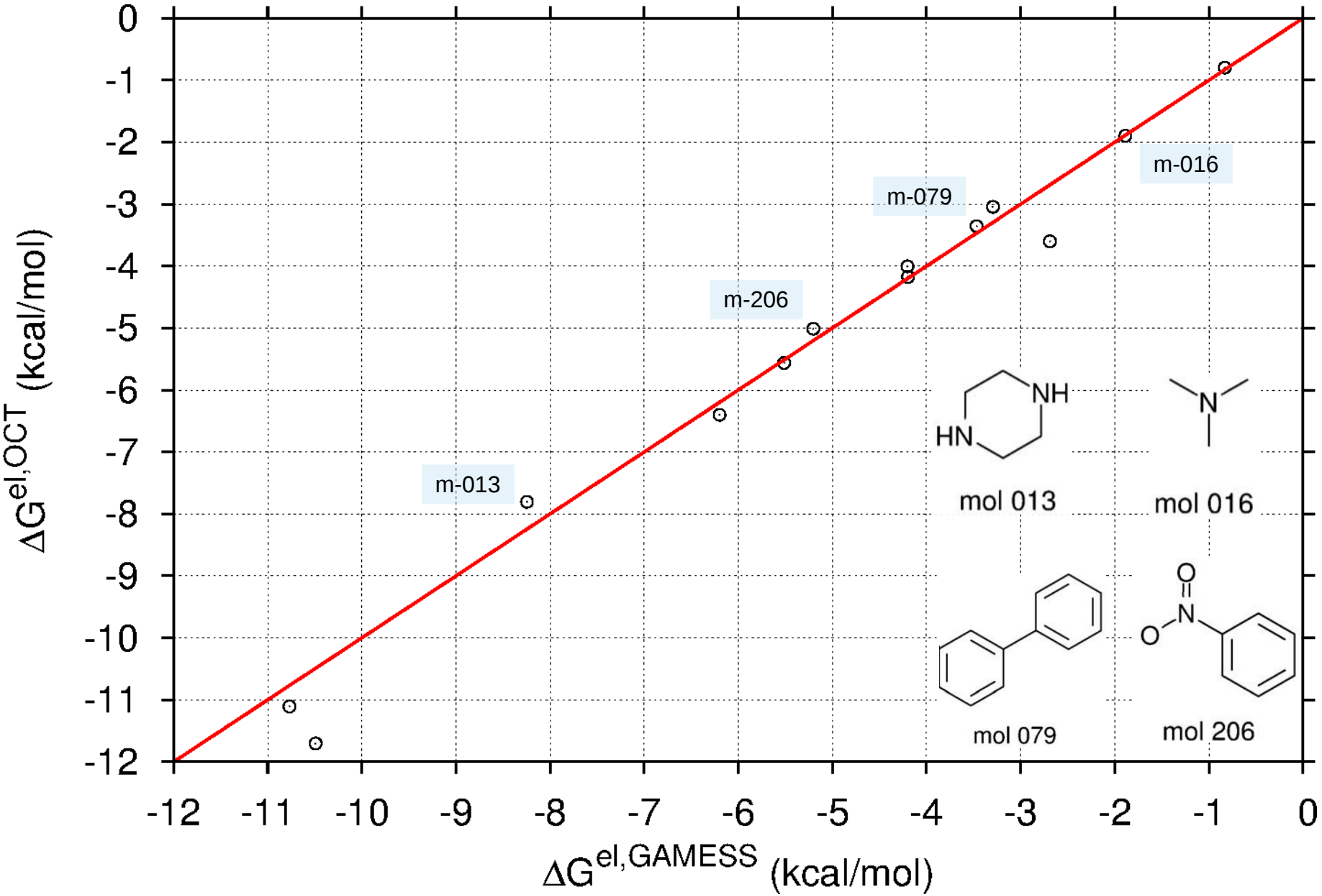
