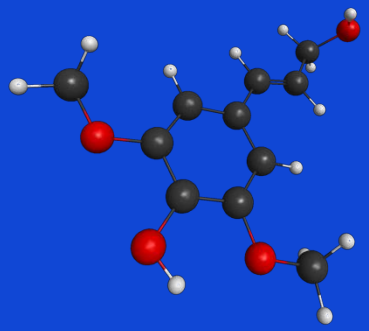
Towards efficient modeling of positronium in heterogeneous environments

Márcio T. do N. Varella

Institute of Physics

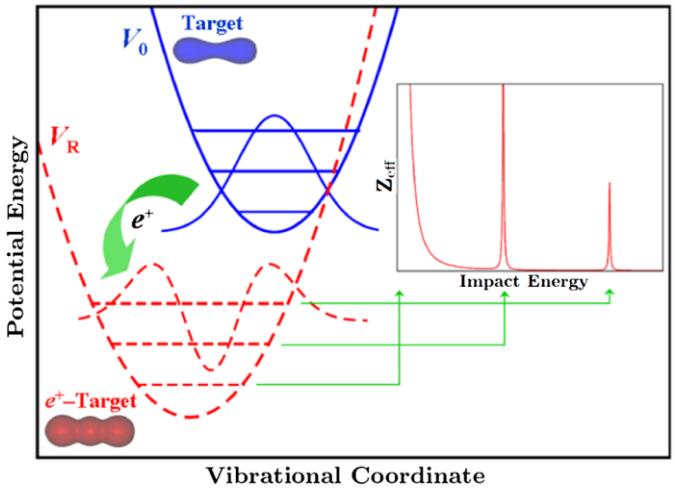
University of São Paulo



Molecular Physics

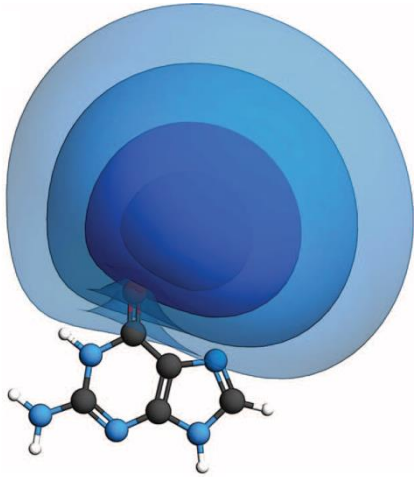
electrons positrons photons

http://fig.if.usp.br/~mvarella/

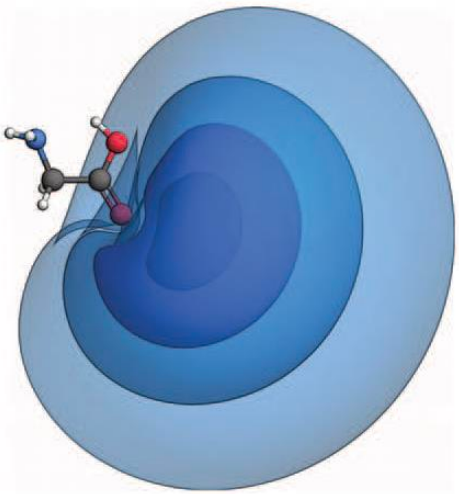


Phys. Rev. Lett. **107**, 103201 (2011)

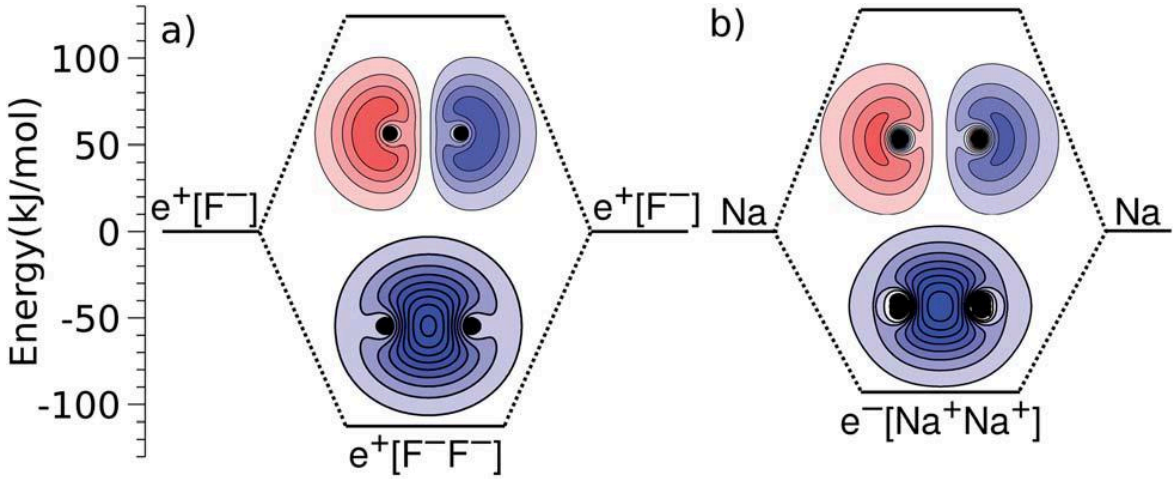
e^+– Uracil



e^+– Glycine



J. Chem. Phys. **141**, 114103 (2014)

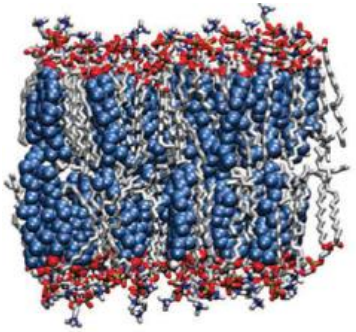


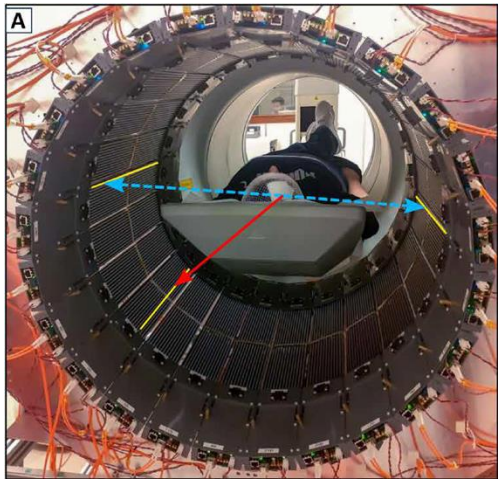
Chem. Sci. **11**, 44 (2020)

