

Polarizable Continuum Model Implementation in the Octopus code

Alain Delgado, Carlo Andrea Rozzi, Stefano Corni



S3 Center, CNR Institute of Nanoscience, Modena, Italy.

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.

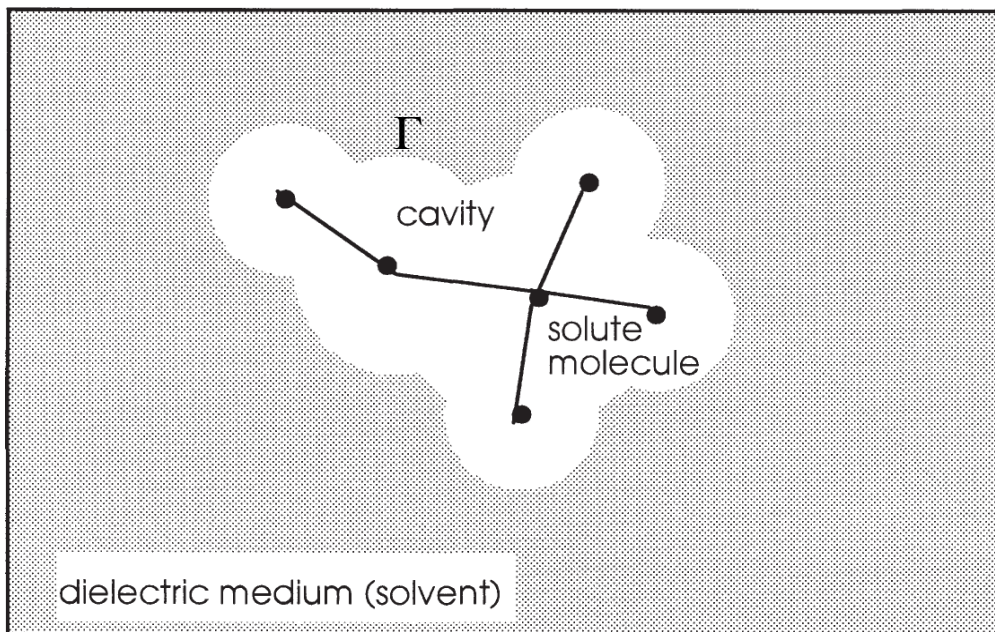
3.1 – Solvation free energies of neutral solutes.

3.2 – Optical absorption spectra of selected molecules.

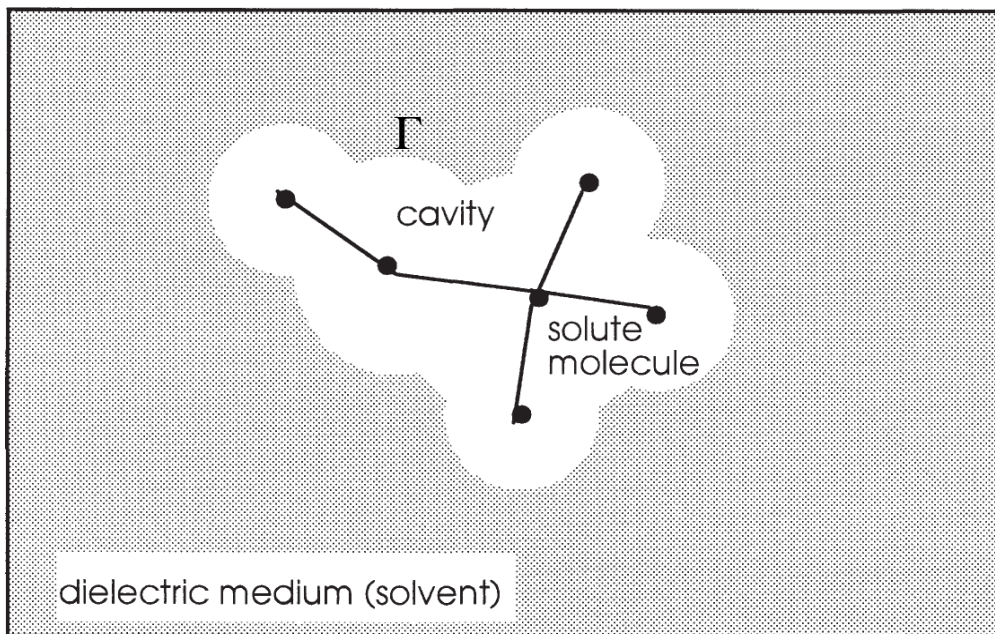
4- What has been coded about PCM in Octopus ?

4.1 – PCM module: main types and subroutines.

5- Conclusions.



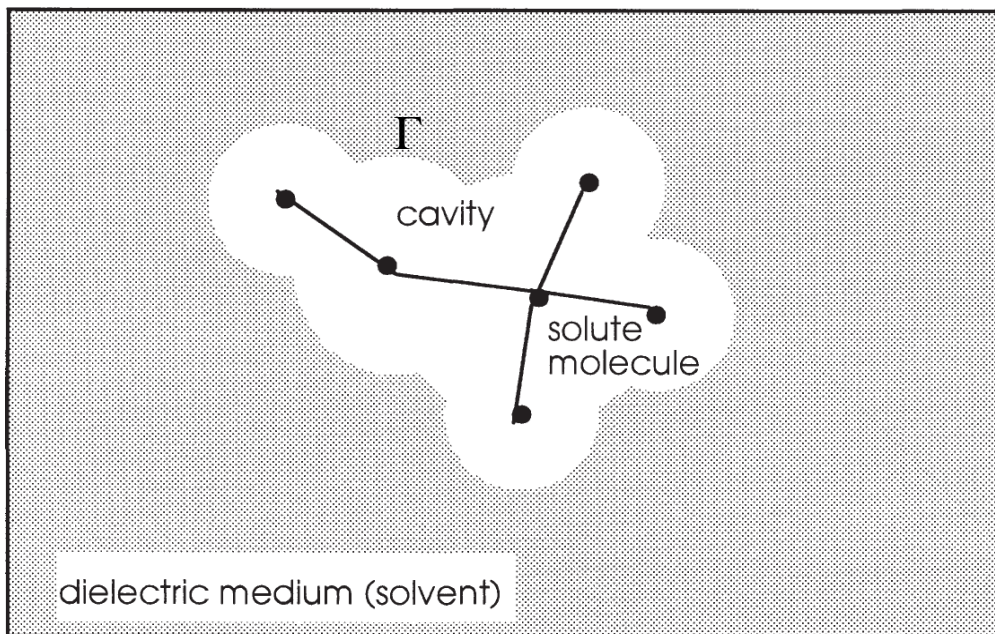
- The solvent is a **continuous dielectric medium** polarized by the solute molecule.
- Solute molecule is hosted by the **cavity** within the surface Γ .
- The **shape of Γ** should reproduce the **molecular shape**.
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Effective Hamiltonian

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



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Poisson equation + boundary conditions at Γ

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

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

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

$$V(\mathbf{r}) = V_M(\mathbf{r}) + v_{\text{PCM}}^e(\mathbf{r}) + v_{\text{PCM}}^n(\mathbf{r}) \longrightarrow \text{Solvent Reaction potentials.}$$

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 $\sigma(\mathbf{s})$:
$$v_{\text{PCM}}(\mathbf{r}) = \int_{\Gamma} \frac{\sigma(\mathbf{s})}{|\mathbf{r} - \mathbf{s}|} d\mathbf{s}$$

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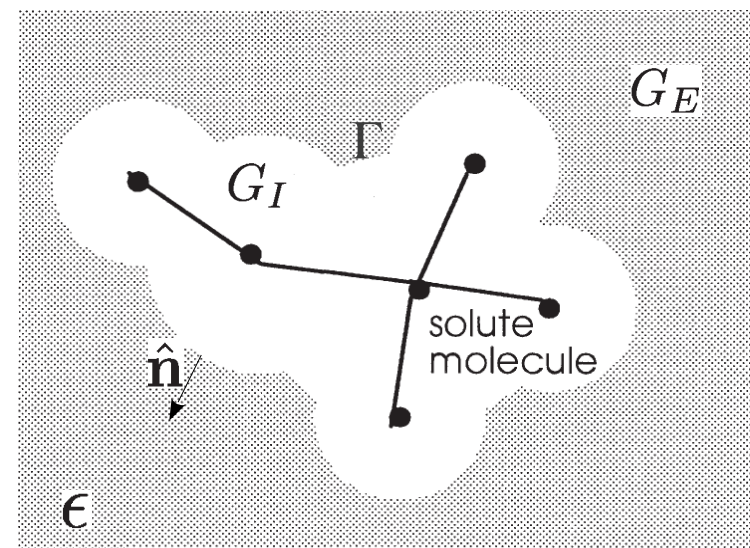
- $\sigma(\mathbf{s})$ is the unique solution of the equation: *Cances et al. J. Math. Chem. 23, 309 (1998)*

$$[S_E(2\pi + D_I^*) + (2\pi - D_E)S_I] \sigma = [S_E S_I^{-1}(2\pi - D_I) - (2\pi - D_E)] V_M$$

Integral operators

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

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



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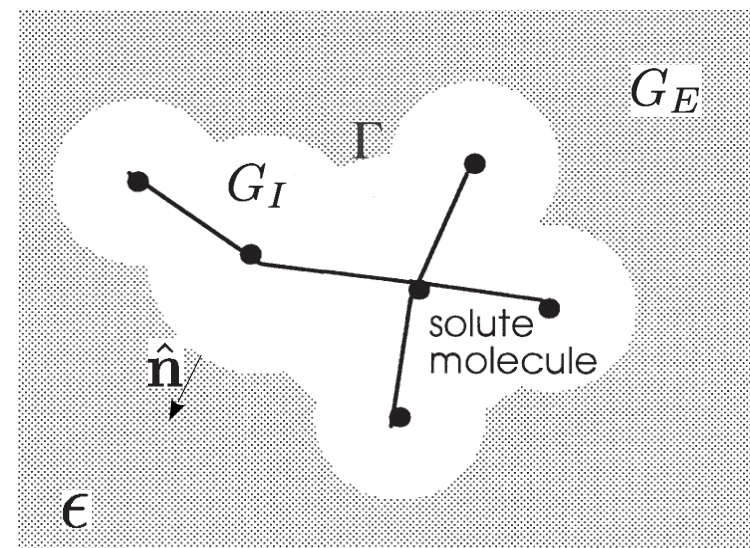
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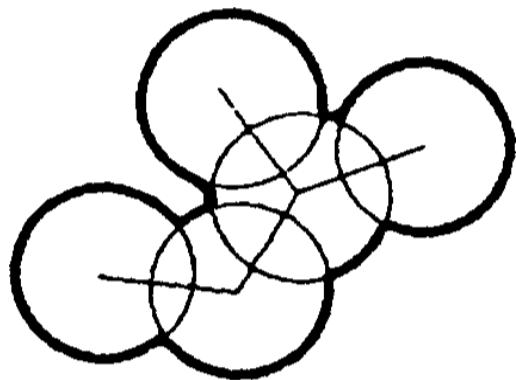
PCM-IEF



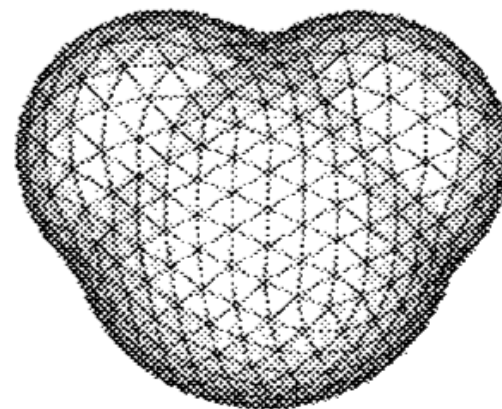
Apparent surface charge method (ASC): *in practice*

- 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.

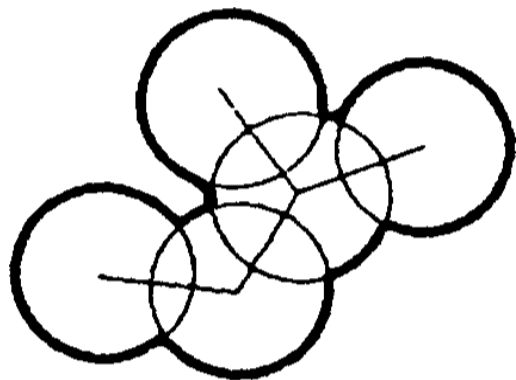


2- Cavity surface *tessellation*: projecting the 60 faces of a pentakis dodecahedron inscribed in each sphere.

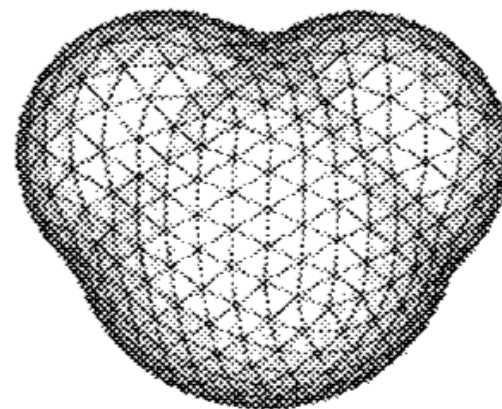
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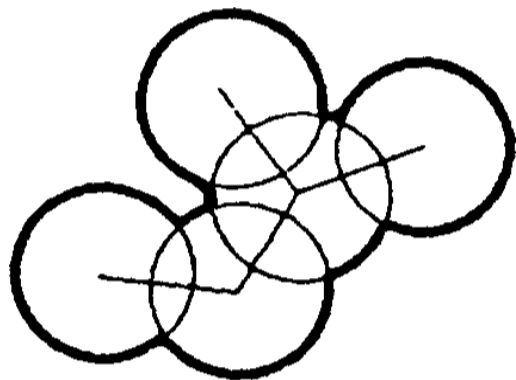
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$$v_{\text{PCM}}(\mathbf{r}) = \int_{\Gamma} \frac{\sigma(\mathbf{s})}{|\mathbf{r} - \mathbf{s}|} d\mathbf{s} \approx \sum_{k=1}^T \frac{\sigma(\mathbf{s}_k) A_k}{|\mathbf{r} - \mathbf{s}_k|} = \sum_{k=1}^T \frac{q_k}{|\mathbf{r} - \mathbf{s}_k|}$$

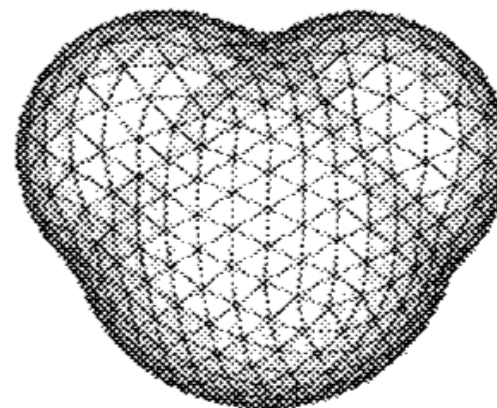
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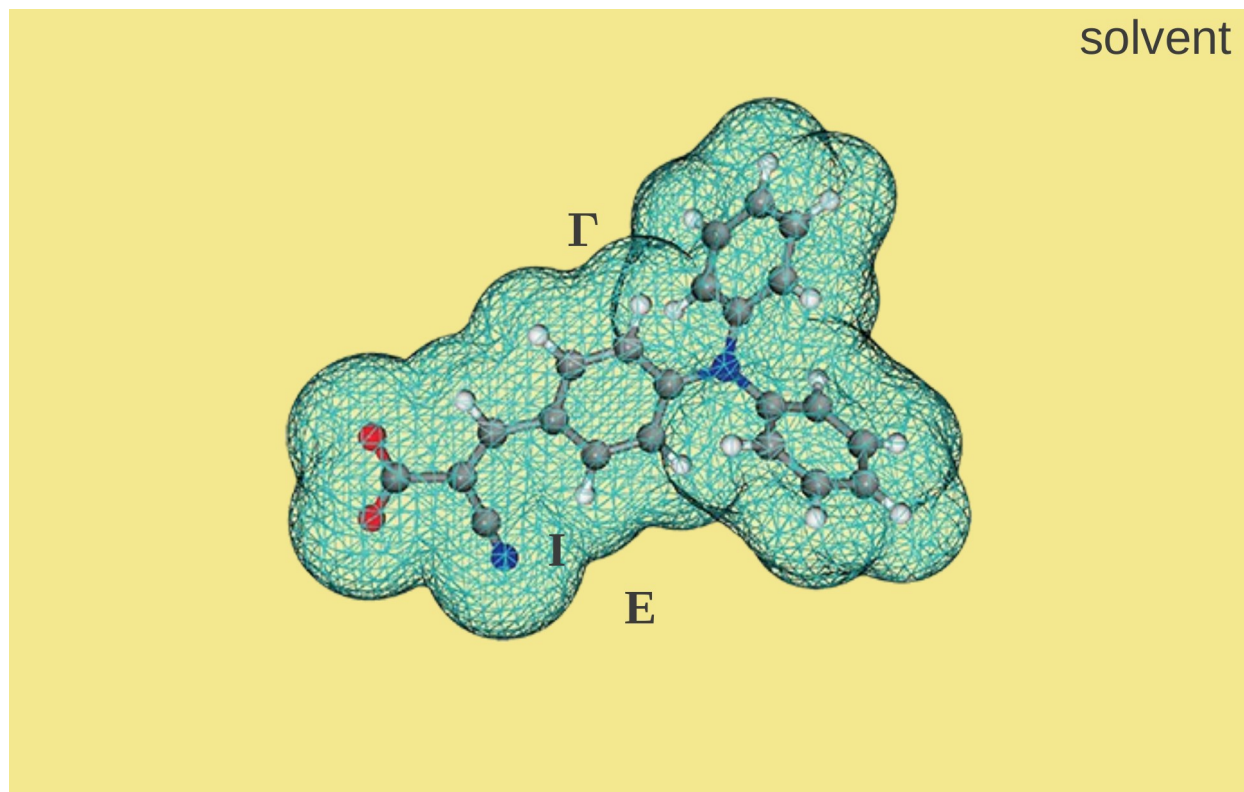
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- Polarization charges are computed by using the PCM matrix (*JCP* 139, 024105 (2013))