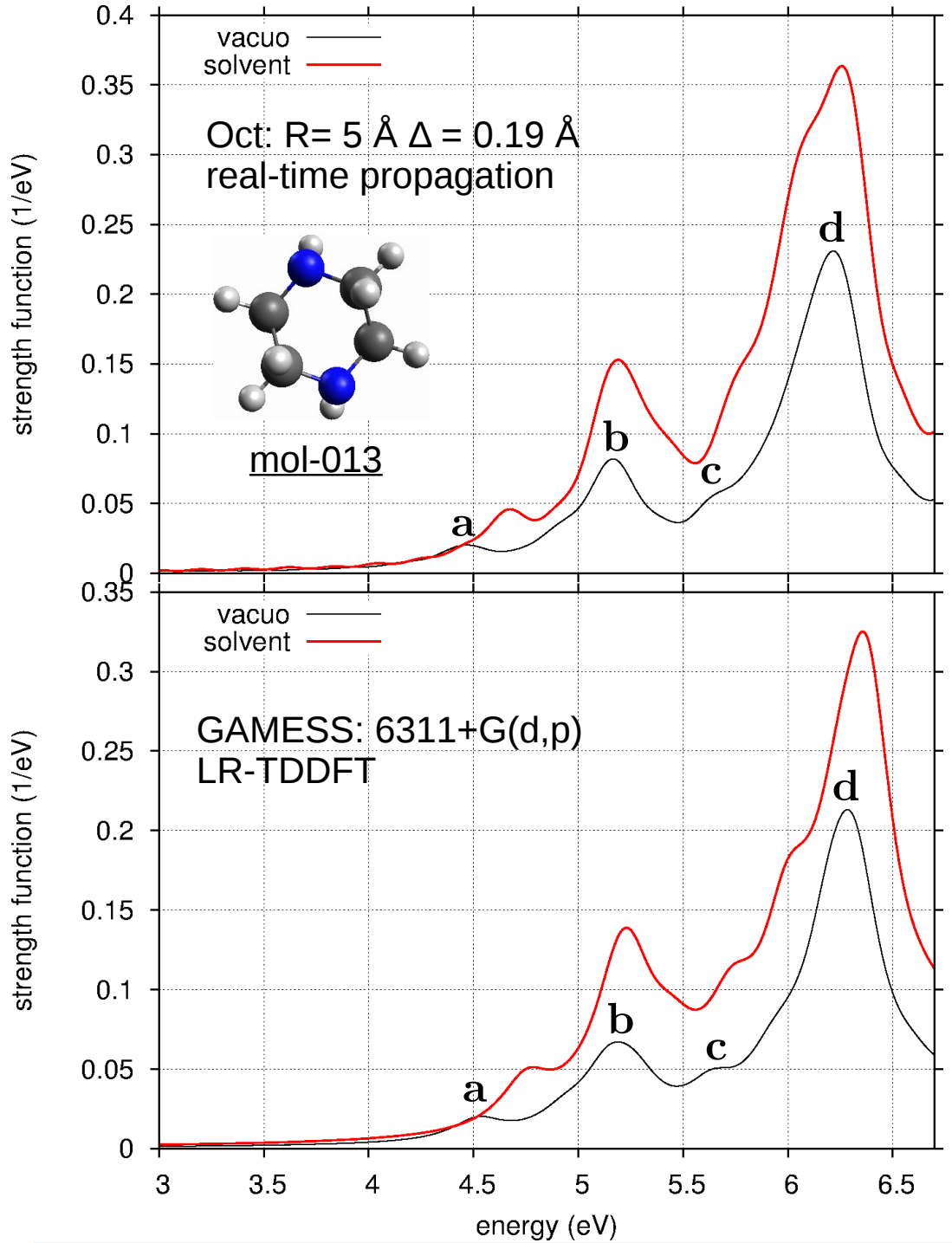