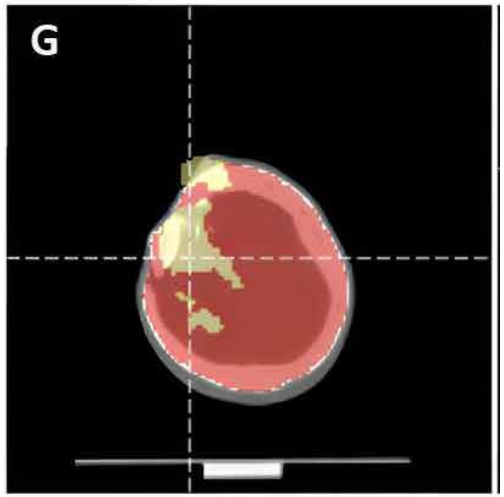
Prof. Andres Reyes
UNAL, Colombia

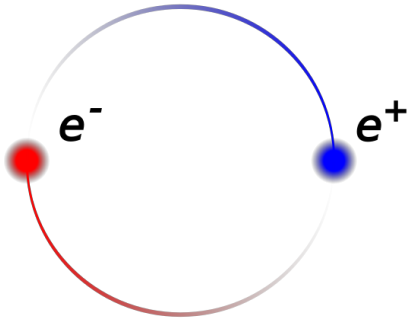
Positron annihilation lifetime spectroscopy (PALS): a probe for molecular organisation in self-assembled biomimetic systems

PCCP **17**, 17527 (2015)







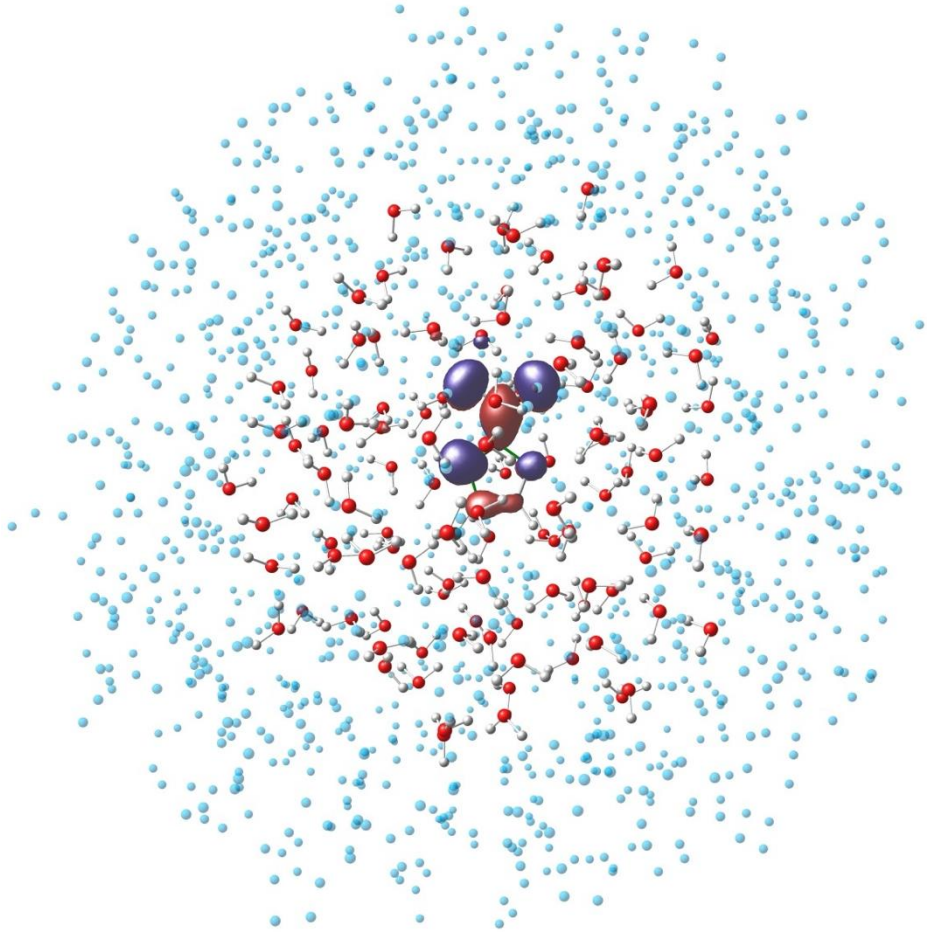


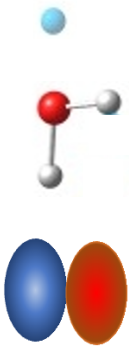
– Cancer diagnosis:
Physics Communications **3** 173 (2020)
Sci. Rep. **13** 7648 (2023)

– Improving PET with Ps imaging:
Reviews of Modern Physics **95** 021002 (2023)
Science Advances **10** eadp2840 (2024)

– Cancer treatment:
Sci. Rep. **11**, 2474 (2021)

Quantum Mechanics/Molecular Mechanics (QM/MM)