$$\mathbf{q} = \mathbf{Q} \mathbf{V}_M$$

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

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

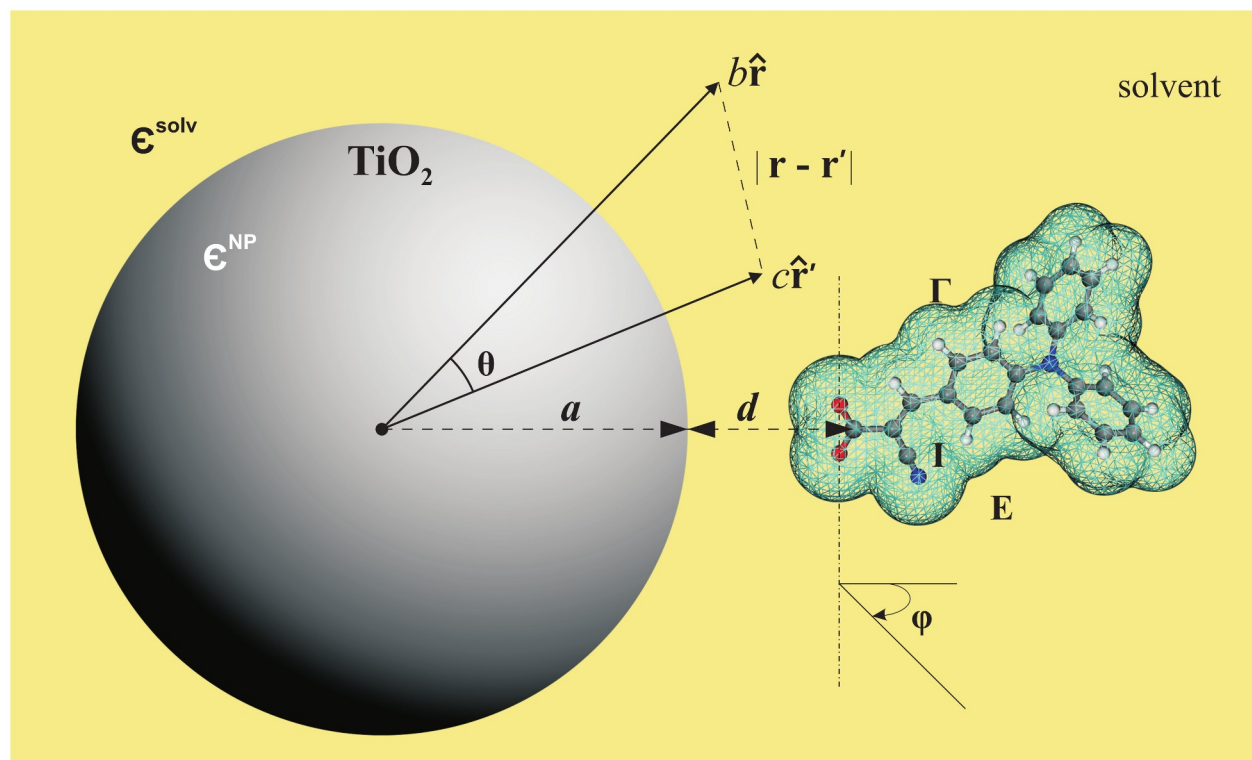


$$G_I(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi|\mathbf{r} - \mathbf{r}'|} \quad \text{Green function in vacuo.}$$

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

$$\mathbf{q} = \mathbf{Q}(\epsilon^{\text{solv}}) \mathbf{V}_M$$

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)

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

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

PCM terms in the Kohn-Sham Eqs.

- The starting point is the free energy functional:

$$\begin{aligned} G[n, n^n] = E^{\text{vac}}[n] &+ \frac{1}{2} \int d\mathbf{r} \, n(\mathbf{r}) \{v_{\text{PCM}}^e[n](\mathbf{r}) + v_{\text{PCM}}^n[n^n](\mathbf{r})\} \\ &+ \frac{1}{2} \int d\mathbf{r} \, n^n(\mathbf{r}) \{v_{\text{PCM}}^e[n](\mathbf{r}) + v_{\text{PCM}}^n[n^n](\mathbf{r})\} \end{aligned}$$

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

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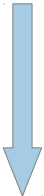
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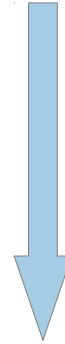
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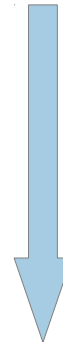

$$= \sum_{i=1}^T \left[\frac{q_i^e + q_i^n}{|\mathbf{r} - \mathbf{s}_i|} \right]$$

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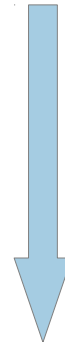


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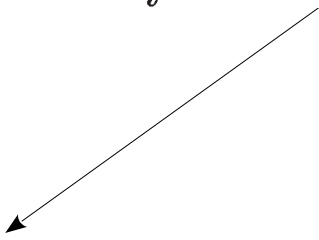
atomic basis set representation: *Gaussian, Gamess, NWChem*


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


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


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

self-consistent term

real-space representation: *Octopus*, ... ?

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

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- How does the PCM field is regularized?

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

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

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

Regularized PCM potential

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with:

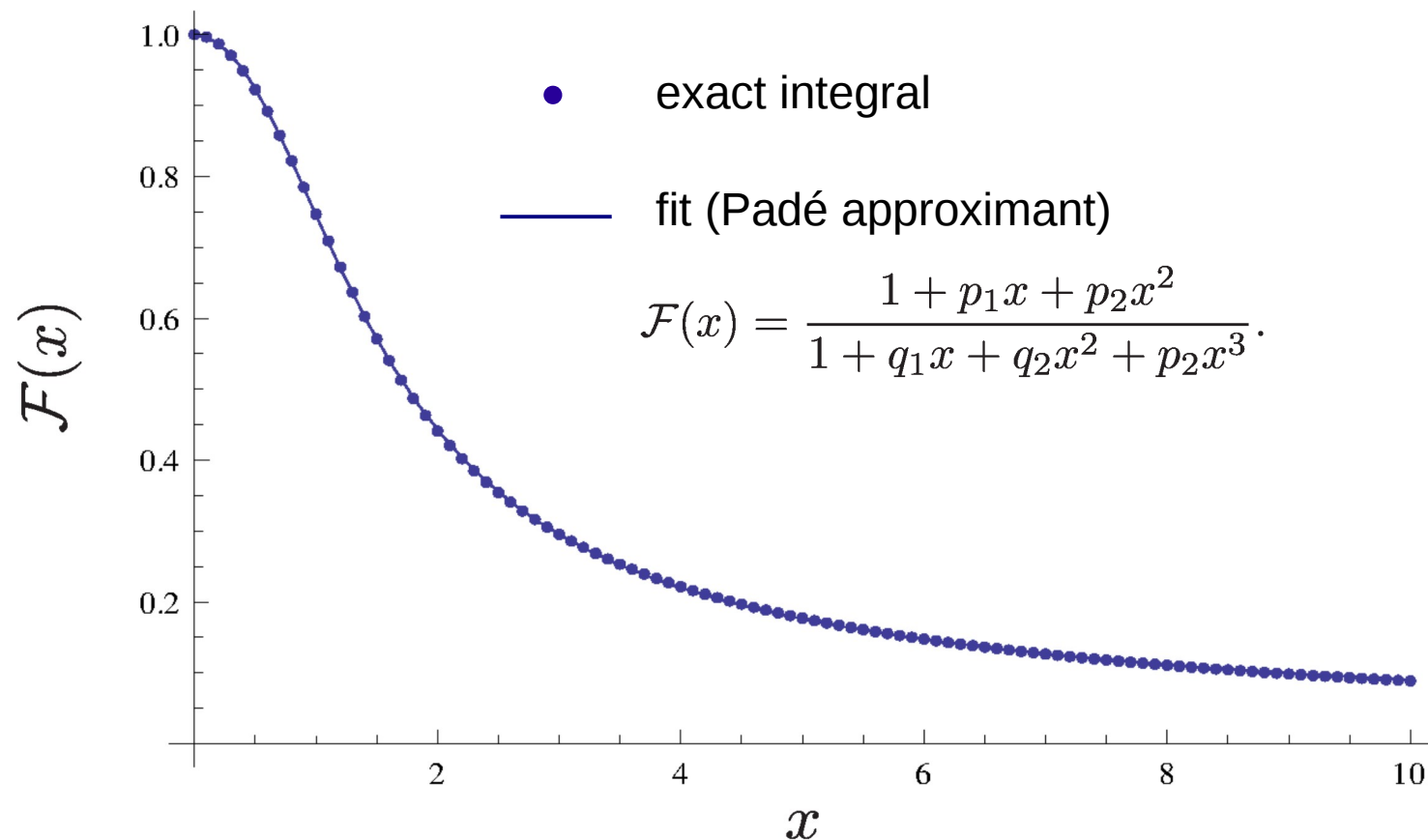
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PCM terms in the ground state energy

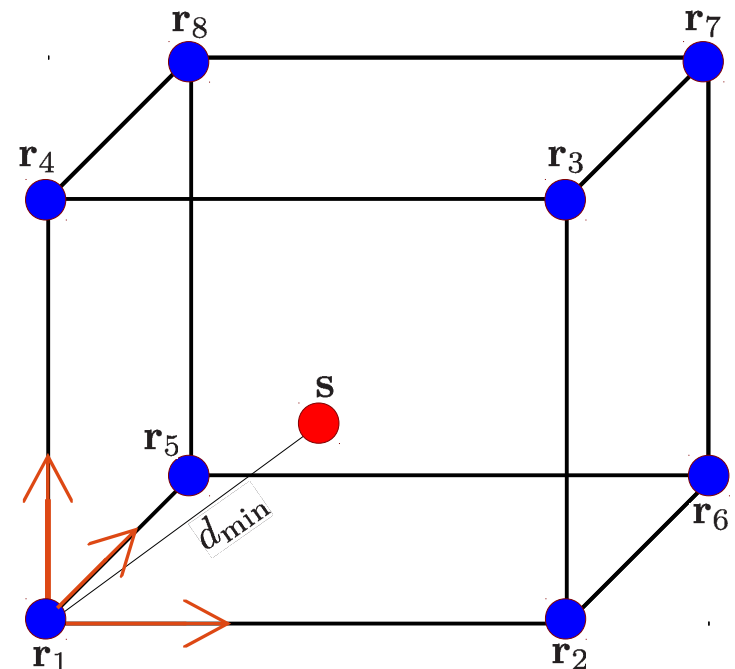
$$\begin{aligned} G[n] = & \sum_{j=1}^{N_{occ}} \varepsilon_j - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} n(\mathbf{r}) v_{xc}[n](\mathbf{r}) + E_{xc}[n] \\ & - \int d\mathbf{r} n(\mathbf{r}) \{v_{\text{PCM}}^e(\mathbf{r}) + v_{\text{PCM}}^n(\mathbf{r})\} \\ & + \frac{1}{2} \sum_{i=1}^T [V_{\text{Hartree}}(\mathbf{s}_i) + V_{\text{Z}_{\text{val}}}(\mathbf{s}_i)] [q^e(\mathbf{s}_i) + q^n(\mathbf{s}_i)] \end{aligned}$$

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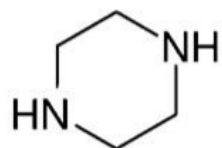
$\mathbf{s}_i \notin$ simulation domain

- Finding the closest grid point for each tessera.
- Building the eight cube's vertices.
- Trilinear interpolation to get $V_{\text{Hartree}}(\mathbf{s})$

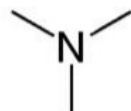


Numerical results: set of molecules to test PCM

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



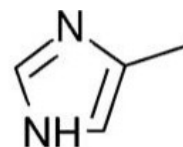
mol 013



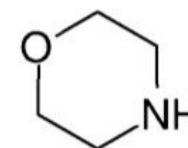
mol 016



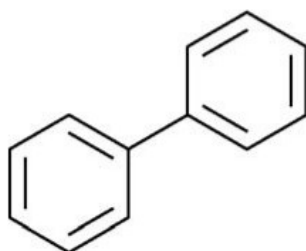
mol 036



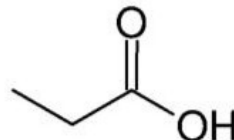
mol 069



mol 090



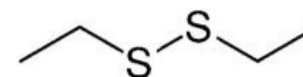
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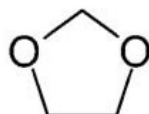
mol 117



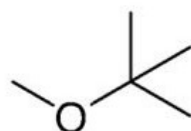
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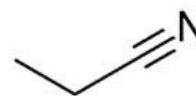
mol 142



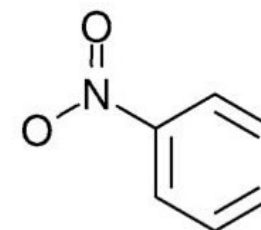
mol 160



mol 163



mol 200

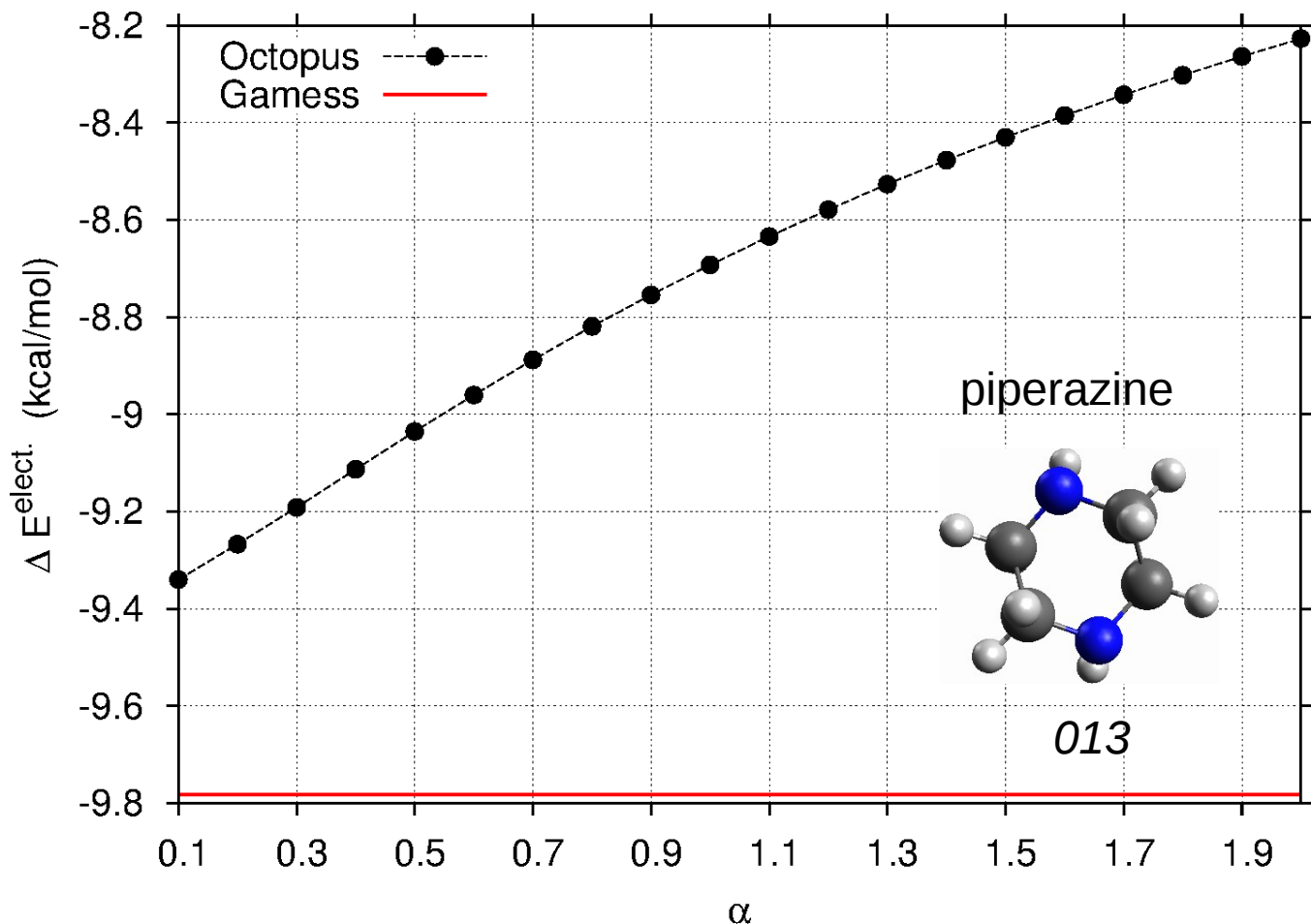


mol 206

solute - solvent electrostatic interaction energy in water

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

- XC = PBE
- Octopus: $R = 5 \text{ \AA}$ $\Delta = 0.15 \text{ \AA}$
- GAMESS: TZ 6311+G(d,p)