Absorption spectra: *selected cases*

- XC = PBE
- Octopus: R= 5 Å Δ = 0.19 Å
- GAMESS: TZ 6311+G(d,p)

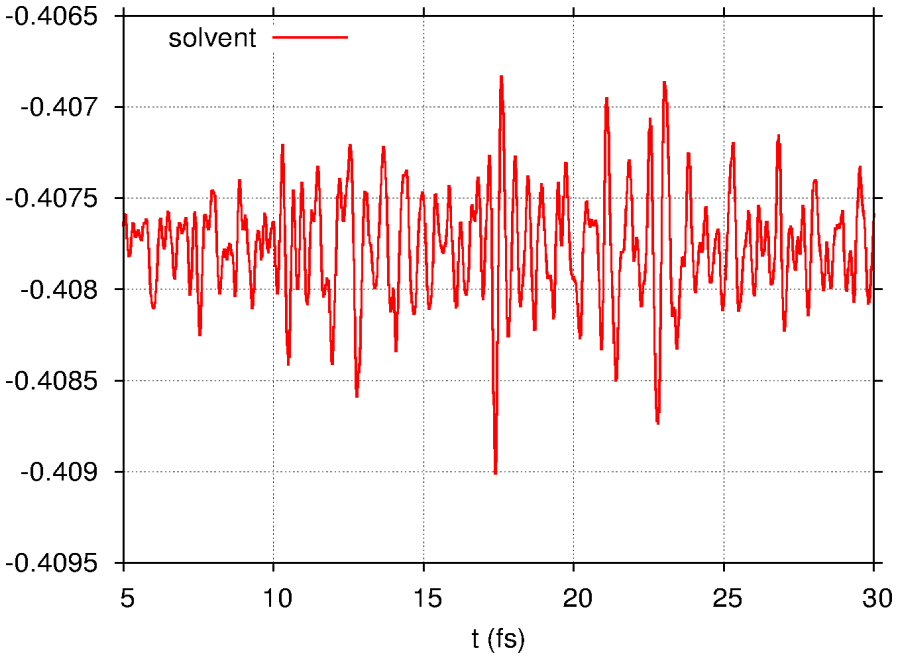


Absorption spectra

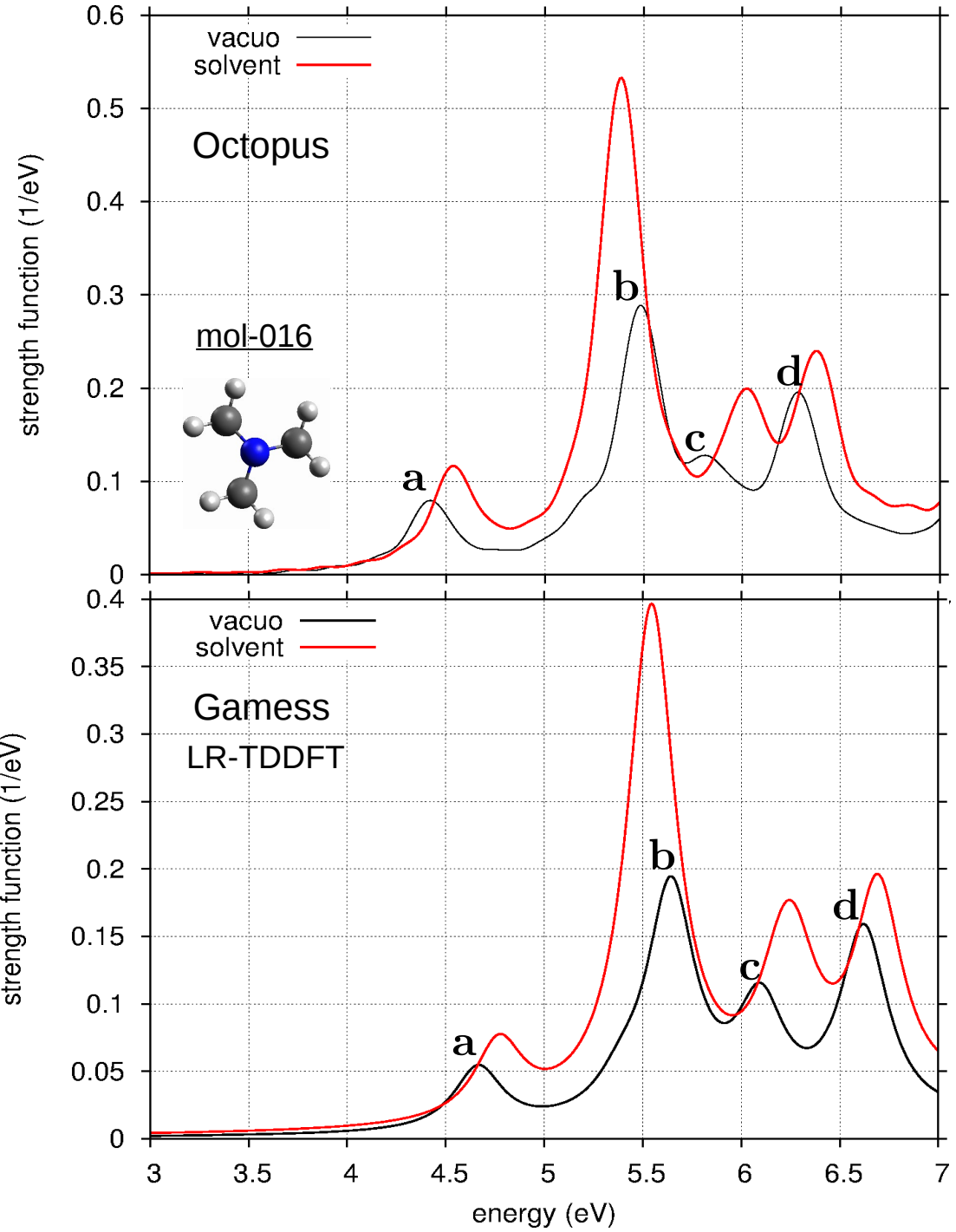


solvatochromic shifts (eV)