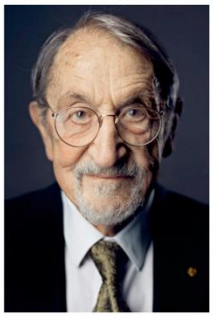
Solvent (MM)

Solvent (QM)

Solute (QM)

Sequential QM/MM:

1) Structure from MM
2) Properties from QM/MM



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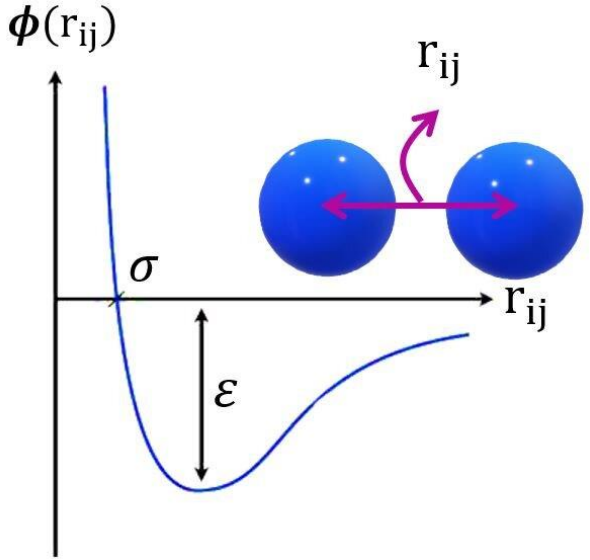
Arieh Warshel

Nobel Prize in Chemistry 2013

Quantum Mechanics/Molecular Mechanics (QM/MM)

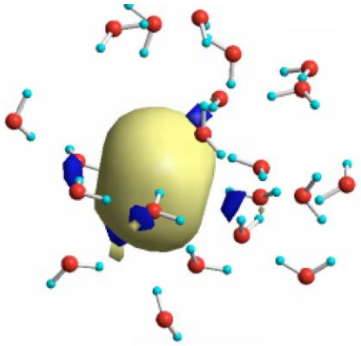


$$V(r_{ij}) = \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}} + \underbrace{4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]}_{\phi(r_{ij})}$$

$$\varepsilon = \sqrt{\varepsilon_i \varepsilon_j}$$

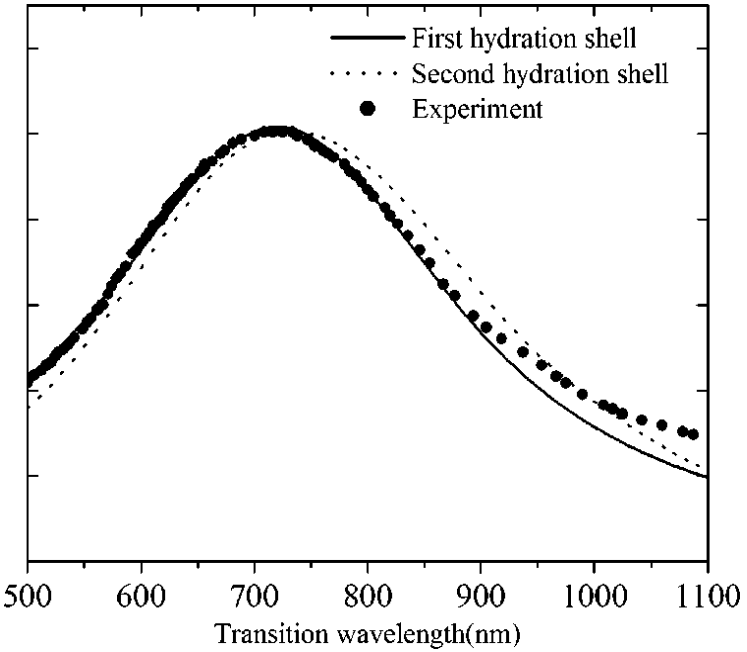
$$\sigma = \sqrt{\sigma_i \sigma_j}$$

Lennard-Jones Potential Energy

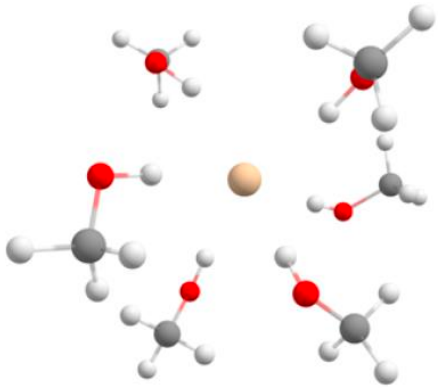


S-QM/MM: Solvated Electron

[Phys. Rev. B 210110 (2004)]



S-QM/MM [Adv. Quantum Chem. **28** 89 (1997)]



DICE
Monte Carlo
Molecular Simulation

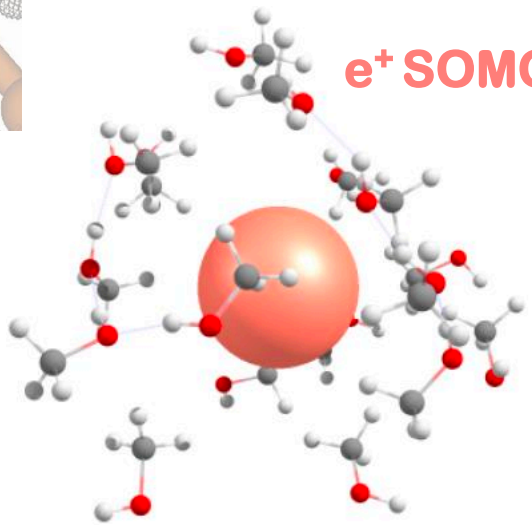
JCIM **60** 3472 (2020)