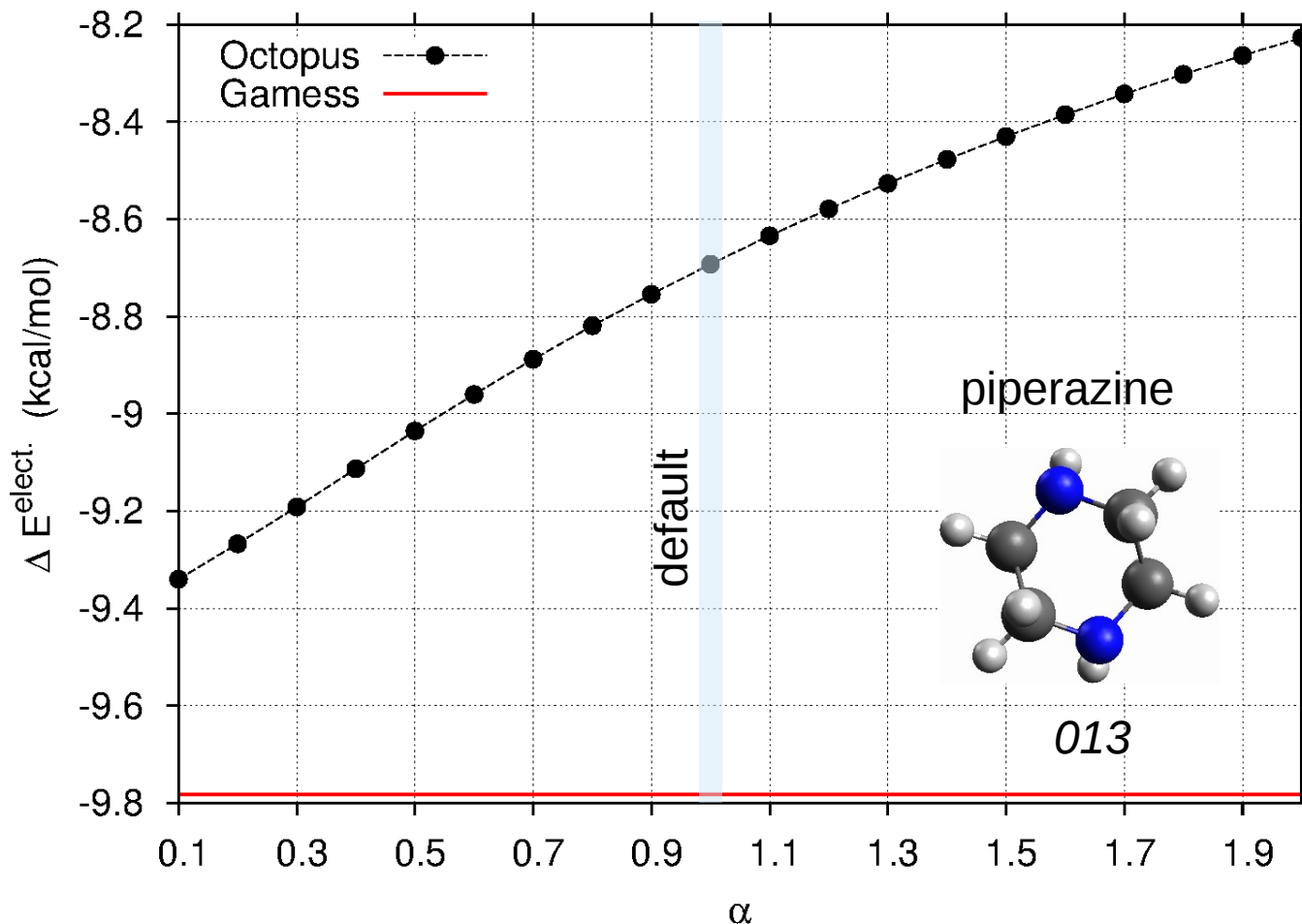


$$\rho_i(\mathbf{r}) = \frac{q_i}{(\alpha\pi A_i)^{3/2}} e^{-|\mathbf{r}-\mathbf{s}_i|^2/\alpha A_i}$$

solute - solvent electrostatic interaction energy in water

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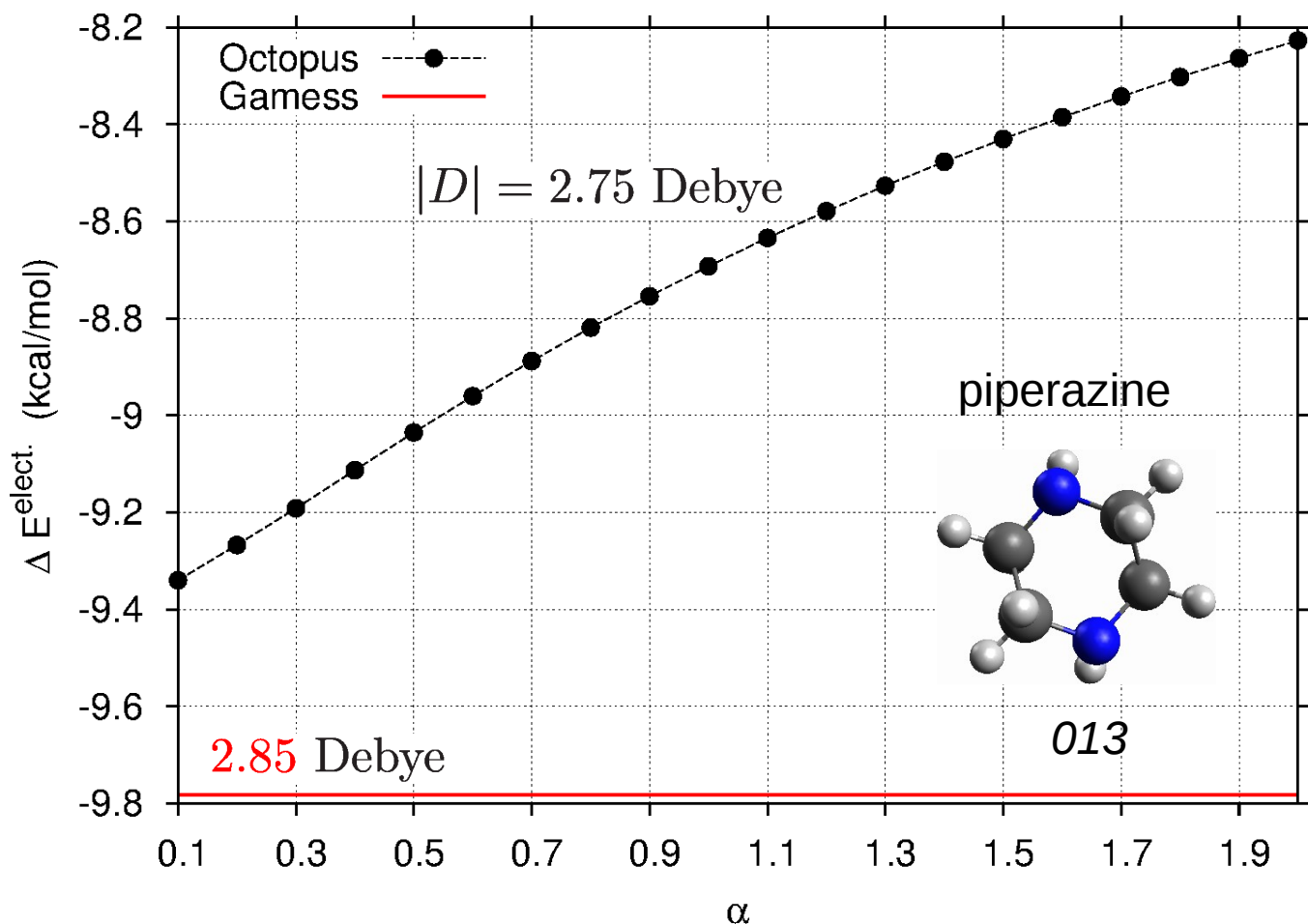


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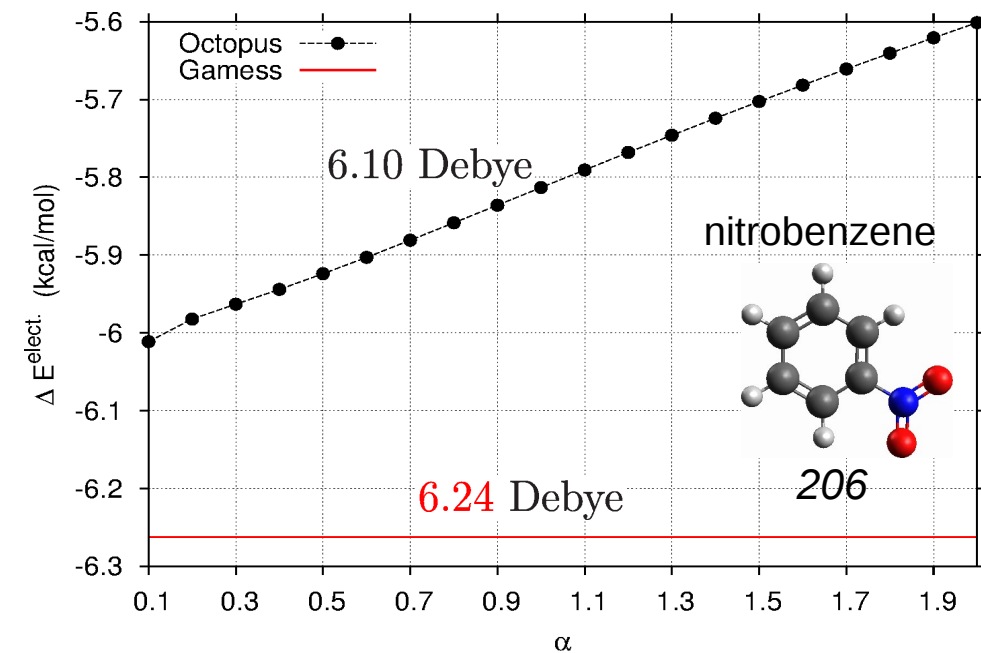
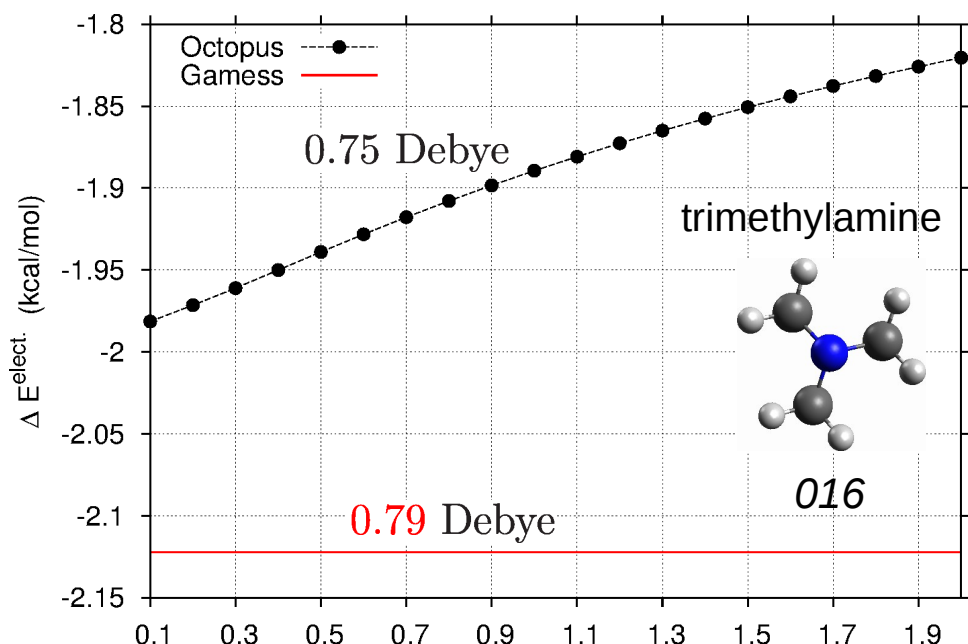
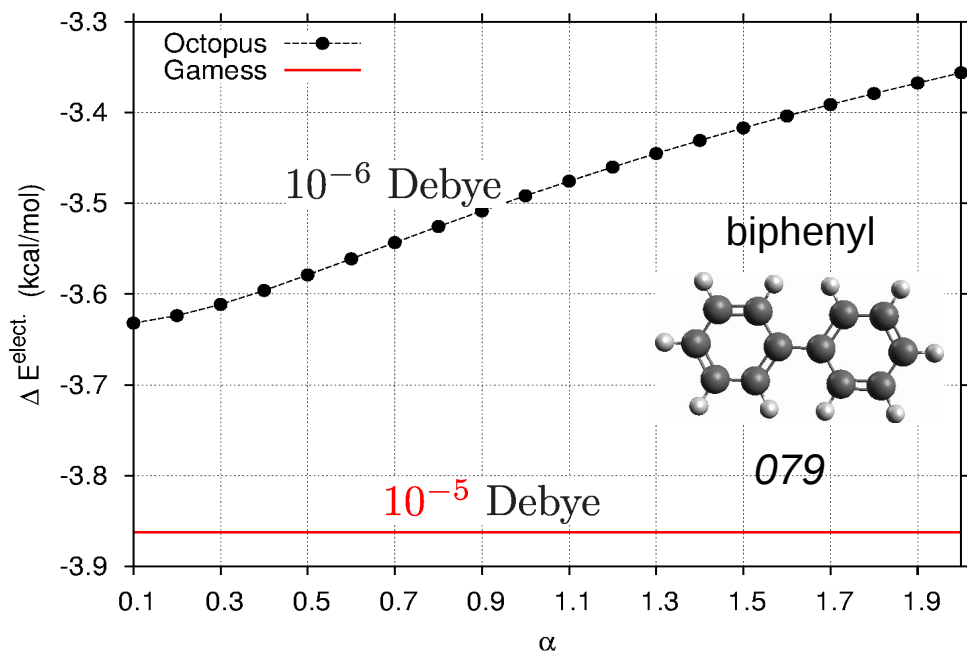
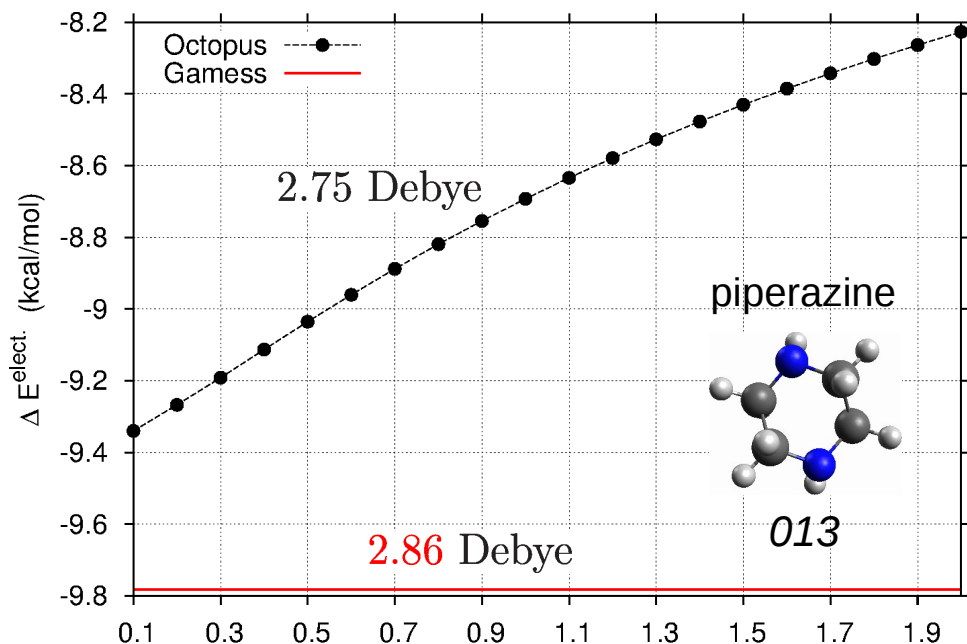
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solute - solvent electrostatic interaction energy in water

