

# Implicit Solvation Models in Q-Chem

(for Ground and Excited States)

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Virtual Winter School on Computational Chemistry  
9 February, 2023

## 0 Philosophy

## 1 Dielectric Boundaries

- Continuum Electrostatics
- Cavity Surface
- Models: PCM vs. SMx

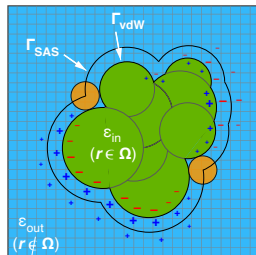
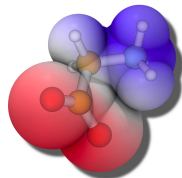
## 2 Solvation Energies

- Nonelectrostatic Terms
- Models: SMx vs. CMIRS

## 3 Nonequilibrium Methods

- $\epsilon_0$  vs.  $\epsilon_\infty$
- Excited States

## 4 Acknowledgements



*Quantum chemistry is not a black box and implicit-solvent models even less so*

- Set your expectations low and you might not be disappointed.
- Best viewed as dielectric boundary conditions.

Model	Cavity		Non-Electrostatic Terms?	Basis Sets Supported
	Construction	Discretization		
Kirkwood-Onsager	spherical	point charges	no	all
Langevin Dipoles	atomic spheres (user-definable)	dipoles in 3-d space	no	all
Poisson Equation Solver	atomic spheres (user-definable)	grid in 3-d space	no	all
C-PCM	atomic spheres (user-definable)	point charges or smooth Gaussians	user-specified	all
SS(V)PE/IEF-PCM	atomic spheres (user-definable)	point charges or smooth Gaussians	user-specified	all
COSMO	predefined atomic spheres	point charges	none	all
Isodensity SS(V)PE	isodensity contour	point charges	none	all
CMIRS	isodensity contour	point charges	automatic	all
SM8	predefined atomic spheres	N/A <sup>a</sup>	automatic	6-31G* 6-31+G* 6-31+G**
SM12	predefined atomic spheres	N/A <sup>a</sup>	automatic	all
SMD	predefined atomic spheres	point charges	automatic	all

<sup>a</sup>Generalized Born electrostatic model; does not require cavity construction.

Implicit solvation models available in Q-Chem

*Quantum chemistry is not a black box and implicit-solvent models even less so*

- Set your expectations low and you might not be disappointed.
- Best viewed as dielectric boundary conditions.
- Don't expect to push one button and obtain a fully satisfactory description.
- There are a lot of models and they are not the same. Read the literature.\*

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Implicit solvation models available in Q-Chem

\* "Dielectric continuum methods for quantum chemistry" [*WIREs Comput. Mol. Sci.* e1519 (2021)]

# Dielectric Boundary Conditions

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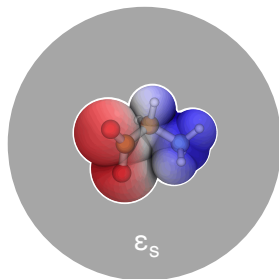
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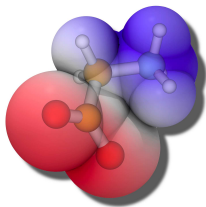
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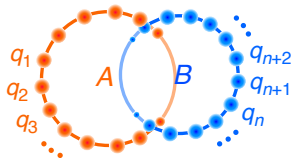
$$\epsilon(\mathbf{r}) = \begin{cases} 1, & \mathbf{r} \in \Omega \\ \epsilon_s, & \mathbf{r} \notin \Omega \end{cases}$$

"Dielectric continuum methods for quantum chemistry" [*WIREs Comput. Mol. Sci.* e1519 (2021)]

# Continuum Electrostatics Problem



Molecular electrostatic potential ( $\mathbf{v}$ ) evaluated on the cavity surface



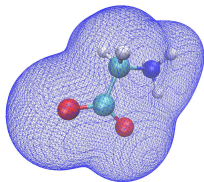
$$\mathbf{K}_\epsilon \mathbf{q} = \mathbf{Y}_\epsilon \mathbf{v}$$

- Solution of the electrostatics problem defines *self-consistent reaction field* (SCRF) theory.
- *Polarizable continuum models* (PCMs) are a widely-used solution.