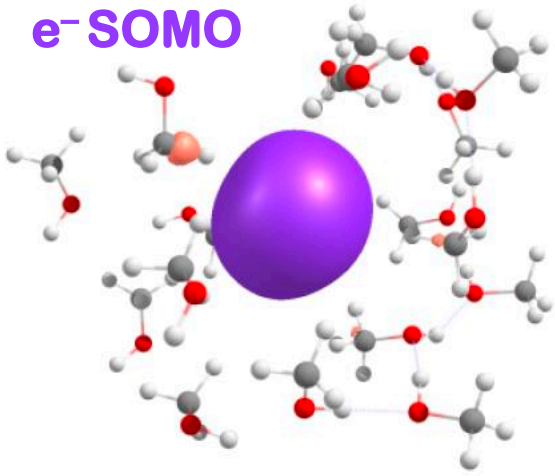
MM Step:
- Monte Carlo simulation
- Coulomb (point-charges) + Lennard-Jones FF

APMO [Int. J. Quantum Chem. **119** e25705 (2019)]

openLOWDIN
Quantum Chemistry Software Package

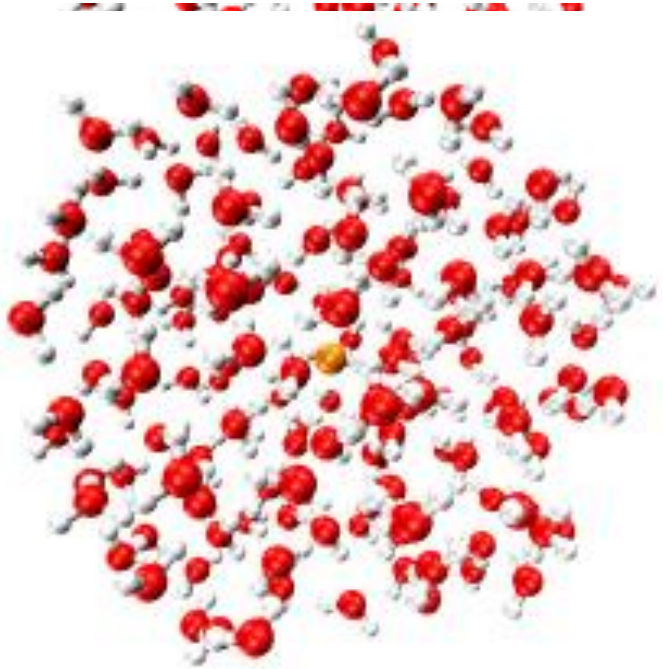
QM Step:
- Hartree-Fock, MP2, Propagators (P2, P3)