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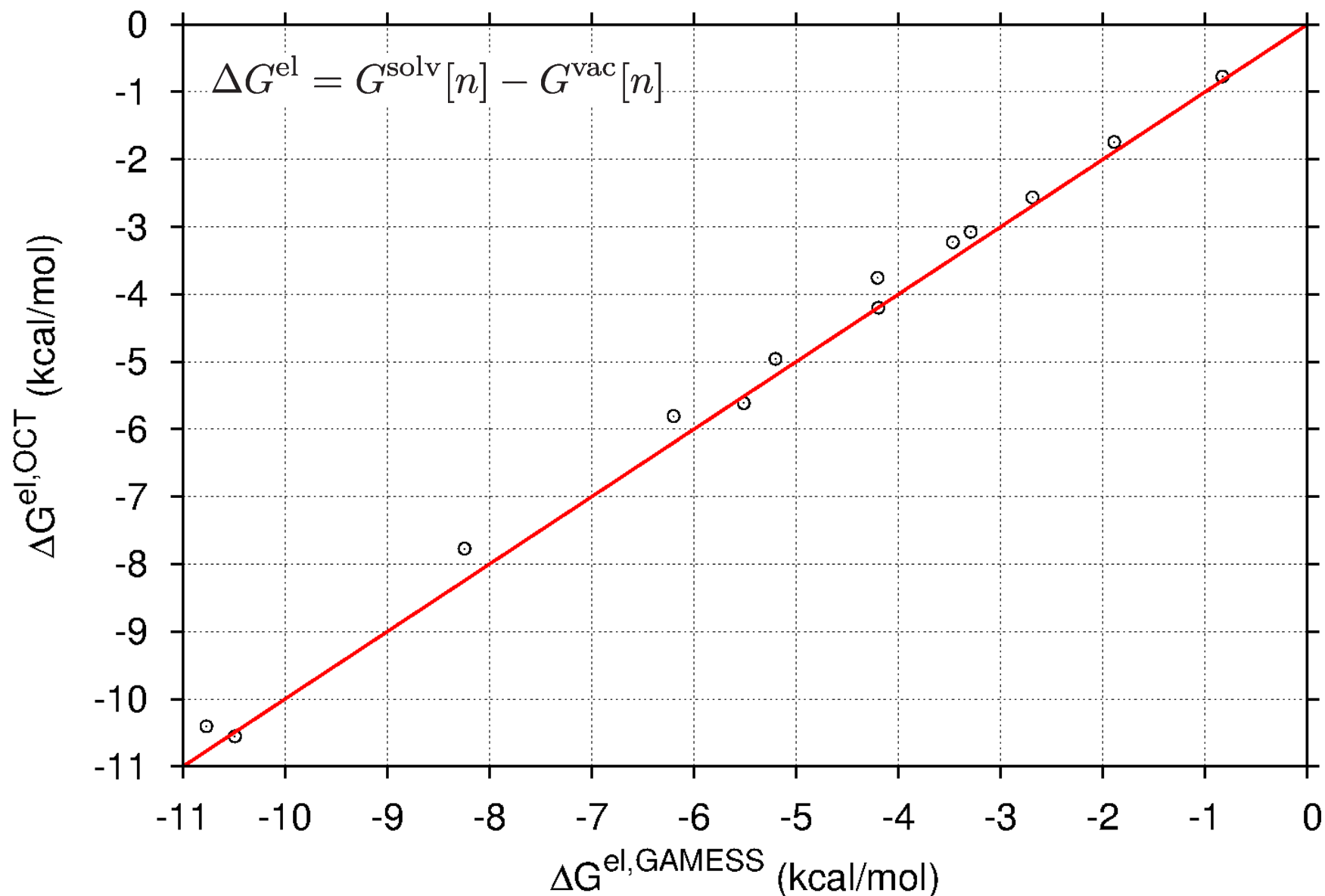
• Octopus: $R = 5 \text{ \AA}$ $\Delta = 0.15 \text{ \AA}$

• GAMESS: TZ 6311+G(d,p)



Solvation free energies in water

- XC = PBE
- Octopus: $R = 5 \text{ \AA}$ $\Delta = 0.15 \text{ \AA}$
- GAMESS: TZ 6311+G(d,p)

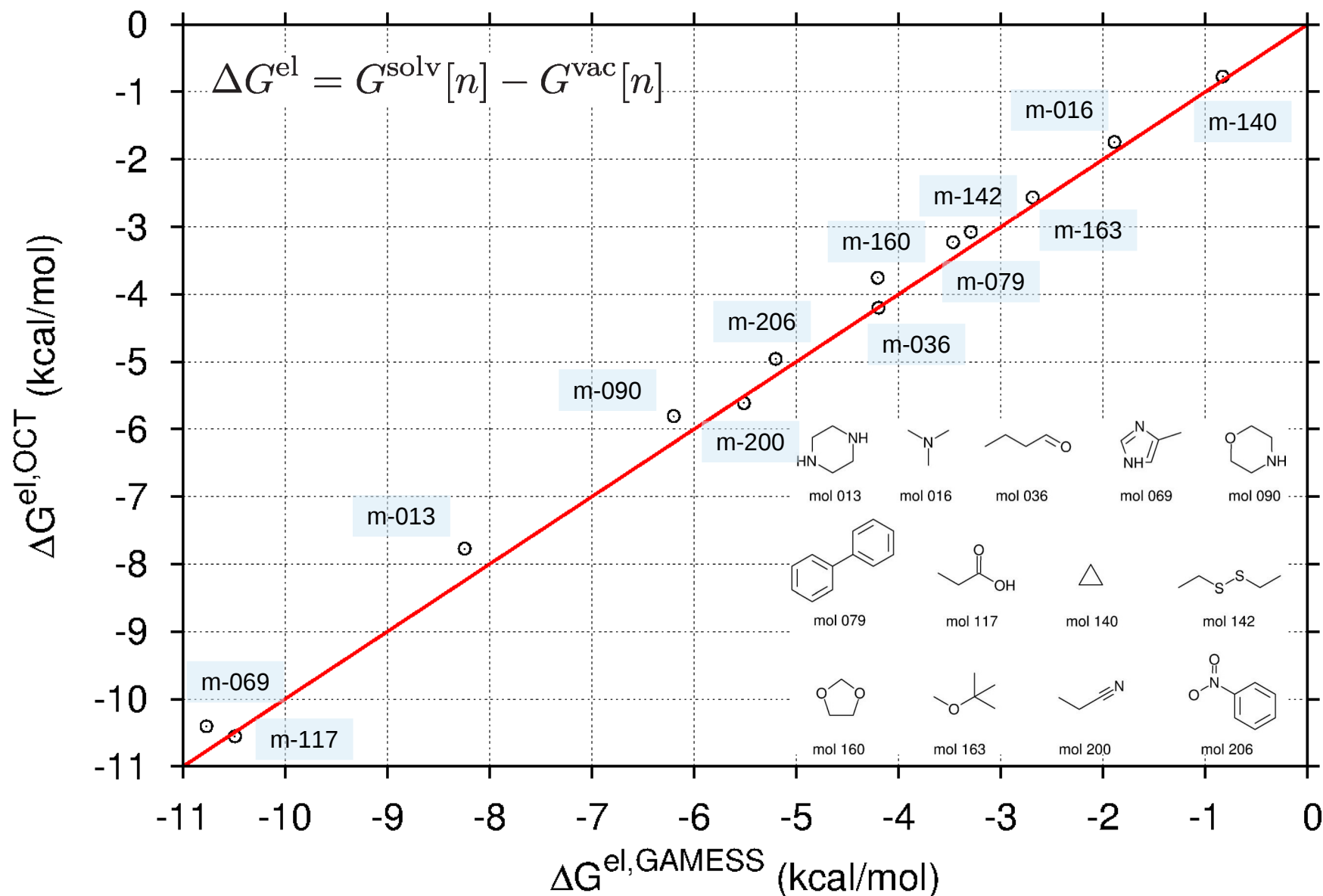


Solvation free energies in water

- XC = PBE

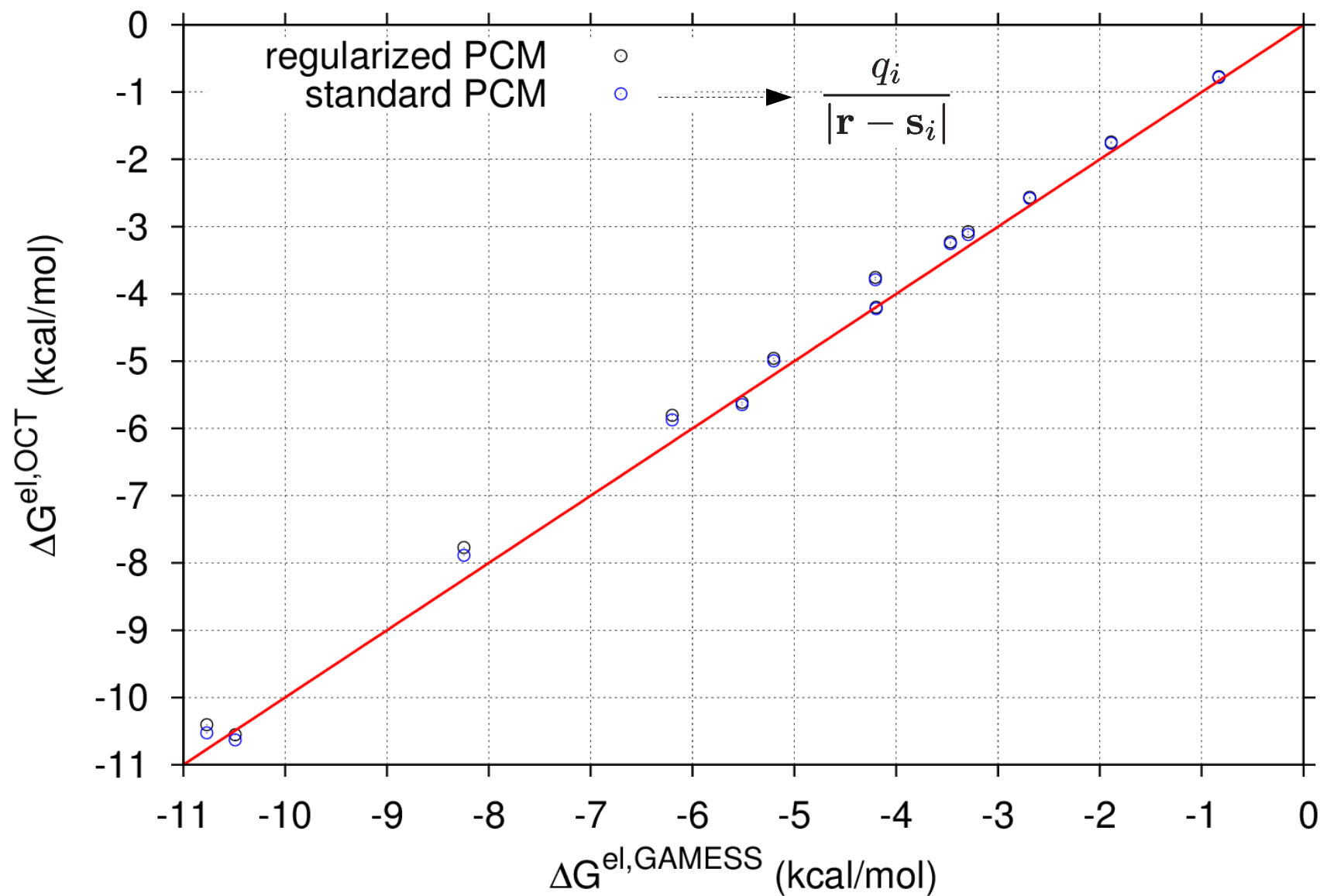
- Octopus: $R = 5 \text{ \AA}$ $\Delta = 0.15 \text{ \AA}$

- GAMESS: TZ 6311+G(d,p)



Solvation free energies in water

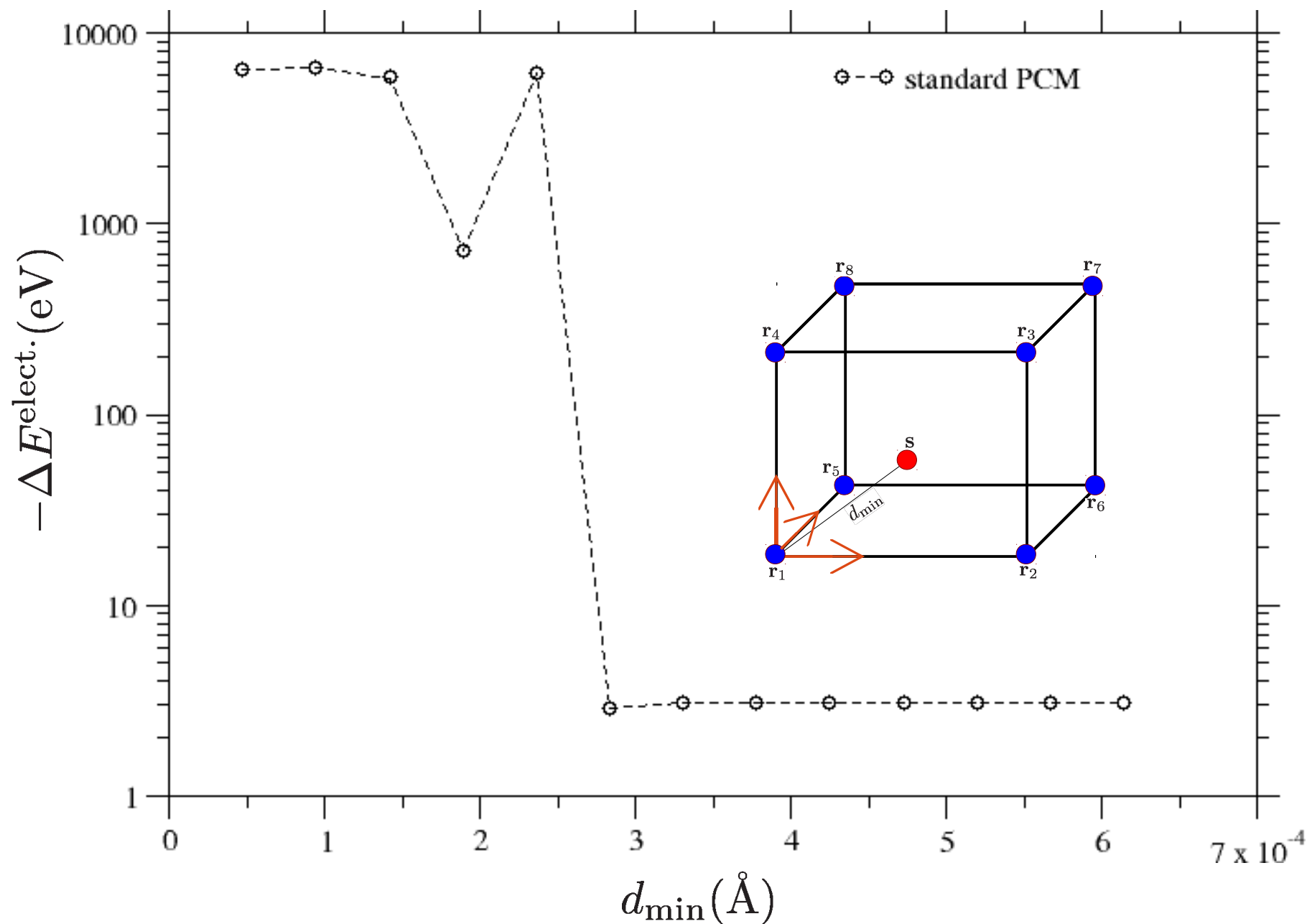
- XC = PBE
- Octopus: $R = 5 \text{ \AA}$ $\Delta = 0.15 \text{ \AA}$
- GAMESS: TZ 6311+G(d,p)