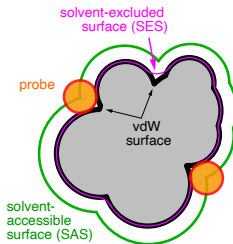
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Lange & Herbert, "A smooth, nonsingular, and faithful discretization scheme..." [*J. Chem. Phys.* **133**, 244111 (2010)]

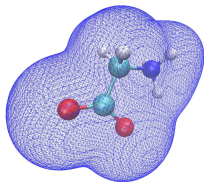
# Solute Cavity Surface



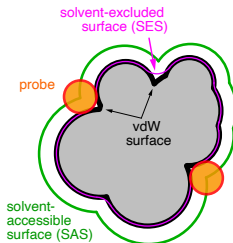
**Isocontour of the electron density**  
( $\rho_0 = 0.001$  a.u.)



**Cavity constructions based on atomic spheres**



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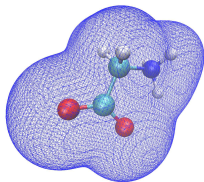


**Cavity constructions based on atomic spheres**

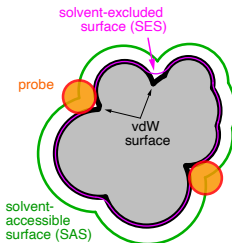
■ **vdW surface:** Union of spheres with radii  $R_A = \alpha R_{A,\text{vdW}}$ .

- ▶ Atomic radii  $\{R_{A,\text{vdW}}\}$  are parameters
- ▶ Typically,  $\alpha = 1.1\text{--}1.4$





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- ▶ Atomic radii  $\{R_{A,\text{vdW}}\}$  are parameters
- ▶ Typically,  $\alpha = 1.1\text{--}1.4$

■ **SAS:** Augmented atomic radii,  $R_A = R_{A,\text{vdW}} + R_{\text{probe}}$

- ▶  $R_{\text{probe}} = 1.4$  Å for water (from the oxygen–oxygen RDF)

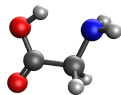
# Cavity Construction Matters!

$$R_A = \alpha R_{A,\text{vdw}} + R_{\text{probe}}$$

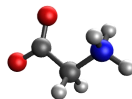
Cavity Type	$\alpha$	$R_{\text{probe}}$ (Å)	Electrostatic Energy (kcal/mol) <sup>a</sup>	
			amino acid	zwitterion
vdW	1.0	0.0	-26.1	-68.2
vdW	1.1	0.0	-20.2	-56.0
<b>vdW</b>	<b>1.2</b>	<b>0.0</b>	<b>-16.1</b>	<b>-46.8</b>
vdW	1.3	0.0	-12.9	-39.0
vdW	1.4	0.0	-10.6	-32.6
SAS	1.0	0.2	-18.0	-51.4
SAS	1.0	0.4	-13.1	-39.8
SAS	1.0	1.4	-4.3	-13.9
<b>isodensity<sup>b</sup></b>			<b>-16.4</b>	<b>-48.1</b>

<sup>a</sup>SS(V)PE @ B3LYP/6-31+G\*

<sup>b</sup>isovalue = 0.001 a.u.