peak	*Octopus*	*Gamess*
a	0.21	0.22
b	0.03	0.04
c	0.10	0.09
d	0.04	0.07



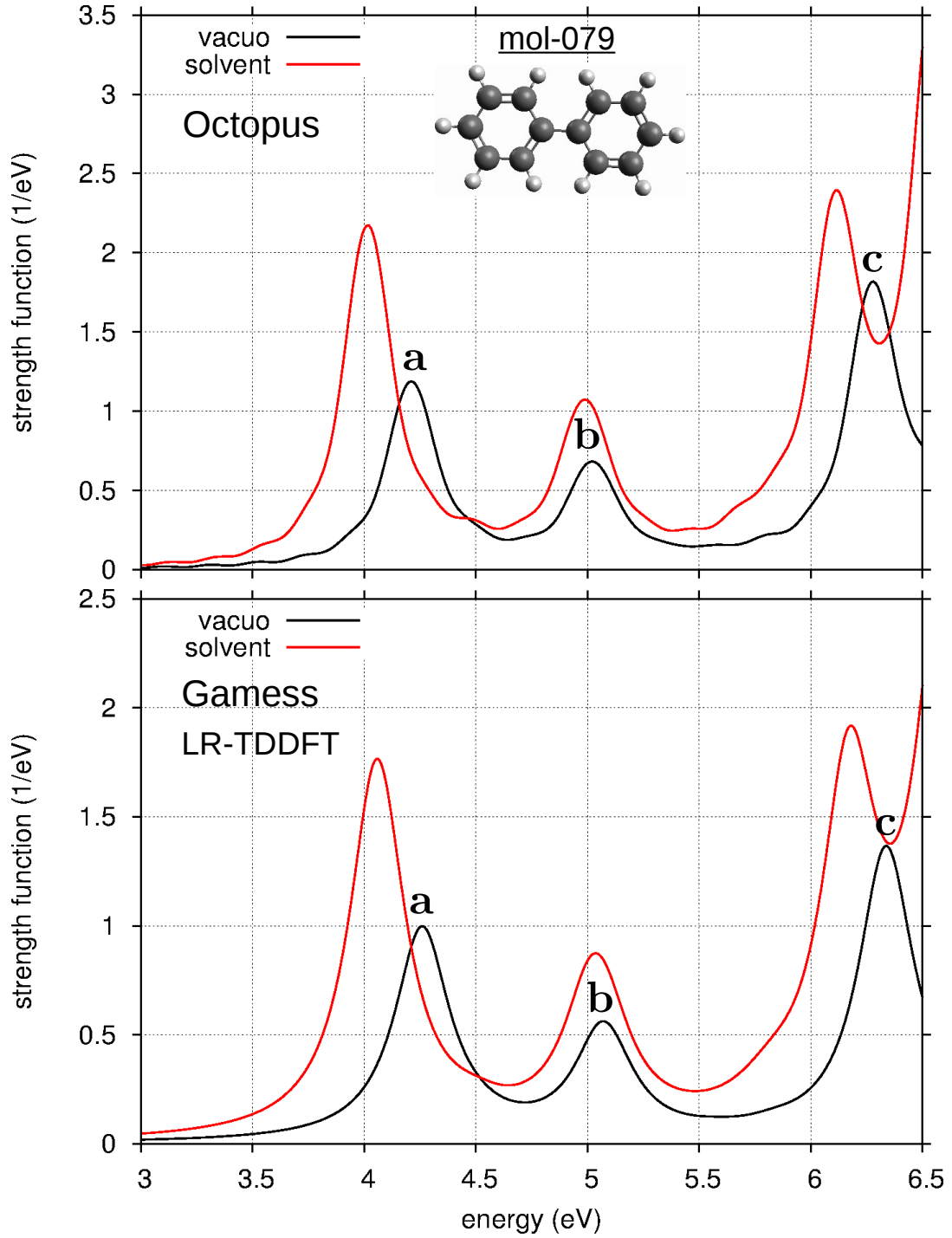
Absorption spectra



solvatochromic shifts (eV)