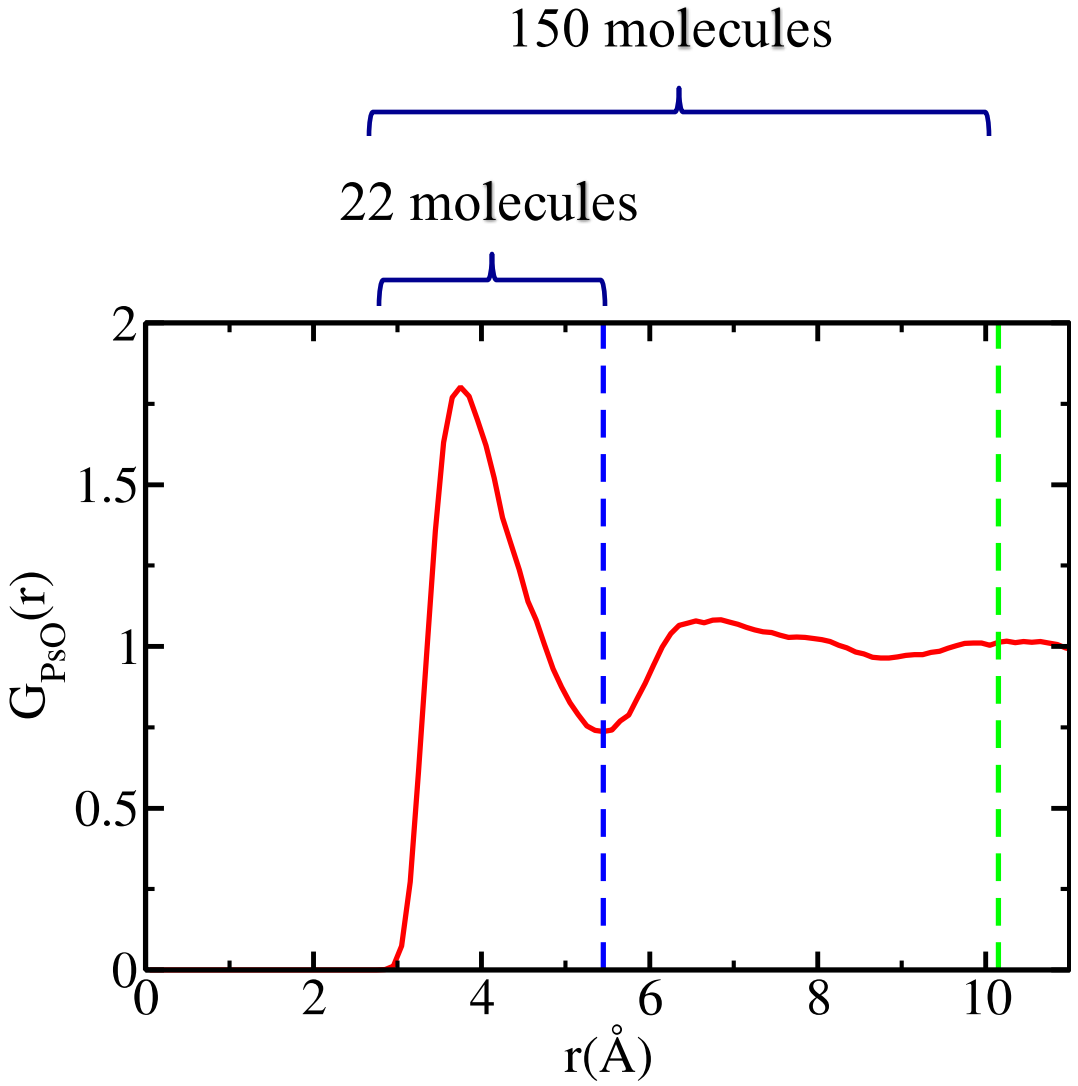


Ps-water QM/MM Model

Ps and 150 water molecules

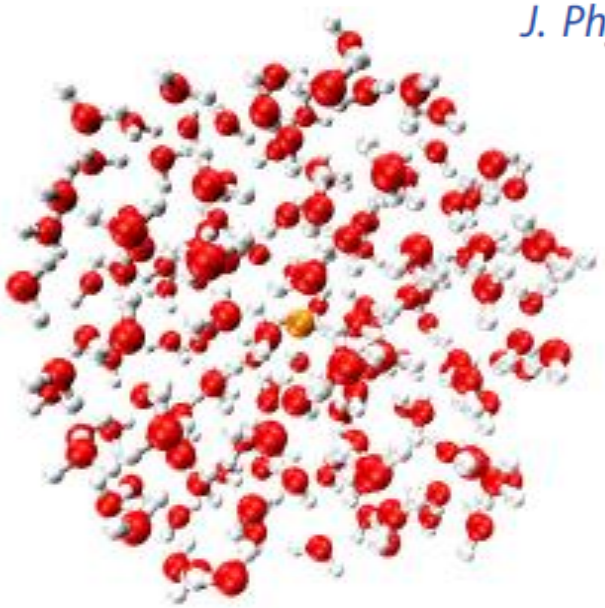


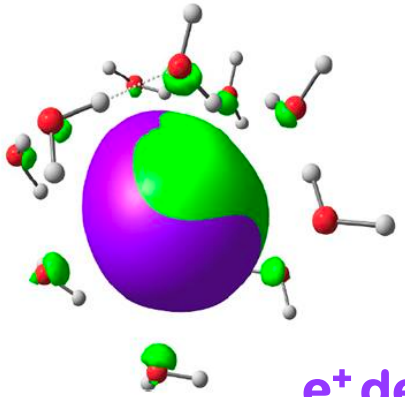
SPC/E (water)
NPT (1 atm, 298 K)



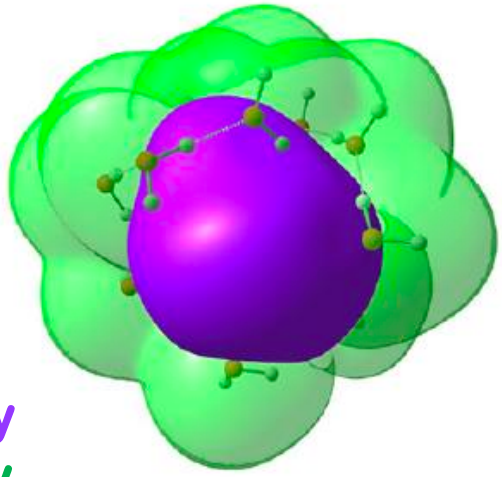
Multicomponent Quantum Mechanics/Molecular Mechanics Study of Hydrated Positronium

J. Phys. Chem. B 2022, 126, 2699–2714





e^+ density
e^- density



6-31G+(d,p)/aug-cc-pVTZ

		KT
e^- VDE	(eV)	4.53 ± 0.04
e^+ VDE	(eV)	5.21 ± 0.04
τ_{Ps}	(ns)	6.7 ± 0.1
τ_{po}	(ns)	7.3 ± 0.1
τ_{co}	(ns)	58.0 ± 0.6

$$\lambda = \pi r_0^2 c \left(S_N + \sum_{i=1}^{N_\alpha} S_i^\alpha + \sum_{j=1}^{N_\beta} S_j^\beta \right),$$