**amino acid**



**zwitterion**

solute	solvent	Electrostatic Energy (kcal/mol)			
		exact <sup>a</sup>	SS(V)PE <sup>b</sup>	C-PCM <sup>c</sup>	
				$\zeta = 0$	$\zeta = 1/2$
H <sub>2</sub> O	toluene	−3.9	−3.9	−4.8	−3.9
CH <sub>3</sub> CONH <sub>2</sub>	toluene	−5.3	−5.0	−5.9	−4.8
NO <sup>+</sup>	toluene	−52.2	−52.2	−52.5	−43.3
CN <sup>−</sup>	toluene	−39.4	−39.4	−39.4	−32.5
H <sub>2</sub> O	water	−8.6	−8.6	−8.6	−8.6
CH <sub>3</sub> CONH <sub>2</sub>	water	−10.9	−10.8	−10.9	−10.8
NO <sup>+</sup>	water	−89.5	−89.5	−89.5	−88.9
CN <sup>−</sup>	water	−67.4	−67.3	−67.3	−66.9

<sup>a</sup>Poisson's equation including outlying charge

<sup>b</sup>Similar to IEF-PCM [*Chem. Phys. Lett.* **509**, 77 (2011)]

<sup>c</sup> $\tilde{f}_\varepsilon(\zeta) = (\varepsilon - 1)/(\varepsilon + \zeta)$

- SS(V)PE / IEF-PCM is formally more correct in low-dielectric solvents but the practical difference is nil
- C-PCM is simpler and has more features available

**Data:** Chipman, "Comparison of solvent reaction field representations" [*Theor. Chem. Acc.* **107**, 80 (2002)]

# Interpreting the Q-Chem Output

- For an SCF calculation with `SOLVENT_METHOD = PCM` in `$rem`:

```
      8  -284.4696326693      1.37e-05
      9  -284.4696330277      4.72e-06  Convergence criterion met
-----
SCF time:   CPU 5.79s  wall 6.00s

***** Final PCM Free Energy Summary *****
G_electrostatic =   -0.07680684 hartree =   -48.19701867 kcal/mol
G_cavitation    =    0.00000000 hartree =    0.00000000 kcal/mol
G_dispersion    =    0.00000000 hartree =    0.00000000 kcal/mol
G_repulsion     =    0.00000000 hartree =    0.00000000 kcal/mol
-----
Non-electrostatic Free Energy =    0.00000000 hartree =    0.00000000 kcal/mol
Total                =   -0.07680684 hartree =   -48.19701867 kcal/mol
-----
SCF Energy (H0 + V/2)          = -284.46963303
Solute Internal Energy (H0)     = -284.39282619
Total Free Energy (H0 + V/2 + non-elec) = -284.46963303 hartree
                                = -178507.38893677 kcal/mol
*****
```

- The **total SCF energy** minimizes a functional

$$G_0[\Psi] = \underbrace{\langle \Psi | \hat{\mathcal{H}}_{\text{vac}} | \Psi \rangle}_{\mathcal{H}_0[\Psi], \text{ "internal energy" }} + \underbrace{\frac{1}{2} \langle \Psi | \hat{\mathcal{R}}_0 | \Psi \rangle}_{G_{\text{elst}} \equiv V/2}$$

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- ▶ “PCM” includes only the electrostatic contribution to the free energy
- ▶  $G_{\text{nonelect}}$  must be parameterized separately

# Solvation Energies

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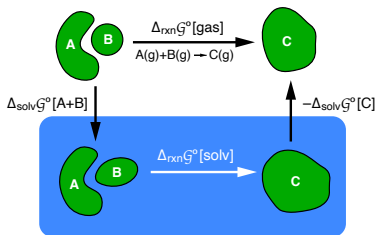
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“Dielectric continuum methods for quantum chemistry” [*WIREs Comput. Mol. Sci.* e1519 (2021)]

# There Is More to Solvation Than Electrostatics!

Error statistics for  $\Delta_{\text{solv}}\mathcal{G}^\circ$ , versus experiment

Data Set	$N_{\text{data}}$	mean unsigned error (kcal/mol)		
		C-PCM only <sup>a</sup>	SMD ( $\mathcal{G}_{\text{elst}} + \mathcal{G}_{\text{nonelst}}$ )	
			(C-PCM) <sup>b</sup>	(IEF-PCM) <sup>c</sup>
aq. neutrals	274	1.6	0.9	0.9
aq. cations	52	7.3	2.9	2.8
aq. anions	60	8.1	3.9	3.9
nonaq. neutrals	666	2.8	0.7	0.7
nonaq. cations	72	12.0	5.4	5.4
nonaq. anions	148	6.6	4.1	4.1
all neutrals	940	2.5	0.8	0.8
all ions	332	8.1	4.1	4.1