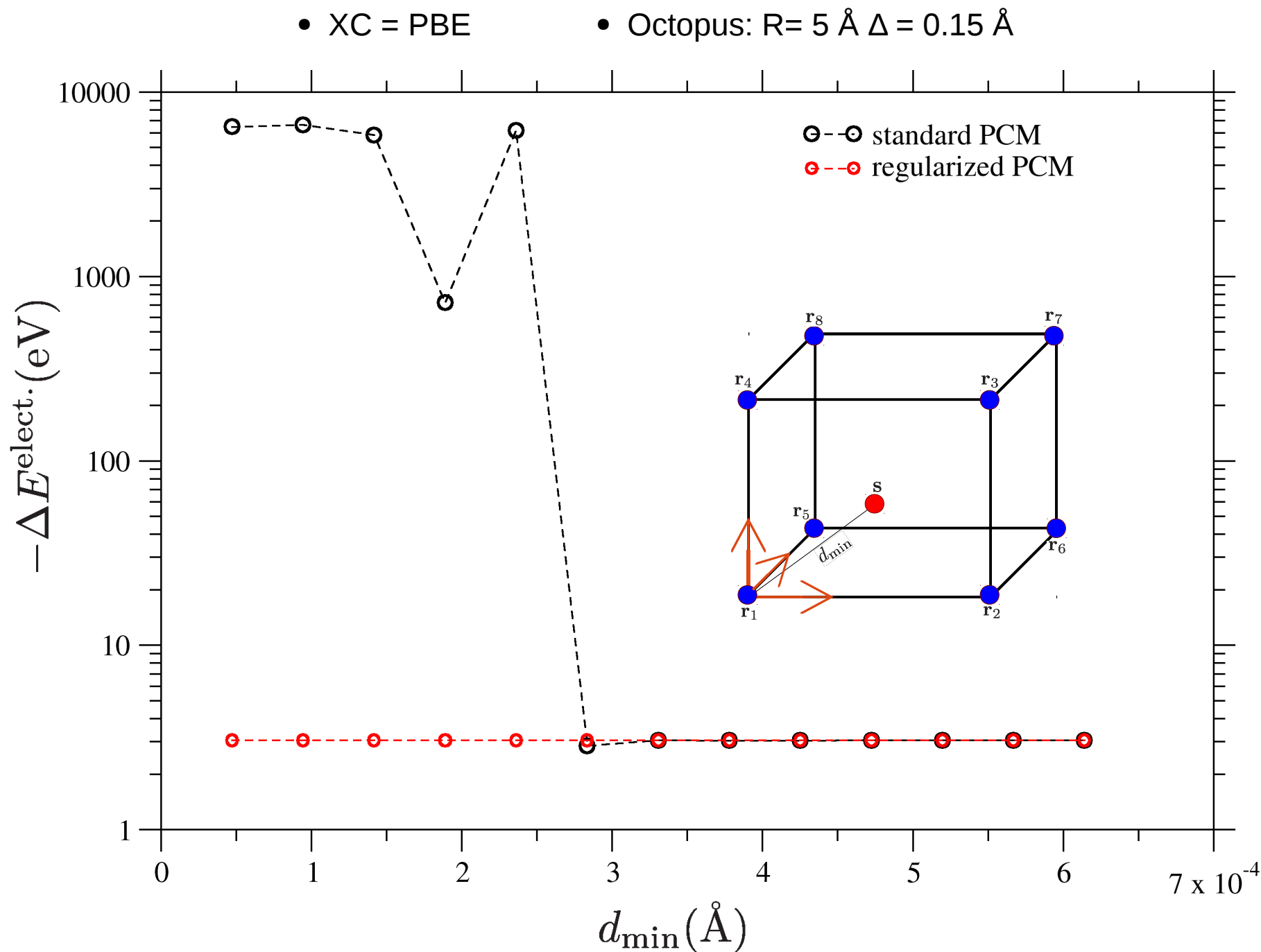
Looking for the singularity: *calculations in Cl⁻*

• XC = PBE

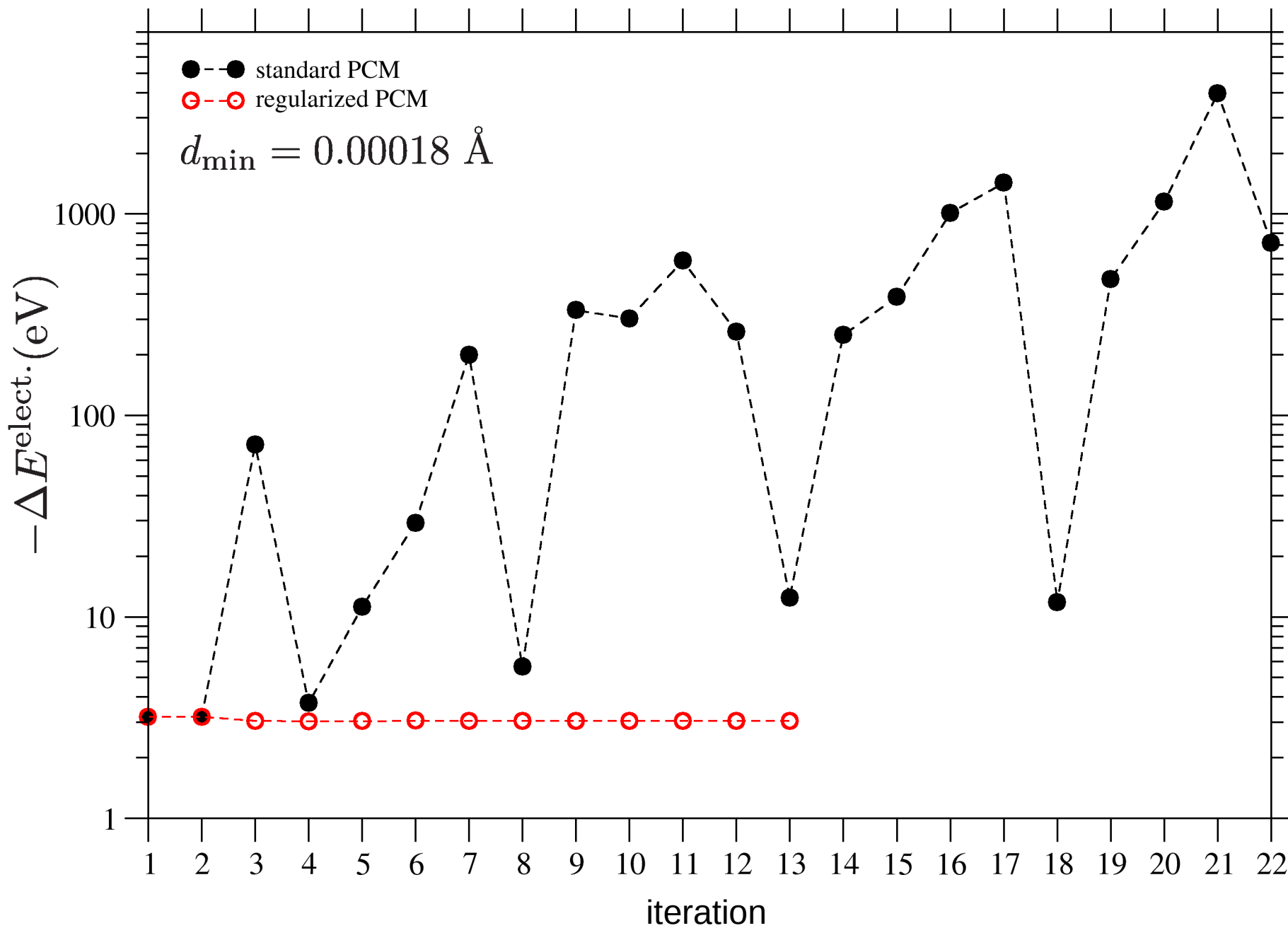
• Octopus: R= 5 Å Δ = 0.15 Å



Looking for the singularity: *calculations in Cl⁻*



Looking for the singularity: *calculations in Cl⁻*

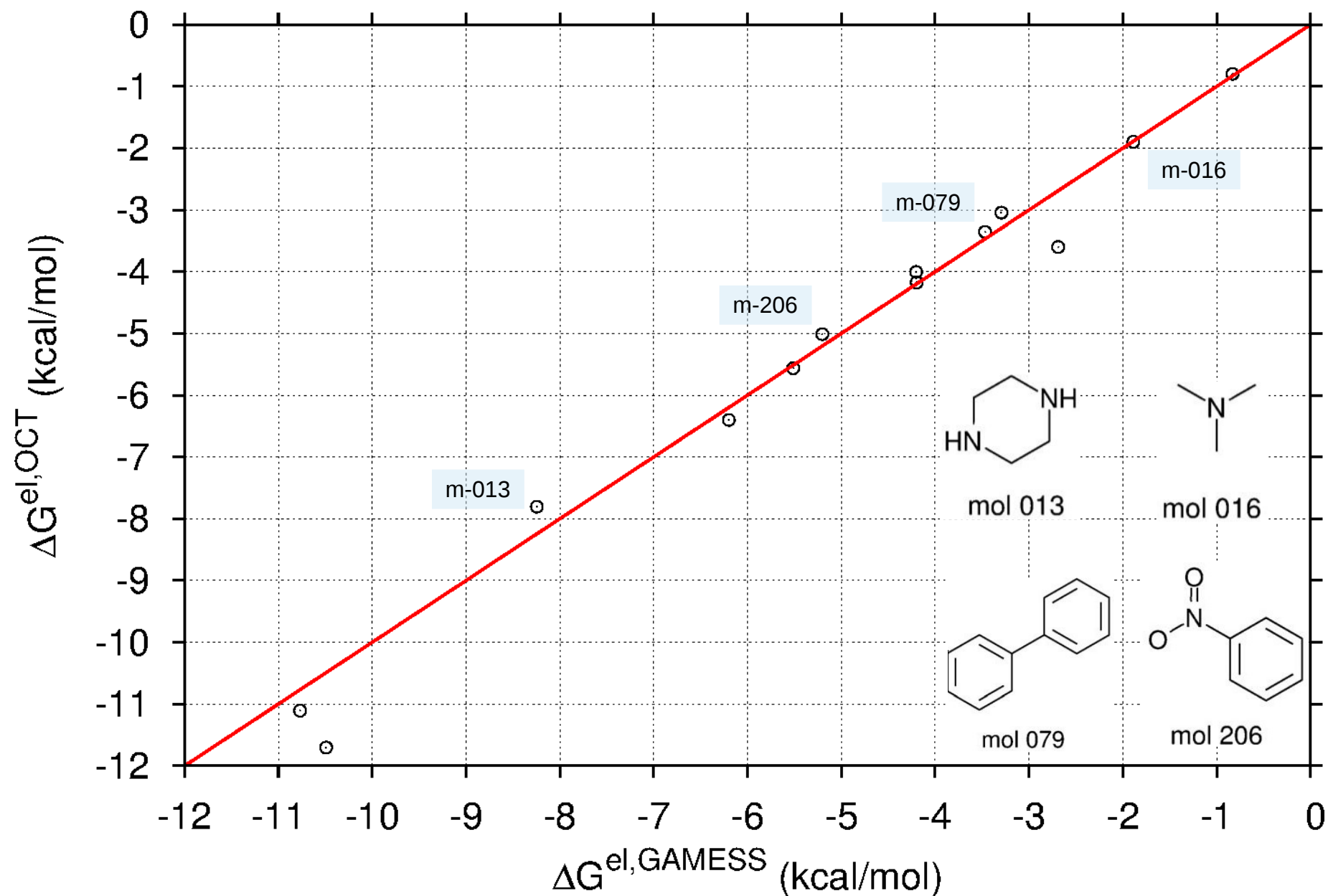


Absorption spectra: *selected cases*

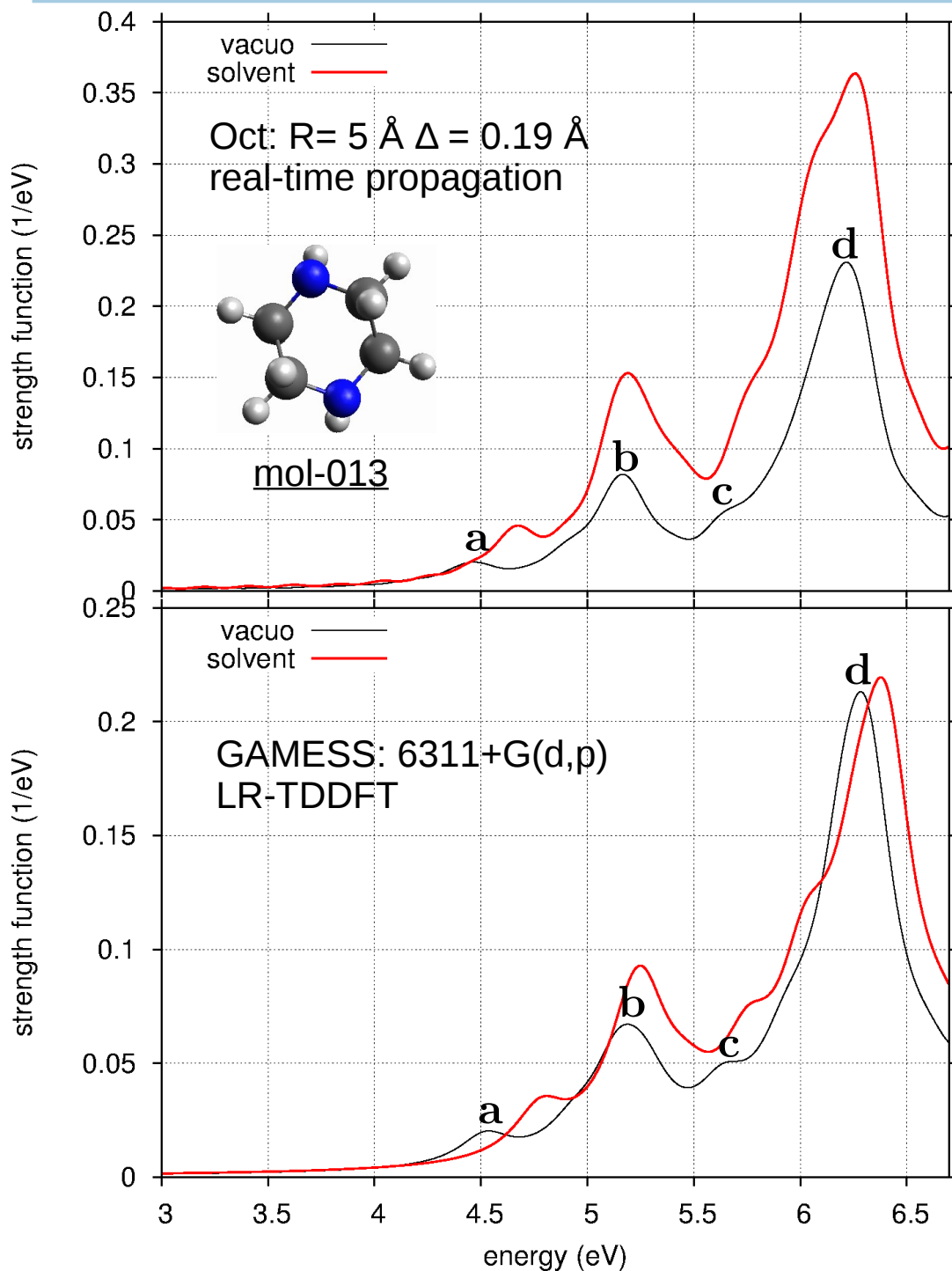
• XC = PBE

• Octopus: $R = 5 \text{ \AA}$ $\Delta = 0.19 \text{ \AA}$

• GAMESS: TZ 6311+G(d,p)