$$\tau = \lambda^{-1}$$

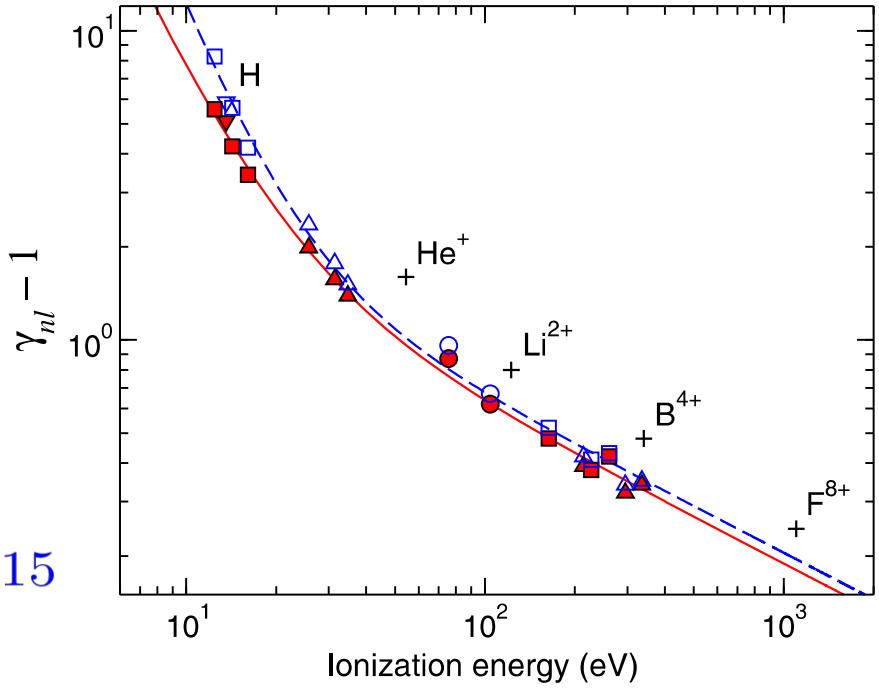
Annihilation Enhancement Factor

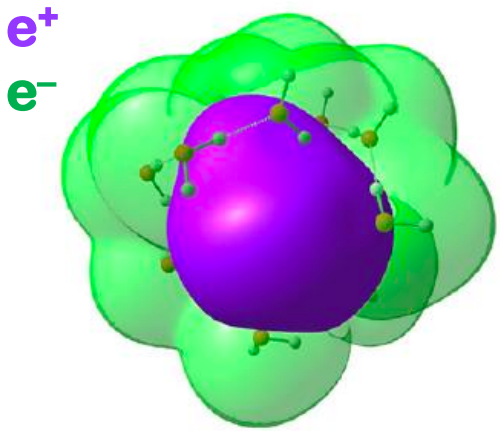
Phys. Rev. Lett. 114, 093201 (2015)

$$\Gamma = \gamma_{nl} \times \Gamma^0$$

$$\gamma_{nl} = 1 + \sqrt{A/I_{nl}} + (B/I_{nl})^{\beta}$$

$$A = 35.7\,\mathrm{eV}\ , \quad B = 22.7\,\mathrm{eV}\ , \quad \beta = 2.15$$





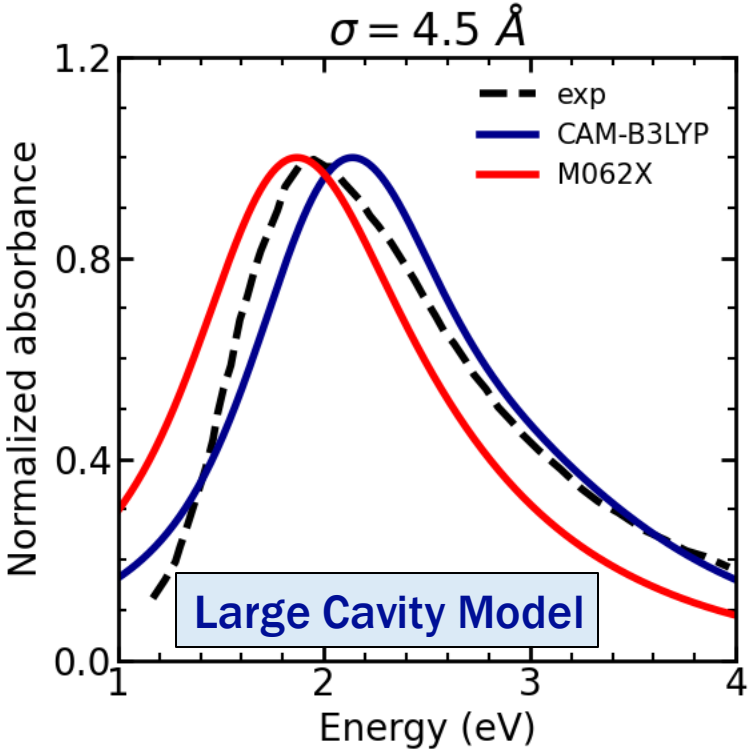
Hydrated Ps (no optimization):

$$\tau_{\mathrm{po}}^0 = (7.3 \pm 0.1)\,\mathrm{ns} \xrightarrow{\gamma_{nl}} \tau_{\mathrm{po}} = (2.27 \pm 0.03)\,\mathrm{ns}$$

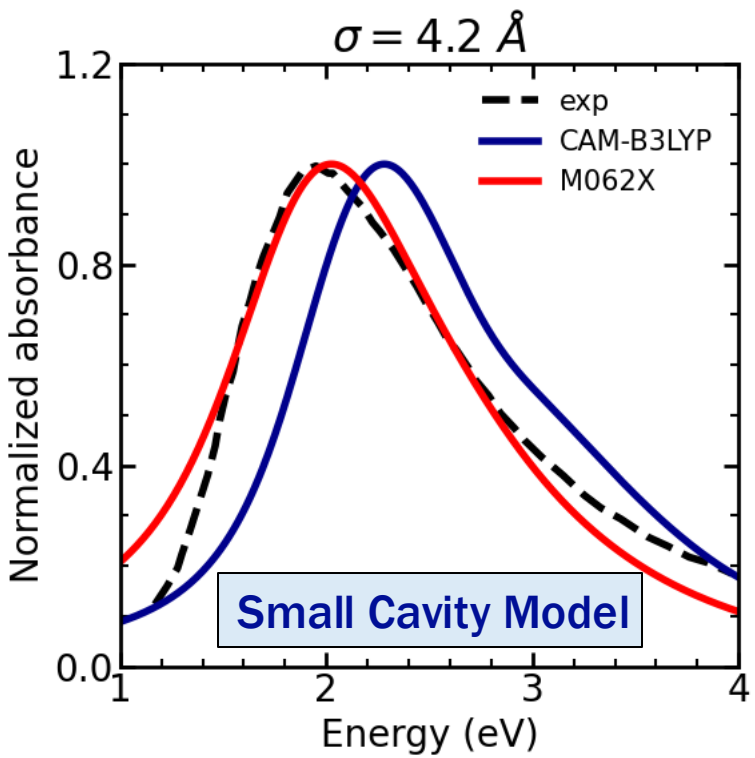
Experiment*: τ_{po} **= 1.85 ns (18%)**

*Chuev et al., Int. J. Quant. Chem. **88**, 634 (2002)

Electron in Methanol



[better overall agreement with CAM-B3LYP and M062X functionals]