<sup>a</sup>Electrostatics-only model

<sup>b</sup> $\mathcal{G}_{\text{elst}}(\text{C-PCM}) + \mathcal{G}_{\text{nonelst}}(\text{SMD})$

<sup>c</sup> $\mathcal{G}_{\text{elst}}(\text{IEF-PCM}) + \mathcal{G}_{\text{nonelst}}(\text{SMD})$

**Data set:** Kelly, Cramer, & Truhlar [*J. Chem. Theory Comput.* **1**, 1133 (2005)]

**Error statistics:** Marenich, Cramer, & Truhlar [*J. Phys. Chem. B* **113**, 6378 (2009)]

## Error statistics for hydration energies, vs. experiment

Data Set	$N_{\text{data}}$	mean unsigned error (kcal/mol)			
		SM8 <sup>a</sup> (GB)	SM12 <sup>a</sup> (GB)	SMD <sup>a</sup> (IEF-PCM)	CMIRS <sup>b</sup> [SS(V)PE]
neutrals	274	0.6	1.3	0.8	0.8
cations	52	2.7	3.5	3.4	1.8
anions	60	4.0	3.8	6.3	2.8
all ions	112	3.4	3.7	4.9	2.4

<sup>a</sup>B3LYP/6-31G\*, using an explicit H<sub>2</sub>O for 31 of the ions<sup>b</sup>B3LYP/6-31+G\*, no explicit water

- Minnesota solvation database
- Experimental uncertainties are  $\pm 0.2$  kcal/mol for neutrals and  $\pm 3$  kcal/mol for ions

---

**SM8:** Marenich, Olson, Kelly, Cramer, & Truhlar [*J. Chem. Theory Comput.* **3**, 2011 (2007)]

**SM12:** Marenich, Cramer, & Truhlar [*J. Chem. Theory Comput.* **9**, 609 (2013)]

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# Vertical Excitation or Ionization

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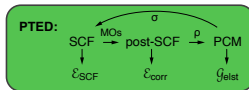
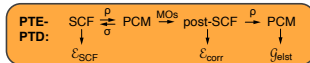
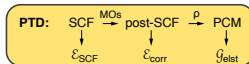
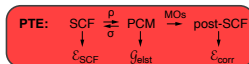
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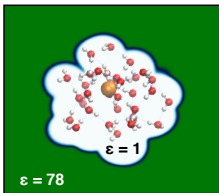
$$\left(\hat{\mathcal{H}}_{\text{vac}} + \hat{\mathcal{R}}_0^s + \hat{\mathcal{R}}_k^f\right) |\Psi_k\rangle = \mathcal{E}_k |\Psi_k\rangle$$



- $\epsilon_0$  = static dielectric constant (orientational + electronic polarization)
- $\epsilon_\infty = n_{\text{refr}}^2$  = “optical” dielectric constant (electronic polarization only)
- Use to partition polarization into two components:
  - ▶ **fast** (remains equilibrated)
  - ▶ **slow** (frozen upon vertical excitation)

<b>solvent</b>	$\epsilon_0$	$\epsilon_\infty$	<b>solvent</b>	$\epsilon_0$	$\epsilon_\infty$
<b>n-hexane</b>	<b>1.9</b>	<b>1.37</b>	ethanol	25.3	1.36
cyclohexane	2.0	1.43	ethylene glycol	42.8	1.43
benzene	2.3	1.50	methanol	33.0	1.33
toluene	2.4	1.50	nitrobenzene	35.6	1.55
diethyl ether	4.3	1.83	acetonitrile	36.6	1.34
chloroform	4.8	1.44	dimethyl acetamide	40.2	1.44
dichloromethane	8.9	1.42	dimethyl sulfoxide	47.2	1.48
2-propanol	20.2	1.38	<b>water</b>	<b>80.2</b>	<b>1.78</b>
acetone	21.1	1.36	formamide	111.8	1.45