peak	*Octopus*	*Gamess*
a	0.12	0.11
b	-0.10	-0.10
c	0.21	0.16
d	0.09	0.08

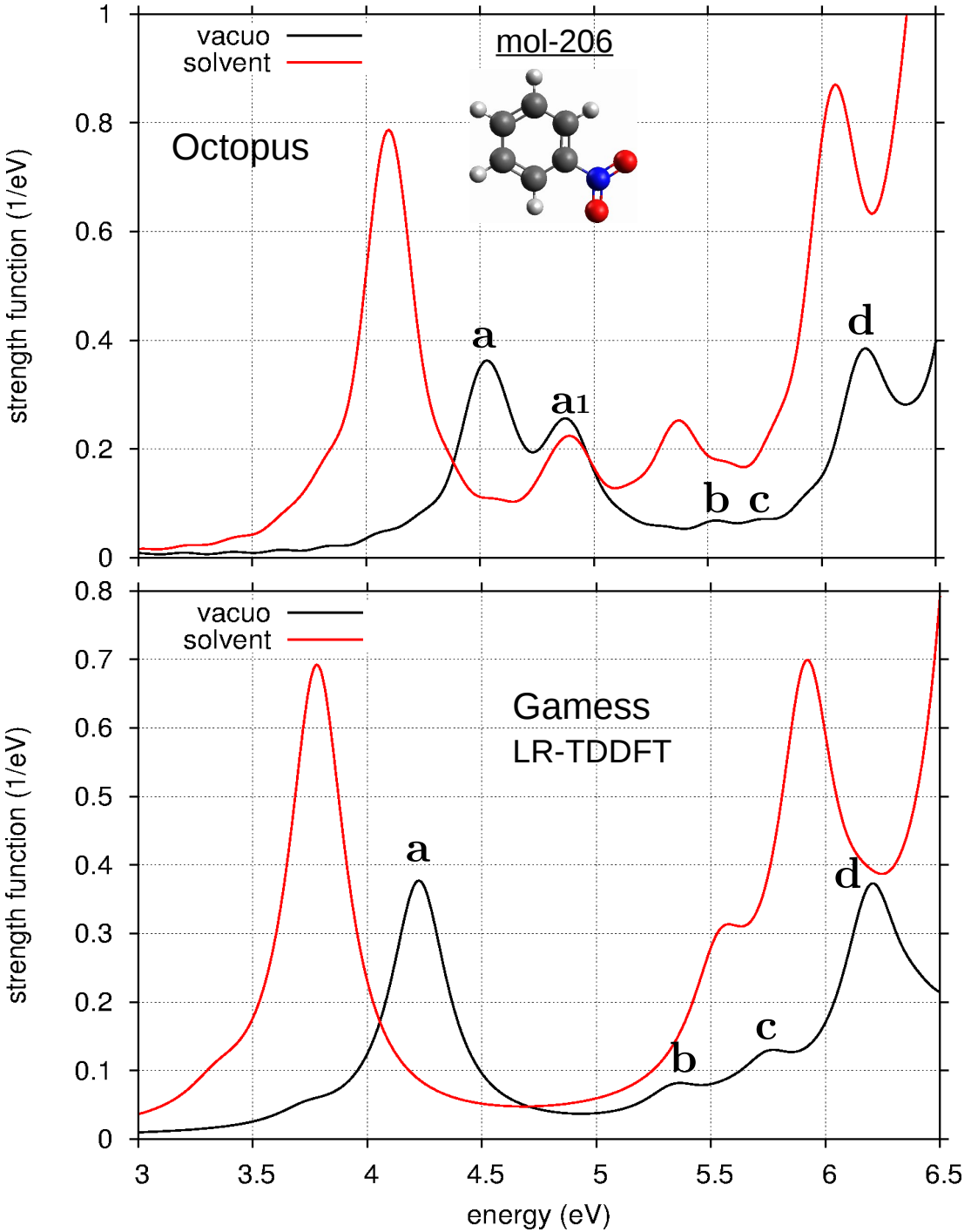
Absorption spectra



solvatochromic shifts (eV)