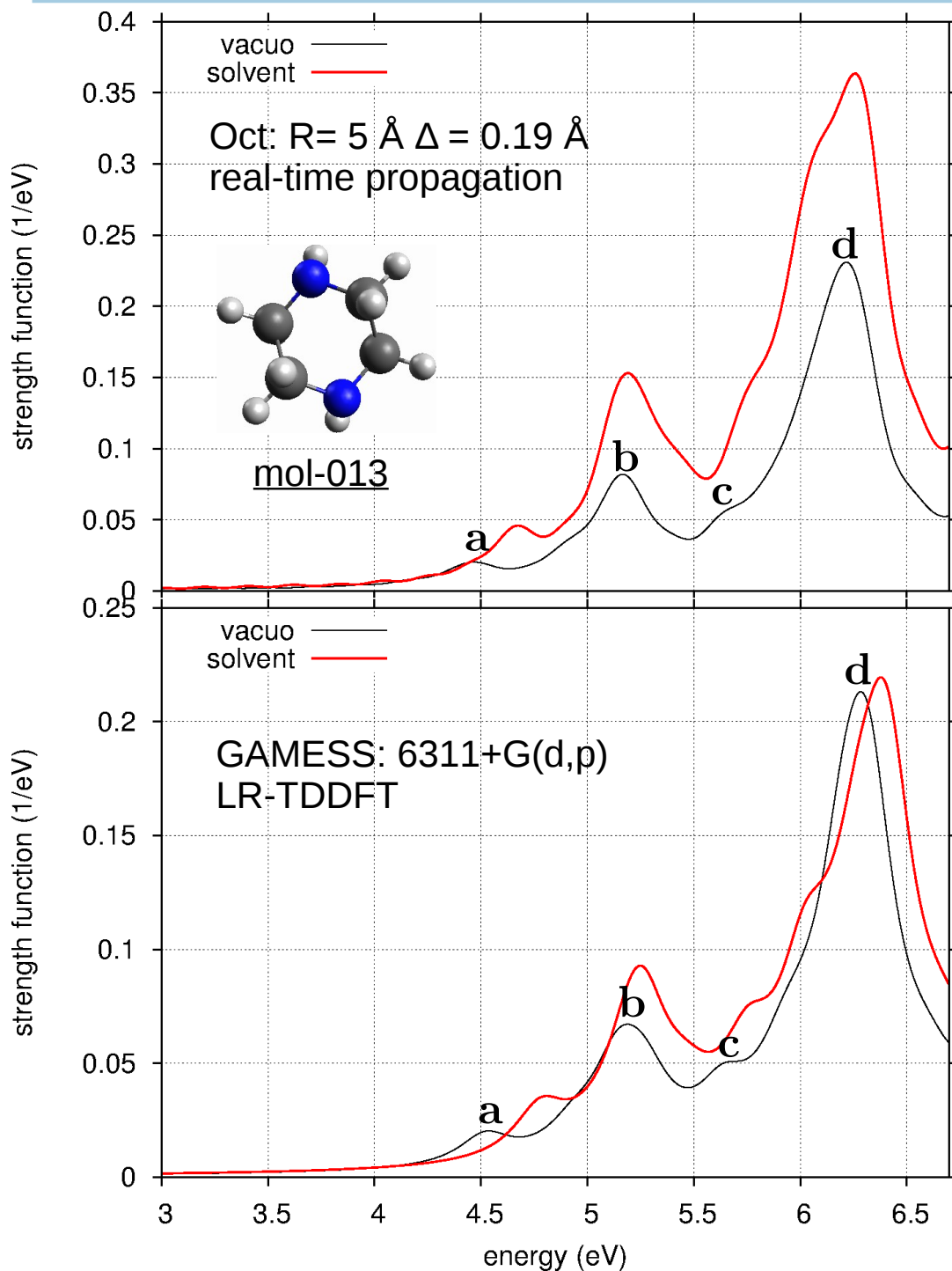
Absorption spectra



solvatochromic shifts (eV)

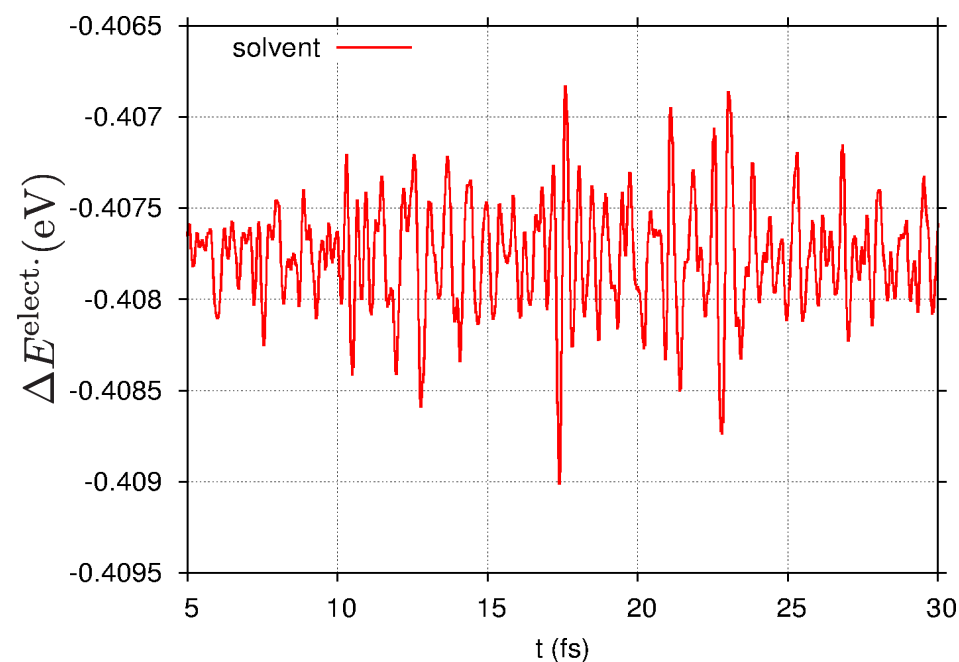
peak	Octopus	Gamess
a	0.21	0.25
b	0.03	0.05
c	0.10	0.10
d	0.04	0.09

Absorption spectra

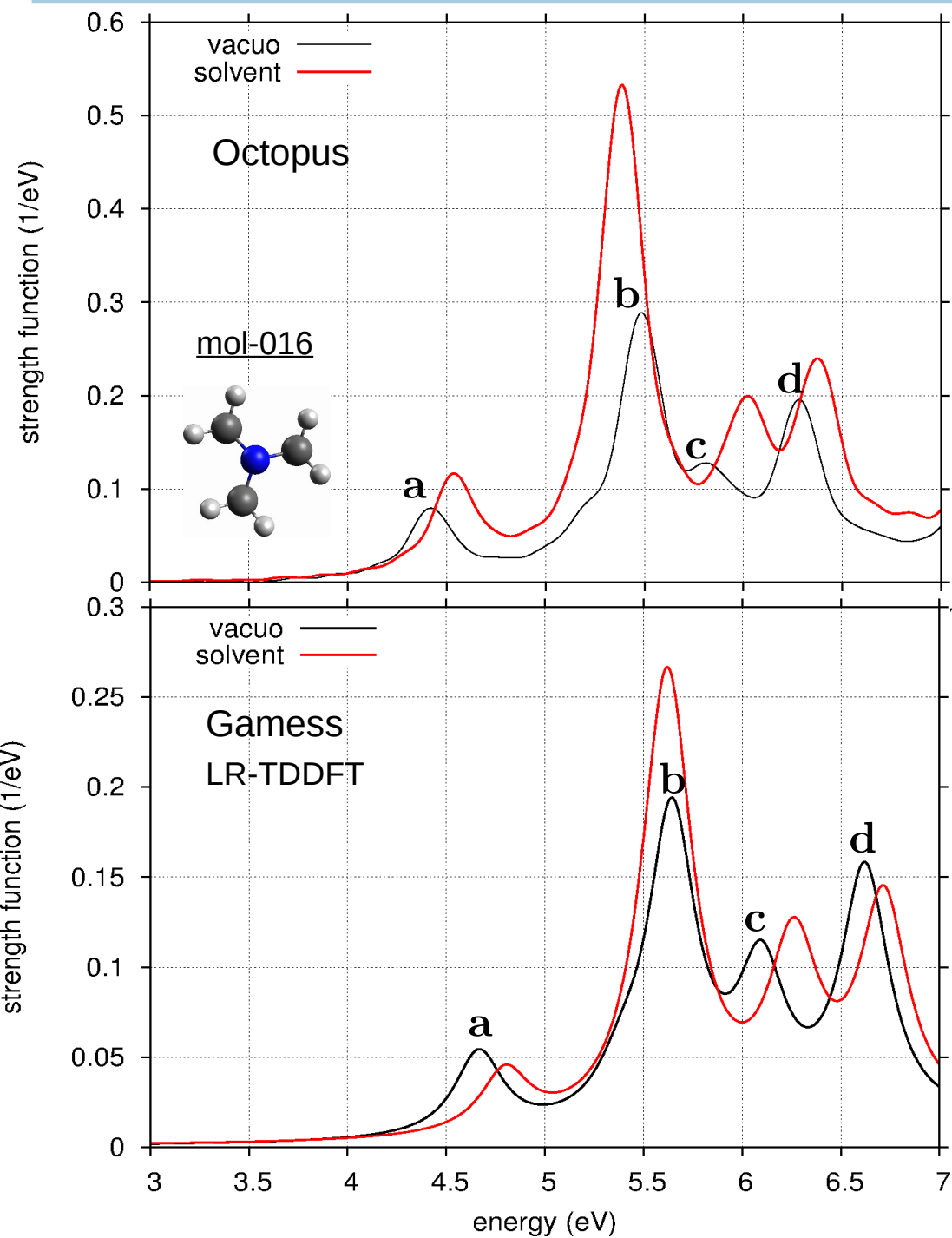


solvatochromic shifts (eV)

<i>peak</i>	<i>Octopus</i>	<i>Gamess</i>
a	0.21	0.25
b	0.03	0.05
c	0.10	0.10
d	0.04	0.09



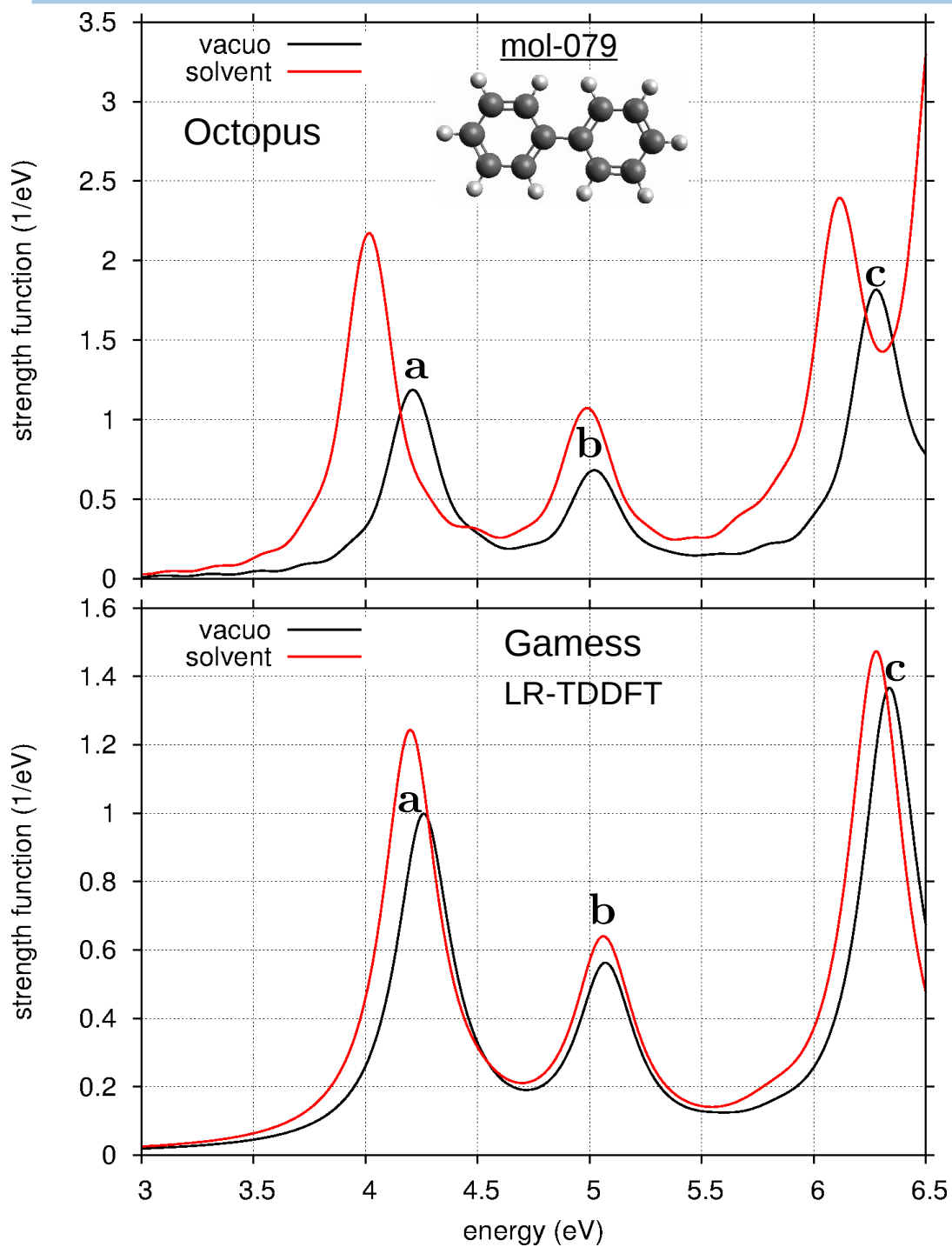
Absorption spectra



solvatochromic shifts (eV)

<i>peak</i>	<i>Octopus</i>	<i>Gamess</i>
a	0.12	0.13
b	-0.10	-0.02
c	0.21	0.17
d	0.09	0.09

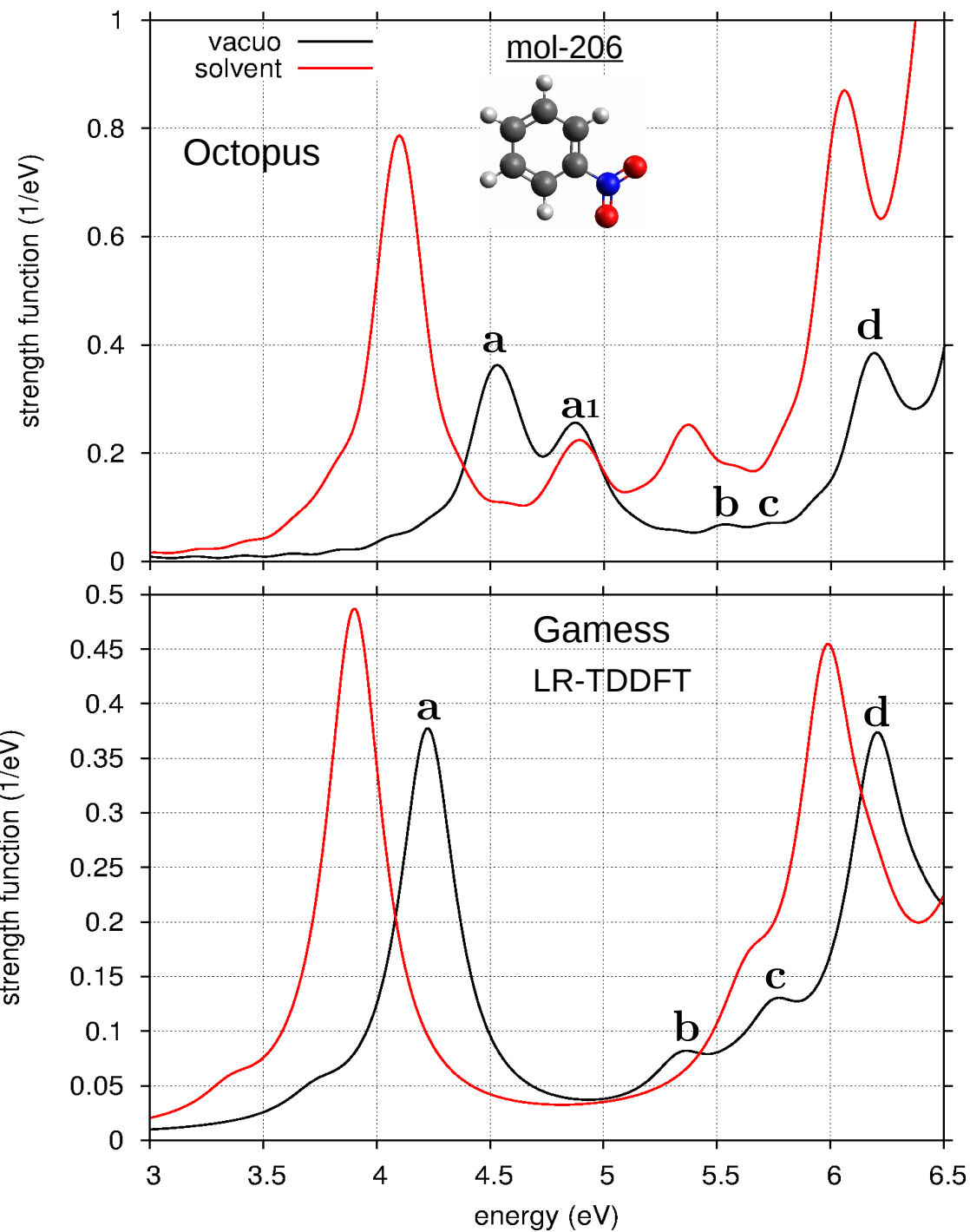
Absorption spectra



solvatochromic shifts (eV)

<i>peak</i>	<i>Octopus</i>	<i>GameSS</i>
a	-0.19	-0.07
b	-0.02	-0.01
c	-0.15	-0.06