## Example: Vertical Ionization Energies (VIEs)



Aqueous VIEs (in eV)

Solute	Expt.	MP2 Calculations				vacuum
		Noneq. PCM		Equil. PCM		
		spherical	SAS	spherical	SAS	
Li <sup>+</sup>	60.4	61.8	61.6	61.3	61.0	64.2
Na <sup>+</sup>	35.4	36.5	36.3	36.0	35.8	38.9
H <sub>2</sub> O	11.7	11.6	11.6	11.1	10.9	13.8
e <sup>−</sup>	3.7	3.2	3.2	2.6	2.6	1.8
F <sup>−</sup>	11.6	11.4	11.5	10.8	10.9	10.0
Cl <sup>−</sup>	9.6	9.4	9.4	8.8	8.8	7.9

Coons & Herbert, "Quantum chemistry in arbitrary dielectric environments..." [*J. Chem. Phys.* **148**, 222834 (2018)]

Herbert, "Dielectric continuum methods for quantum chemistry" [*WIREs Comput. Mol. Sci.* e1519 (2021)]

## ■ Input

```

$rem
exchange          cam-b3lyp
basis             6-31+G*
cis_n_roots       5
cis_triplets      false
solvent_method    pcm
cis_relaxed_density true
$end

$pcm
NonEquilibrium
StateSpecific      perturb
$end

$solvent
Dielectric         35.7 ! MeCN
OpticalDielectric  1.81
$end

```

cost similar to gradient,  
but unrelaxed is not the  
true ex. state density

without this, you are  
only getting 0th-order  
solvation

## Input

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exchange          cam-b3lyp
basis             6-31+G*
cis_n_roots       5
cis_triplets      false
solvent_method    pcm
cis_relaxed_density true
$end

$pcm
NonEquilibrium
StateSpecific      perturb
$end

$solvent
Dielectric         35.7 ! MeCN
OpticalDielectric  1.81
$end
```

cost similar to gradient,  
but unrelaxed is not the  
true ex. state density

without this, you are  
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## Output

```
*****
*      Excited-state properties with relaxed density      *
*****

----- SUMMARY OF LR-PCM AND SS-PCM -----

Relaxed singlet excited state 1:
Total 1st-order corrected excitation energy = 3.987746 eV
```

$$\hbar\omega_{0k}^{\text{neq}} = \Delta\mathcal{E}_k^{(0)} + \text{corrections}$$

```
Relaxed singlet excited state 4:
Total 1st-order corrected excitation energy = 4.777083 eV
1st-order SS-PCM corrected excitation energy = 4.879918 eV
1st-order LR-PCM corrected excitation energy = 4.854926 eV
0th-order excitation energy = 4.957760 eV
SS-PCM correction = -0.077842 eV
LR-PCM correction = -0.102834 eV
Charge-separation penalty = 0.143565 eV
Dipole Mom. (Debye): -0.0002 X 0.0002 Y -11.5623 Z
Strength |mu - mu_0| (Debye): 5.0806
```

- 0th-order excitation energy is  $\Delta\mathcal{E}_k^{(0)} = \mathcal{E}_k^{(0)} - \mathcal{E}_0$ .
- 1st-order corrections within the state-specific (SS) and linear-response (LR) formalisms are also provided.

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Herbert, "Dielectric continuum methods for quantum chemistry" [*WIREs Comput. Mol. Sci.* e1519 (2021)]

Mewes *et al.*, *J. Phys. Chem. A* **119**, 5446 (2015)



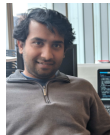
Adrian Lange  
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Zhi-Qiang You  
OSC



Marc Coons  
Dow Chemical

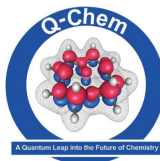


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Bushra Alam

- **Webinar:** <https://www.q-chem.com/webinars/51>
- **Reading:** *WIREs Comput. Mol. Sci.* e1519 (2021)
- **Further Discussion:** <https://talk.q-chem.com>



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