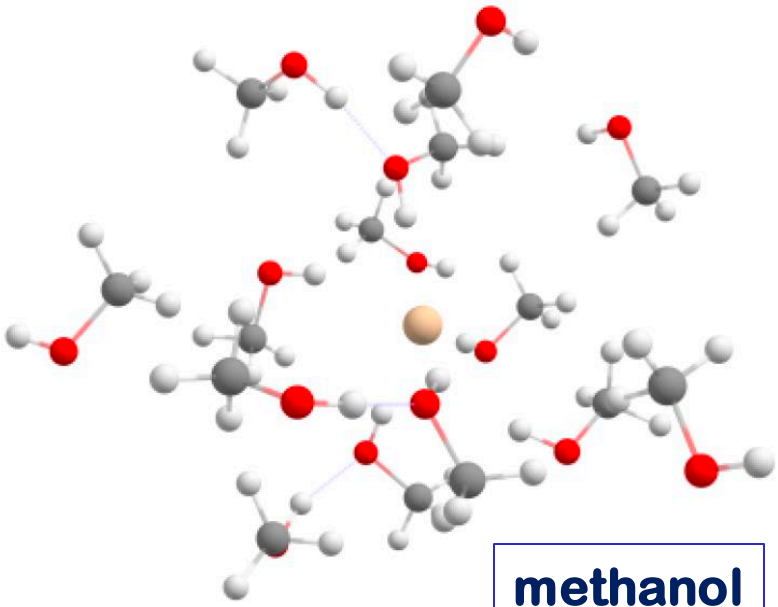


[better possible agreement with M062X functional]

Model: TDDFT/6-31G++(d,p)/6QM+200MM

Experiment: Jou & Freeman, J. Phys. Chem. **81**, 909 (1977)

Electron in Methanol



methanol

Model: DFT/M06-2X/6-31G++(d,p)/14QM+200MM

MetOH: Jorgensen, JCP **90** 1276 (1986)
NPT (1 atm, 298 K)

Vertical Binding Energy (VBE)

$$\mathrm{VBE} = (3.36 \pm 0.03)\,\mathrm{eV} \quad (\sigma = 4.2\,\text{Å})$$

"small cavity"

$$\mathrm{VBE} = (3.15 \pm 0.04)\,\mathrm{eV} \quad (\sigma = 4.5\,\text{Å})$$

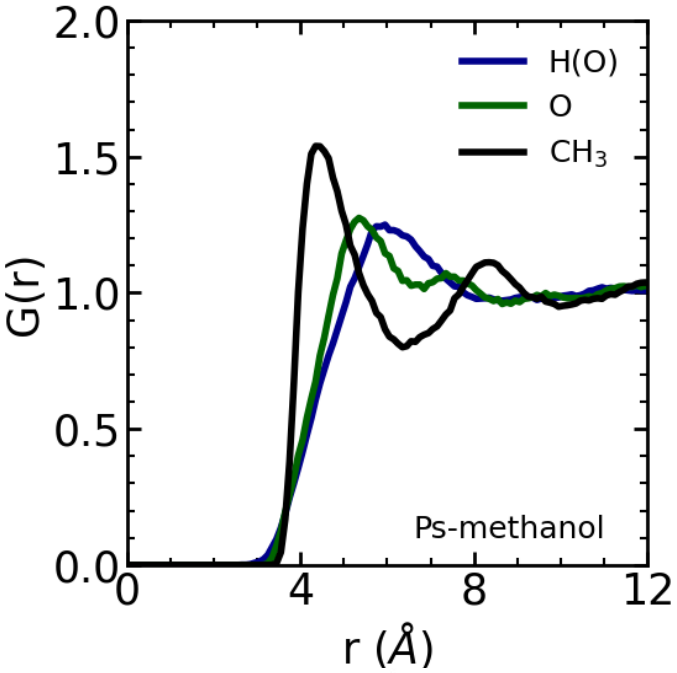
"large cavity"

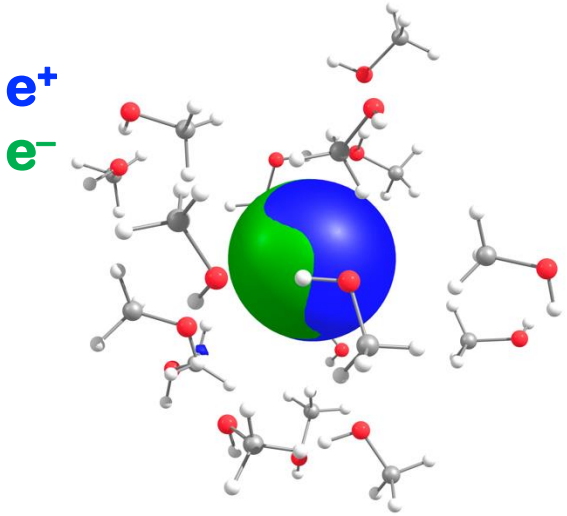
$$\text{Experiment}: 3.1\,\mathrm{eV}^{a} \text{ or } 3.4\,\mathrm{eV}^{b}$$

[a] Chem. Lett. **39** 668 (2010)

[b] Sience Adv. **5** 6896 (2019)

Ps in Methanol





APMO/HF/aug-cc-pVTZ/6-31++G**

Large Cavity Model

N_{QM}	τ^0_{po}(ns)	τ_{po}(ns)
10	(22.1 ± 0.91)	(4.90 ± 0.20)
16	(21.6 ± 0.77)	(4.72 ± 0.17)

Experiment*: τ_{po} = 3.58 ns (24% to 27%)