Absorption spectra

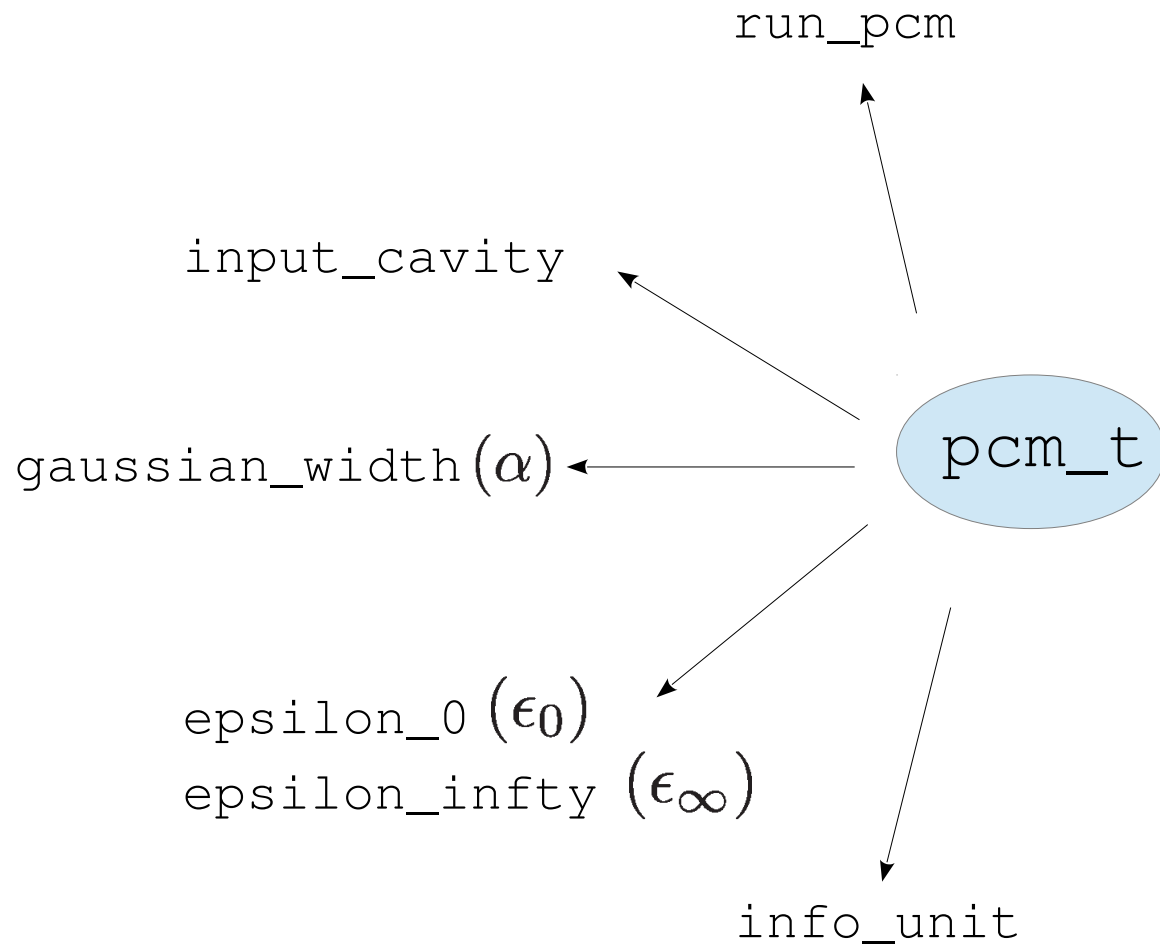


solvatochromic shifts (eV)

<i>peak</i>	<i>Octopus</i>	<i>Gamess</i>
a	-0.42	-0.32
a1	0.02	
b	-0.17	
c	-0.13	-0.13
d	-0.12	-0.21

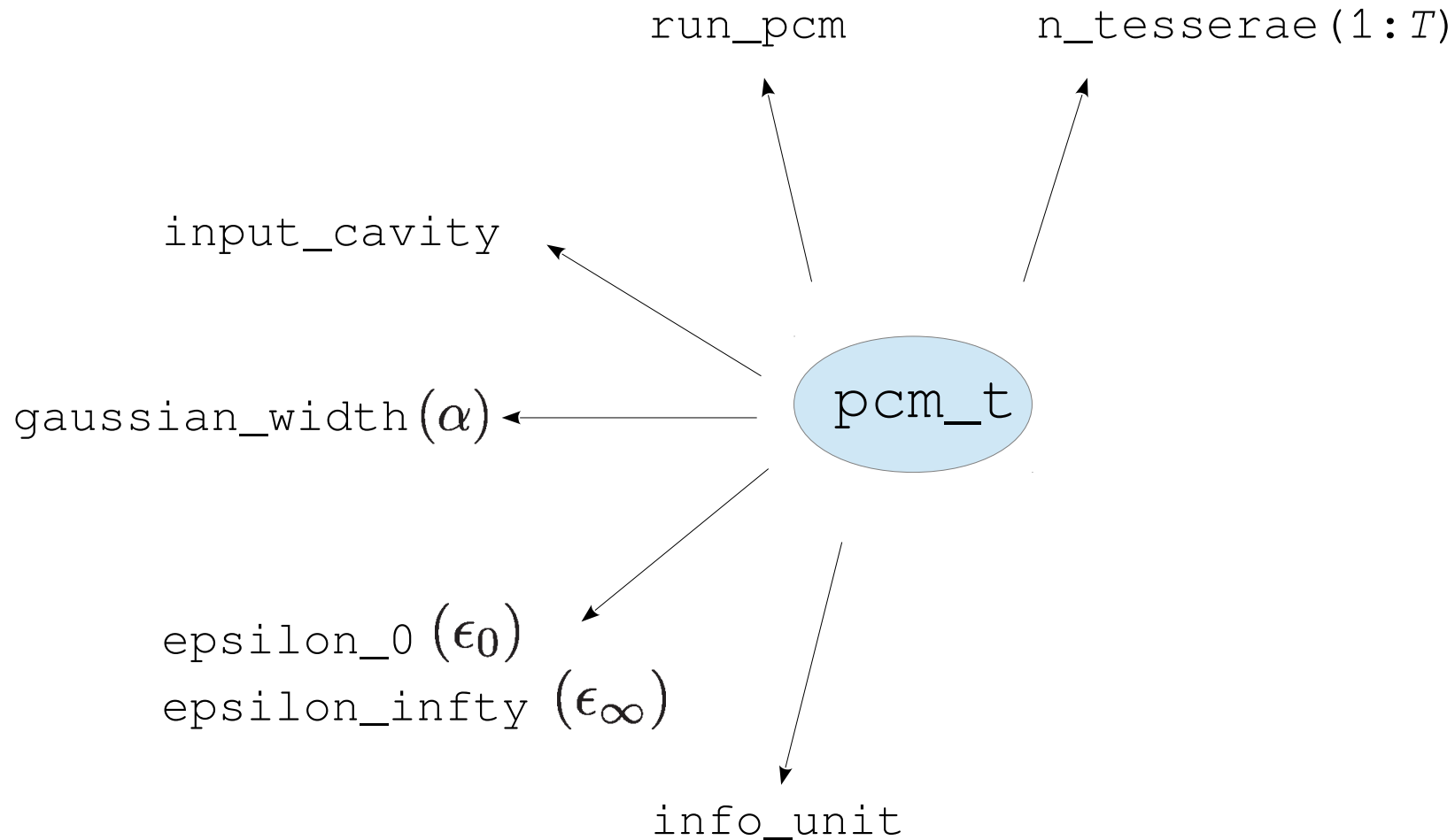
Structure of the PCM type

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



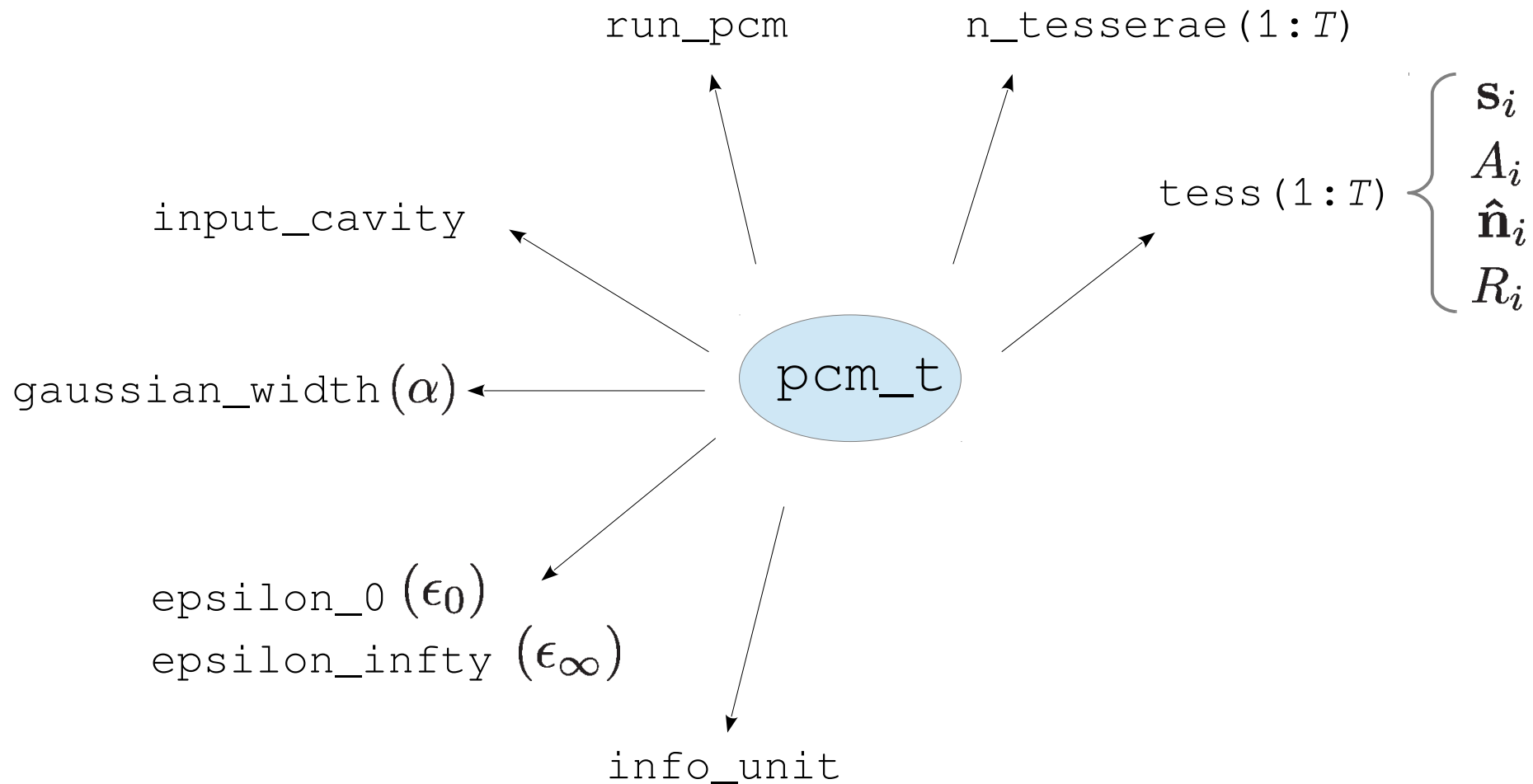
Structure of the PCM type

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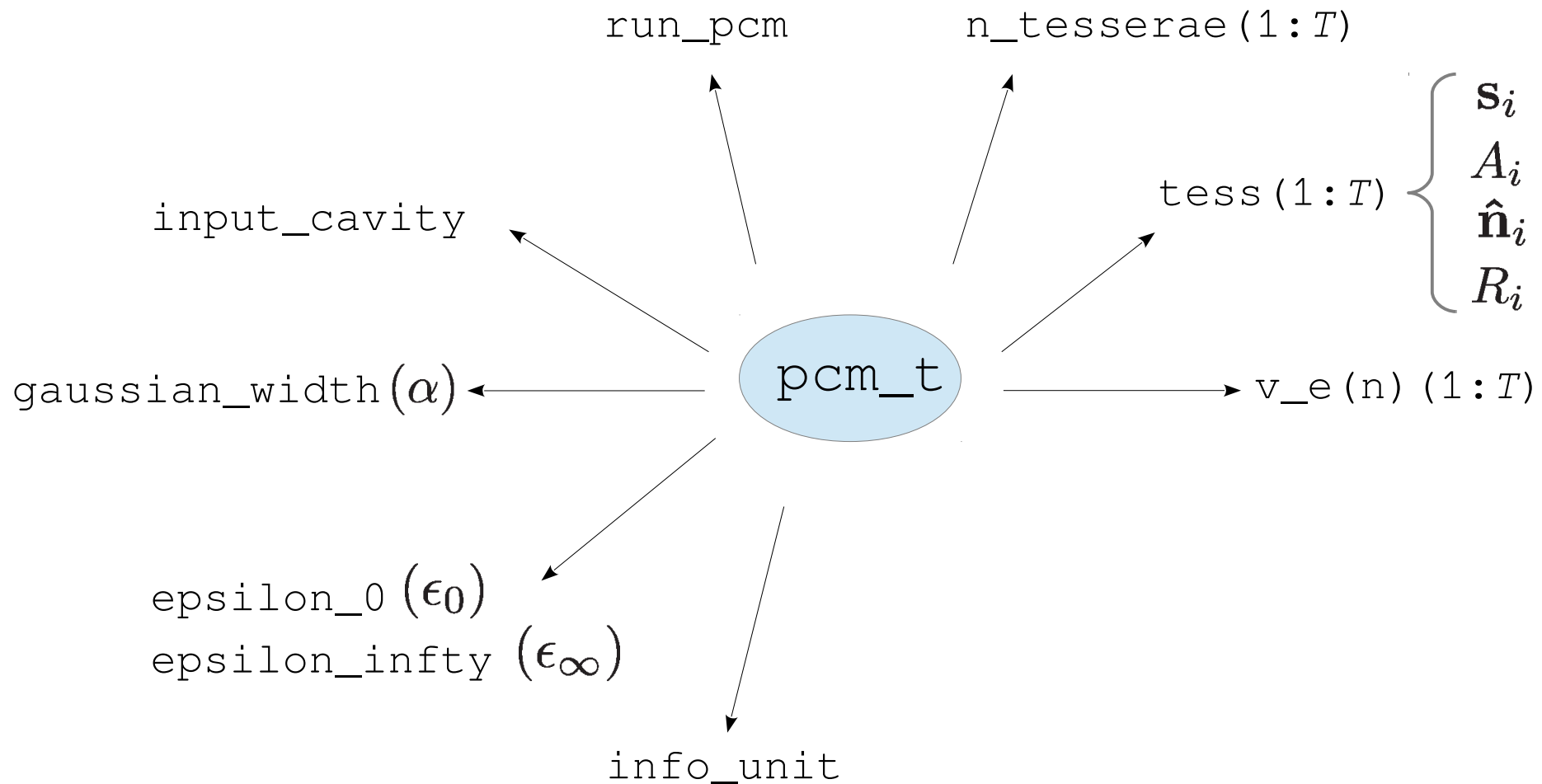
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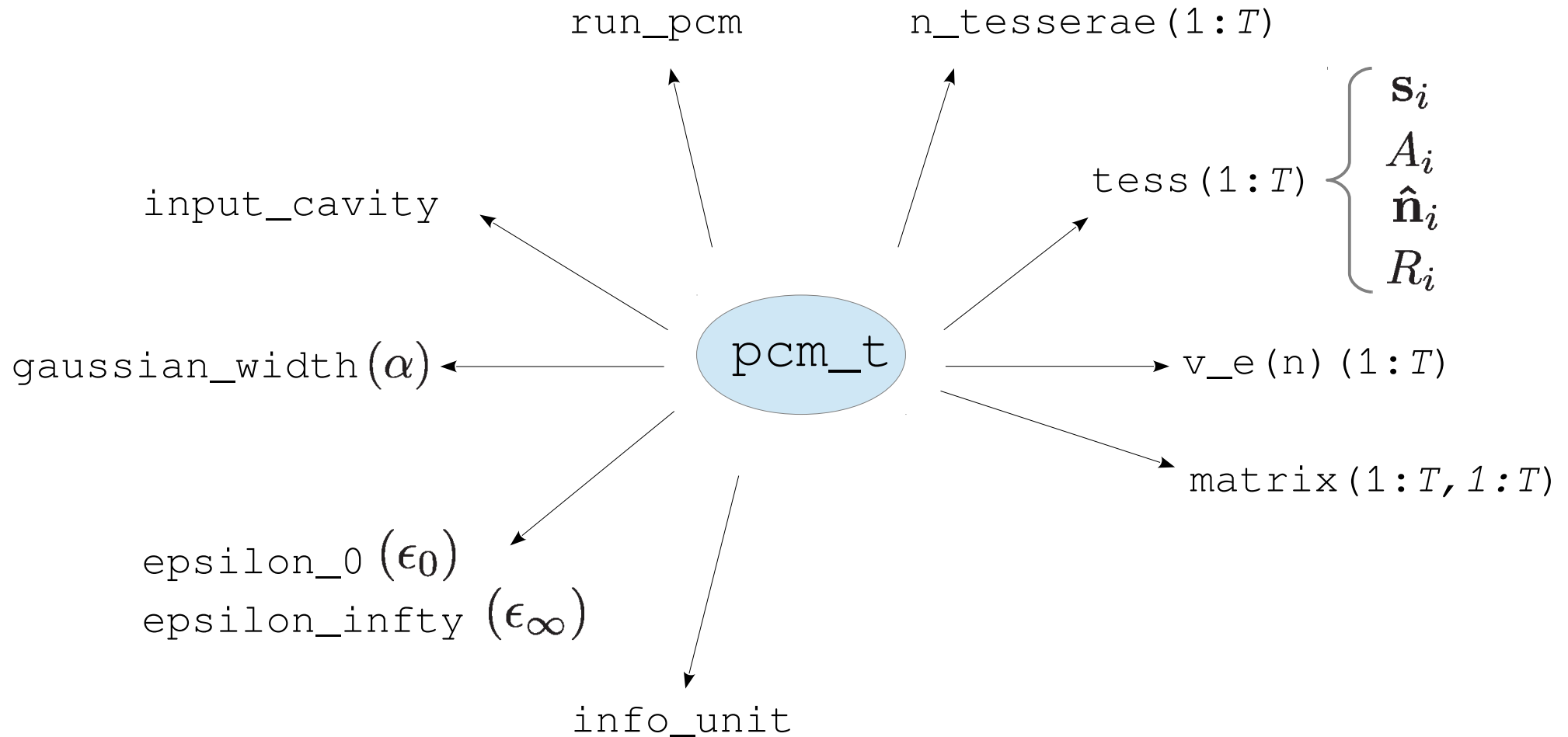
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`pcm` variable is of type `pcm_t` and can be accessed through any variable of type `hamiltonian_t`