peak	*Octopus*	*Gamess*
a	-0.19	-0.19
b	-0.02	-0.03
c	-0.15	-0.15

Absorption spectra

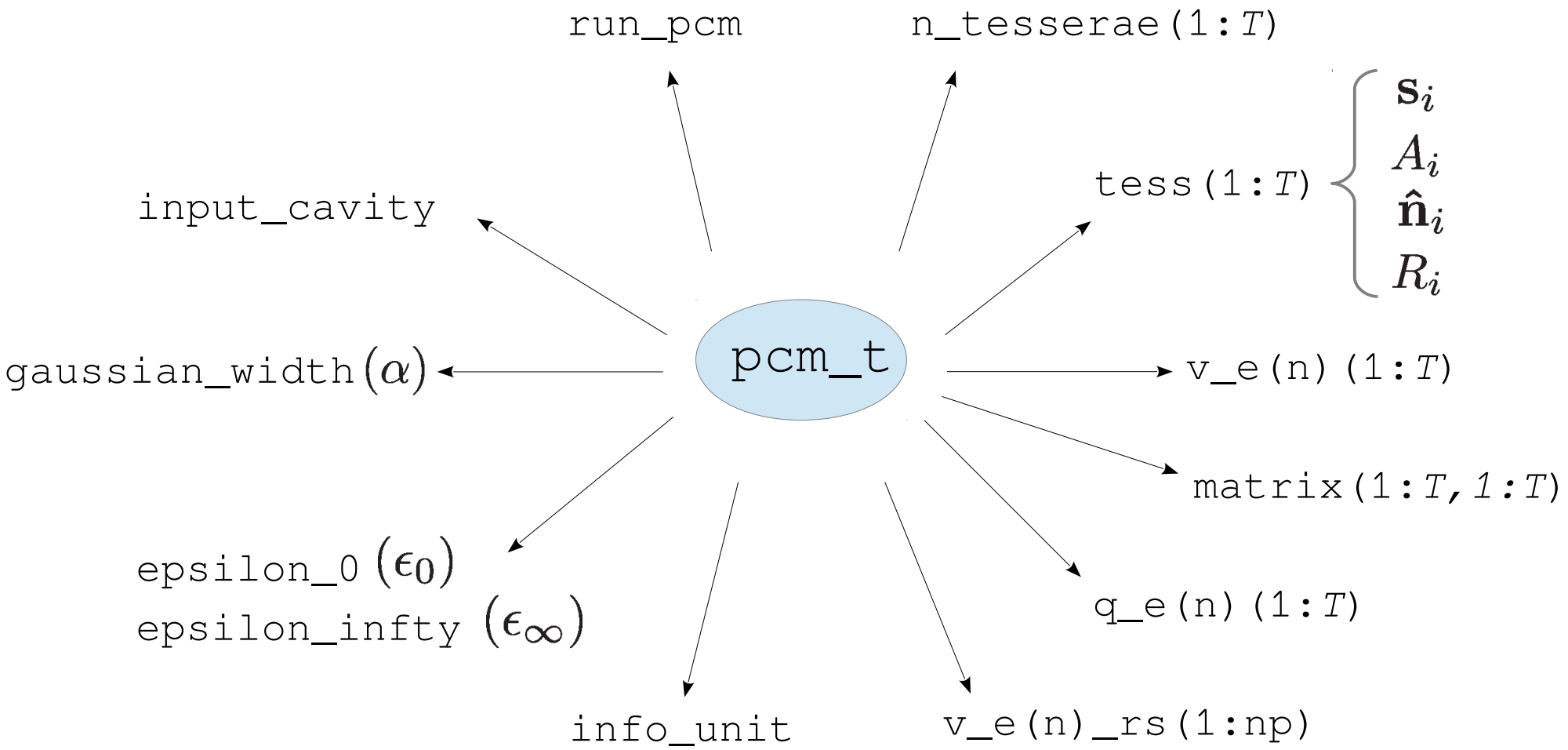


solvatochromic shifts (eV)

peak	*Octopus*	*Gamess*
a	-0.42	-0.43
a1	0.02	
b	-0.17	
c	-0.13	-0.18
d	-0.12	-0.28

Structure of the PCM type

`pcm` variable is of type `pcm_t` and can be accessed through any variable of type `hamiltonian_t`



main pcm subroutines

main program

```
.
.
call hamiltonian_init(..)
    call pcm_init(..)
```

end program

main pcm subroutines

main program

.

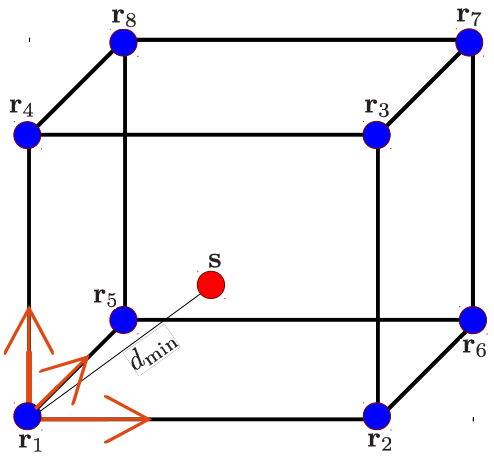
.

```
call hamiltonian_init(..)
```

```
    call pcm_init(..)
```

- read the cavity geometry from a external file

```
    call nearest_cube_vertices(..)
```



end program

main pcm subroutines

main program

.

.

```
call hamiltonian_init(..)
```

```
    call pcm_init(..)
```

- read the cavity geometry from a external file

```
    call nearest_cube_vertices(..)
    call pcm_matrix( .., pcm%matrix )
```

$$\begin{aligned} \mathbf{Q} &= \left[\mathbf{S}_E(2\pi\mathbf{I}+\mathbf{D}_I^*)+(2\pi\mathbf{I}-\mathbf{D}_E)\mathbf{S}_I\right]\mathbf{A}^{-1}\Big]^{-1} \\ &\times \left[\mathbf{S}_E(\mathbf{S}_I)^{-1}(2\pi\mathbf{I}-\mathbf{D}_I)-(2\pi\mathbf{I}-\mathbf{D}_E)\right] \end{aligned}$$