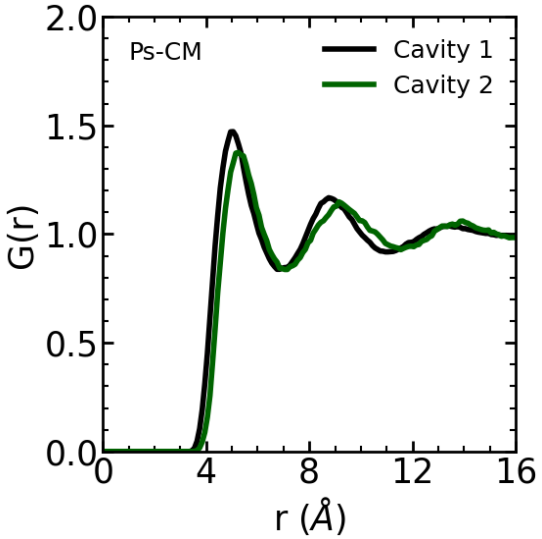
Small Cavity Model

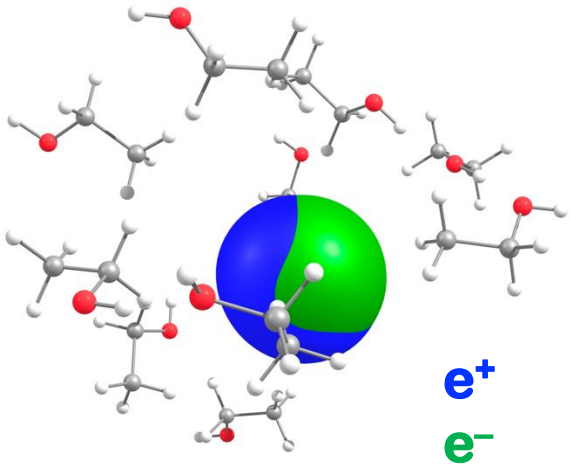
N_{QM}	τ^0_{po}(ns)	τ_{po}(ns)
10	(19.8 ± 0.97)	(4.32 ± 0.31)
16	(16.4 ± 0.93)	(3.60 ± 0.12)

Experiment*: τ_{po} = 3.58 ns (1% to 17%)

***Experiment: Mogensen & Jacobsen, Chem. Phys. 73, 223 (1982)**

Ps in Ethanol





Model: HF/aug-cc-pVTZ/6-31++G**
10QM+200MM

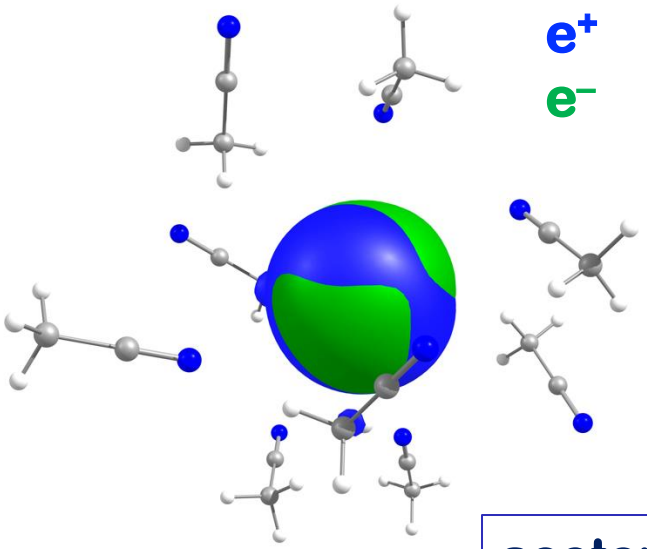
work in progress

cavity	τ^0_{po}(ns)	τ_{po}(ns)
small	(16.1 ± 0.57)	(3.59 ± 0.13)
large	(21.6 ± 0.93)	(4.81 ± 0.22)

[a]Experiment: τ_{po} = 3.50 ns (2% to 27%)
[b]Experiment: τ_{po} = 3.58 ns (0.3% to 25%)

[a]Experiment: Mogensen & Jacobsen, Chem. Phys. **73**, 223 (1982)
[b]Experiment: Castellaz et al., J. Nuc. Rad. Sci. **3**, R1 (2002)

Ps in Acetonitrile



acetonitrile

– Solvated electron ✓

– Classical model ✓

work in progress

Jorgensen, JCP **63** 547 (1988)
NPT (1 atm, 298 K)

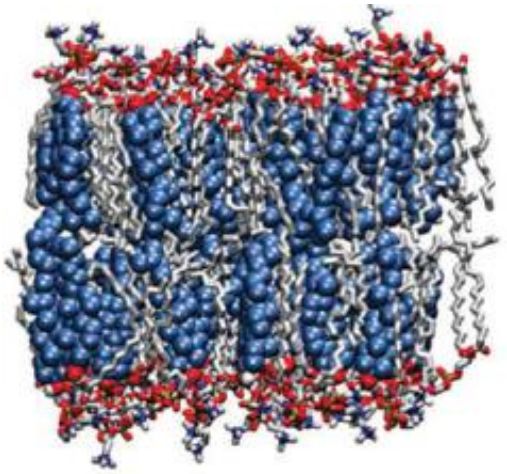
τ^0_{po}(ns)	τ_{po}(ns)
(13.9 ± 0.57)	(3.19 ± 0.09)

Model: HF/aug-cc-pVTZ/6-31++G**
12QM+200MM

[a]**Experiment:** τ_{po} **= 3.30 ns (3%)**

Conclusions & Outlook

- S-QM/MM approach to solvated Ps is promising
- Reoptimize Ps Lennard-Jones parameters (H, C, N, O)
- Universal parametrization? Chemical groups?
- Reoptimize enhancement factors
- Molecular dynamics with Ps
- Fully classical (?)



Support

Students

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Leonardo B. Martins (PhD)


FAPESP

CNPq

Conselho Nacional de Desenvolvimento Científico e Tecnológico

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