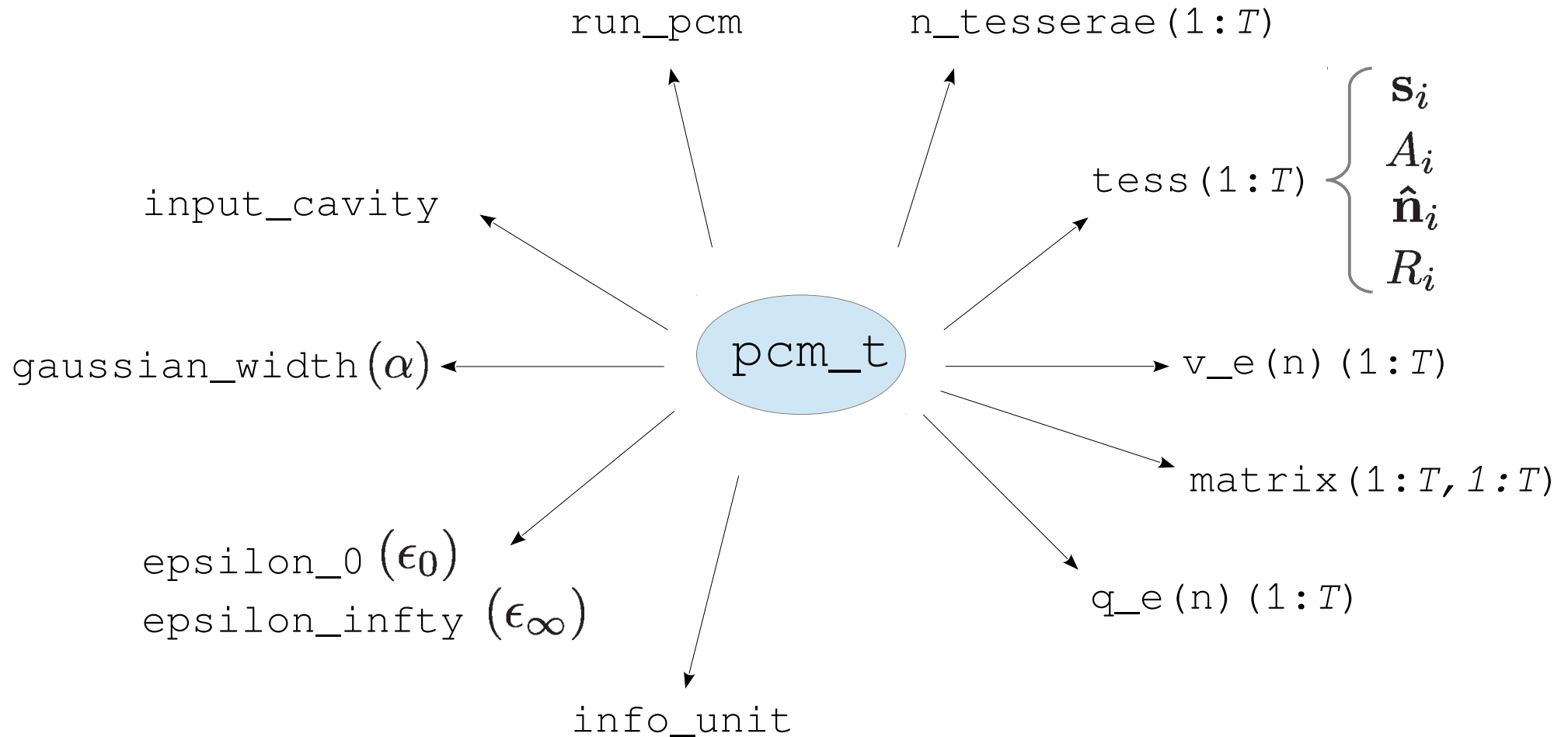
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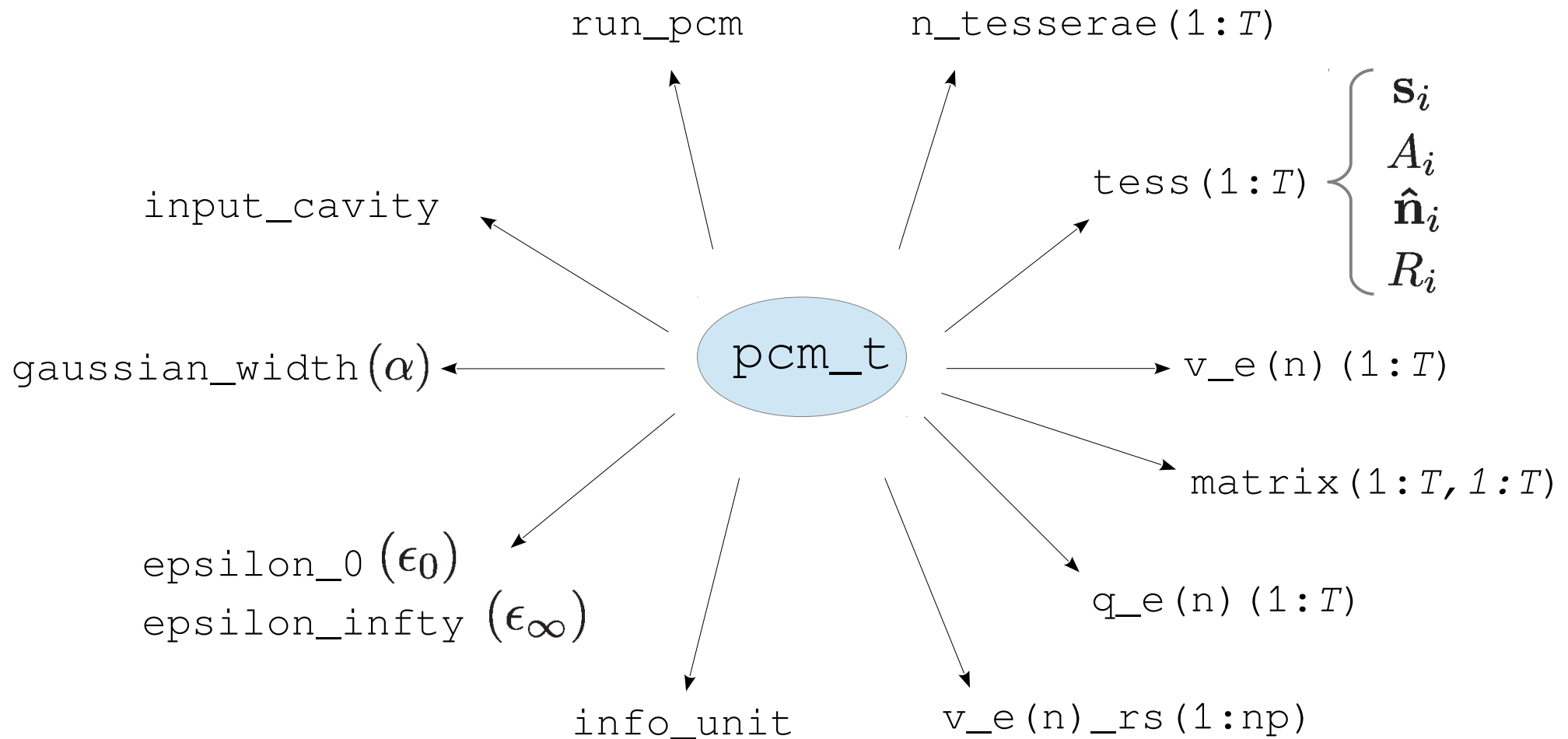
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main pcm subroutines

main program

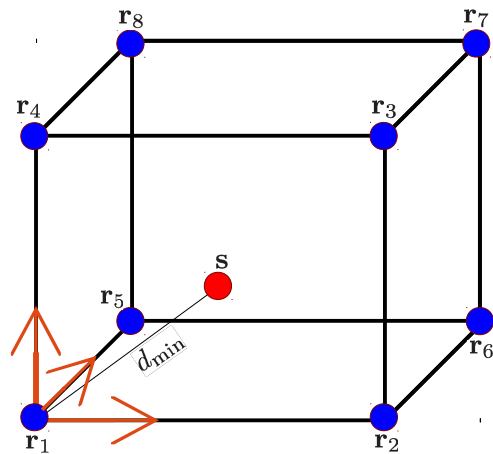
```
.  
call hamiltonian_init(...)  
    call pcm_init(...)
```

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

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```

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

hamiltonian_update

```
graph TD  
    A["call v_nuclei_cav(hm%pcm%v_n, ..)  
call pcm_charges (hm%pcm%q_n, ..)  
call pcm_pot_rs  (hm%pcm%v_n_rs, ..)"] -.-> C[hamiltonian_update]  
    B["call v_electrons_cav_li(vhartree, ..)  
call pcm_charges (hm%pcm%q_e, ..)  
call pcm_pot_rs  (hm%pcm%v_e_rs, ..)"] -.-> C
```

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(..)
```

end program

hamiltonian_update

```
graph TD; A[pcm_pot_rs] -.-> B[hamiltonian_update]; B -.-> C[pcm_pot_rs];
```

main pcm subroutines

main program

```
.  
call hamiltonian_init(..)  
    call pcm_init(..)  
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    call pcm_matrix( .., pcm%matrix )
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```
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```
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    call pcm_pot_rs   (hm%pcm%v_n_rs, ..)
```

```
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```

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

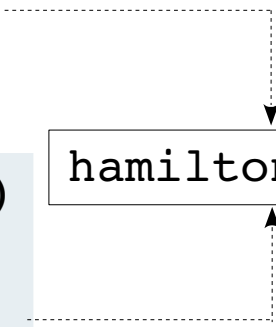
```
call energy_calc_total(..)
```

```
    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.

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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).

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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.

Acknowledgements

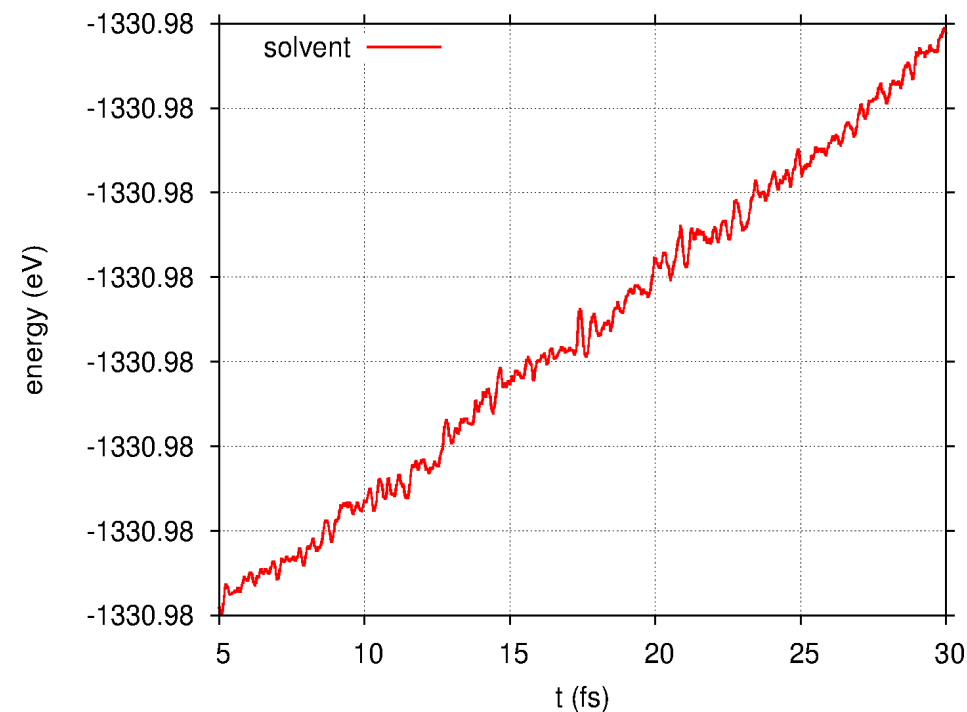
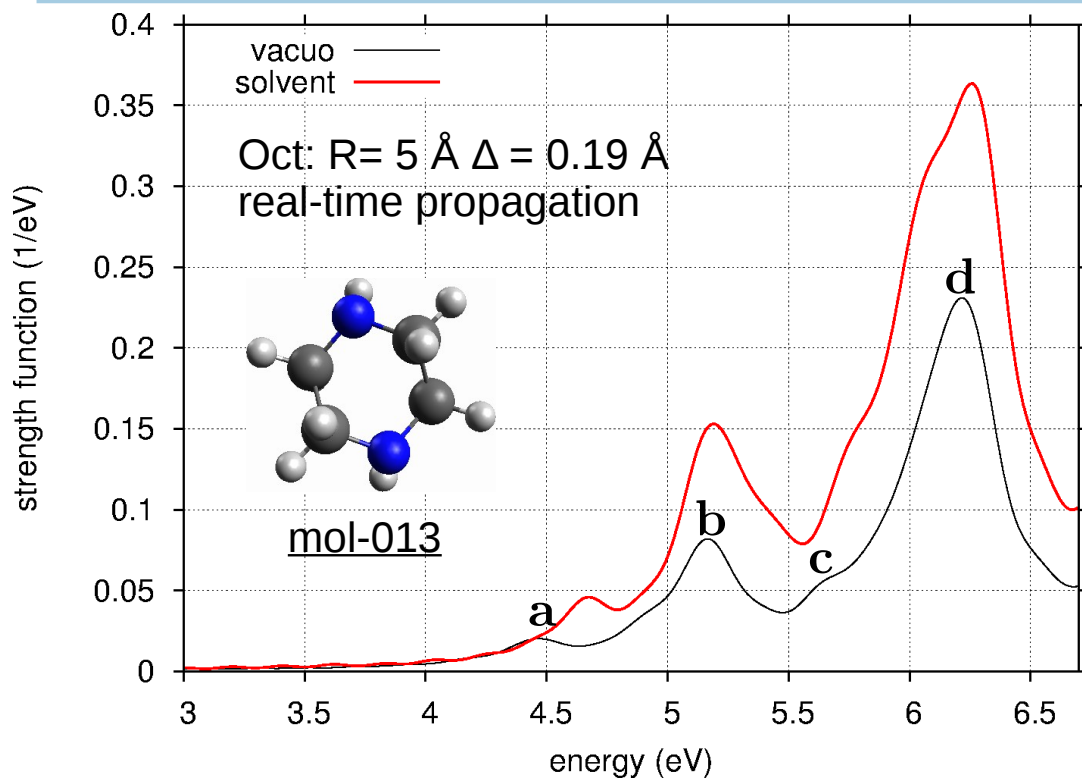


- HPC-ISCRA projects OCT_PCM & DEMOOPT.



- FP7 *CRONOS* grant – 280879.
- FP7 *HY-SUNLIGHT* grant - 252906.

Absorption spectra



solvatochromic shifts (eV)

peak	Octopus	Gamess
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b	0.03	0.05
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