end program

main pcm subroutines

main program

```
.
.
call hamiltonian_init(..)
```

```
    call pcm_init(..)
```

- read the cavity geometry from a external file

```
      call nearest_cube_vertices(..)
      call pcm_matrix( .., pcm%matrix )
```

```
call hamiltonian_epot_generate(..)
```

```
   call v_nuclei_cav(hm%pcm%v_n, ..)
   call pcm_charges (hm%pcm%q_n, ..)
   call pcm_pot_rs  (hm%pcm%v_n_rs, ..)
```

end program

main pcm subroutines

main program

.

.

```
call hamiltonian_init(..)
```

```
    call pcm_init(..)
```

- read the cavity geometry from a external file

```
      call nearest_cube_vertices(..)
      call pcm_matrix( .., pcm%matrix )
```

```
call hamiltonian_epot_generate(..)
```

```
   call v_nuclei_cav(hm%pcm%v_n, ..)
   call pcm_charges (hm%pcm%q_n, ..)
   call pcm_pot_rs  (hm%pcm%v_n_rs, ..)
```

```
 call v_ks_hartree(..)
```

```
   call v_electrons_cav_li(vhartree, ..)
   call pcm_charges (hm%pcm%q_e, ..)
   call pcm_pot_rs  (hm%pcm%v_e_rs, ..)
```

end program

main pcm subroutines

main program

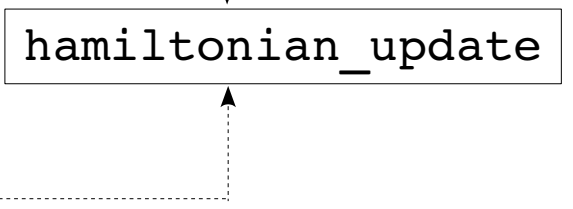
```
.
.
call hamiltonian_init(..)
    call pcm_init(..)
```

- read the cavity geometry from a external file

```
      call nearest_cube_vertices(..)
      call pcm_matrix( .., pcm%matrix )

call hamiltonian_epot_generate(..)
   call v_nuclei_cav(hm%pcm%v_n, ..)
   call pcm_charges (hm%pcm%q_n, ..)
   call pcm_pot_rs  (hm%pcm%v_n_rs, ..)

 call v_ks_hartree(..)
   call v_electrons_cav_li(vhartree, ..)
   call pcm_charges (hm%pcm%q_e, ..)
   call pcm_pot_rs  (hm%pcm%v_e_rs, ..)
```



end program

main pcm subroutines

main program

```
.
.
call hamiltonian_init(..)
    call pcm_init(..)
```

- read the cavity geometry from a external file

```
      call nearest_cube_vertices(..)
      call pcm_matrix( .., pcm%matrix )

call hamiltonian_epot_generate(..)
   call v_nuclei_cav(hm%pcm%v_n, ..)
   call pcm_charges (hm%pcm%q_n, ..)
   call pcm_pot_rs  (hm%pcm%v_n_rs, ..)

 call v_ks_hartree(..)
   call v_electrons_cav_li(vhartree, ..)
   call pcm_charges (hm%pcm%q_e, ..)
   call pcm_pot_rs  (hm%pcm%v_e_rs, ..)

 call energy_calc_total(..)
   call pcm_elect_energy(..)
```

hamiltonian_update

end program

main pcm subroutines

main program

```
.
.
call hamiltonian_init(..)
    call pcm_init(..)
```

- read the cavity geometry from a external file

```
      call nearest_cube_vertices(..)
      call pcm_matrix( .., pcm%matrix )

call hamiltonian_epot_generate(..)
   call v_nuclei_cav(hm%pcm%v_n, ..)
   call pcm_charges (hm%pcm%q_n, ..)
   call pcm_pot_rs  (hm%pcm%v_n_rs, ..)

 call v_ks_hartree(..)
   call v_electrons_cav_li(vhartree, ..)
   call pcm_charges (hm%pcm%q_e, ..)
   call pcm_pot_rs  (hm%pcm%v_e_rs, ..)

 call energy_calc_total(..)
   call pcm_elect_energy(..)
 call pcm_end
.
.
end program
```

hamiltonian_update

Conclusions

1. About PCM.

- The PCM model was implemented within Octopus to solve the KS equations in real-space.
- The Integral Equation Formalism (IEF) has been used to solve the electrostatic problem molecule + solvent.
- The proposed PCM potential in real-space regularizes the Coulomb singularity for grid points infinitesimally close the solute cavity surface.

2. About the results.

- The solvation free energies were calculated for 13 organic molecules in water and shown to be in excellent agreement with similar results obtained with GAMESS.
- In all cases, the solute-solvent interaction energy shows a smooth behavior as the regularization parameter α is varied around its default value (1.0).
- The optical absorption spectra for selected systems (piperazine, trimethylamine, biphenyl, nitrobenzene) were calculated in vacuo and in water. The solvatochromic shifts found with Octopus (TD-DFT) compare qualitatively well with those obtained with GAMESS (LR-TDDFT).

3. About future implementations.

- Coding a subroutine in Octopus to generate the solute cavity surface.
- Inclusion of the non-equilibrium effects within the PCM to model consistently the real-time polarization response.
- Extending the PCM implementation to perform the real-time electron-nuclei dynamics.
- Extending the PCM implementation to perform linear-response TDDFT calculations.
- Generalization of the PCM Eqs. to address more complex dielectric environments.

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