Positronic Molecules

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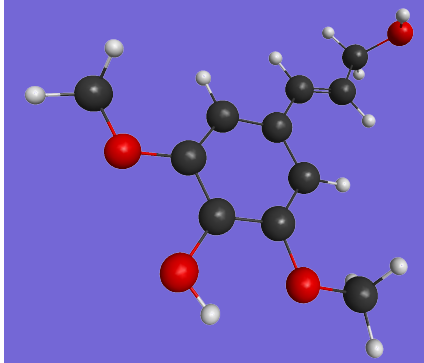
October 17th 2019



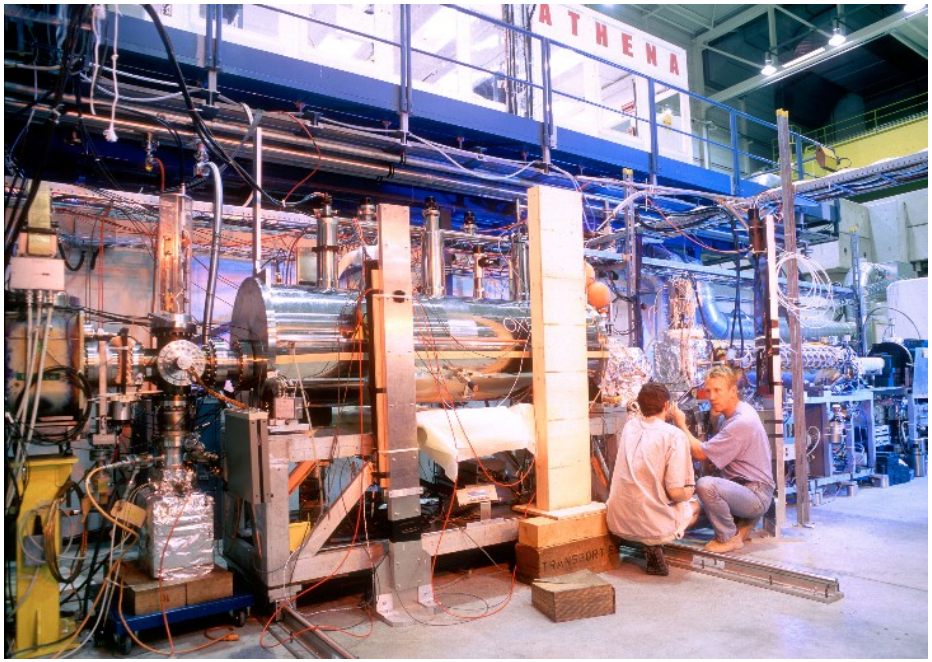
Molecular Physics and Modelling Group

Interactions with electrons, positrons and photons

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

Positron Physics: Motivation

- Astrophysics
- Anti-H, anti-H_2, cold anti-matter, QED Tests (CPT, Anti-Gravity)
  http://athena.web.cern.ch/athena/
  http://hussle.harvard.edu/~atrap/
  http://www.if.ufrj.br/~lenz/lenz.html
  http://www.positron.edu.au
- Ps_2[a], Ps spectroscopy[b], Ps scattering[c], Ps^-[d], annihilation control[e]



[a]Nature **449**, 195 (2007)

[b]PRL **108** 043401 (2012); PRL **117** 073302 (2016)

[c]Science **330**, 789 (2010); PRL **115** 223201 (2015)

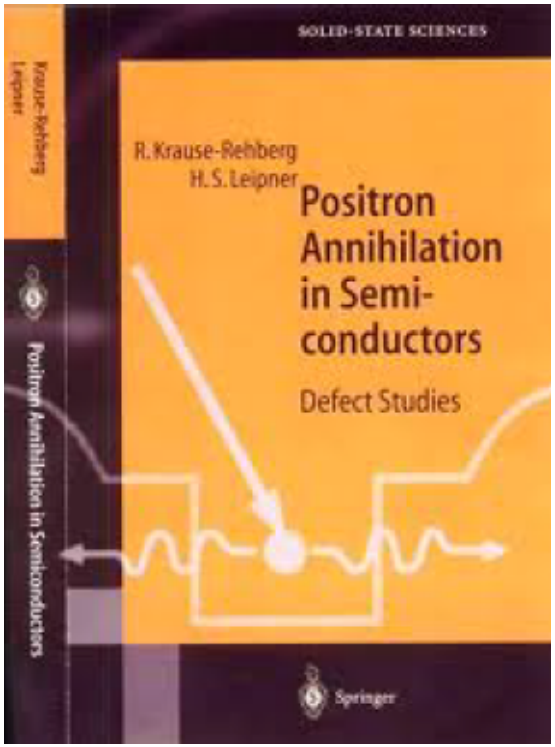
[d]Nat. Commun. **7**, 11060 (2016)

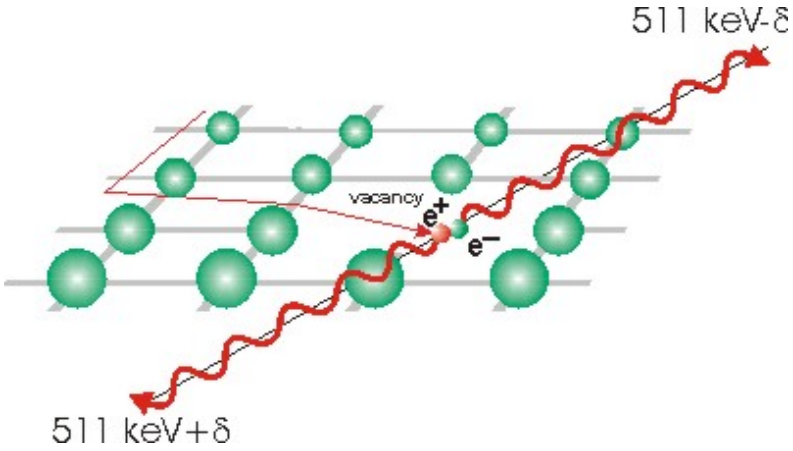
[e]PRL **115**, 183401 (2015)

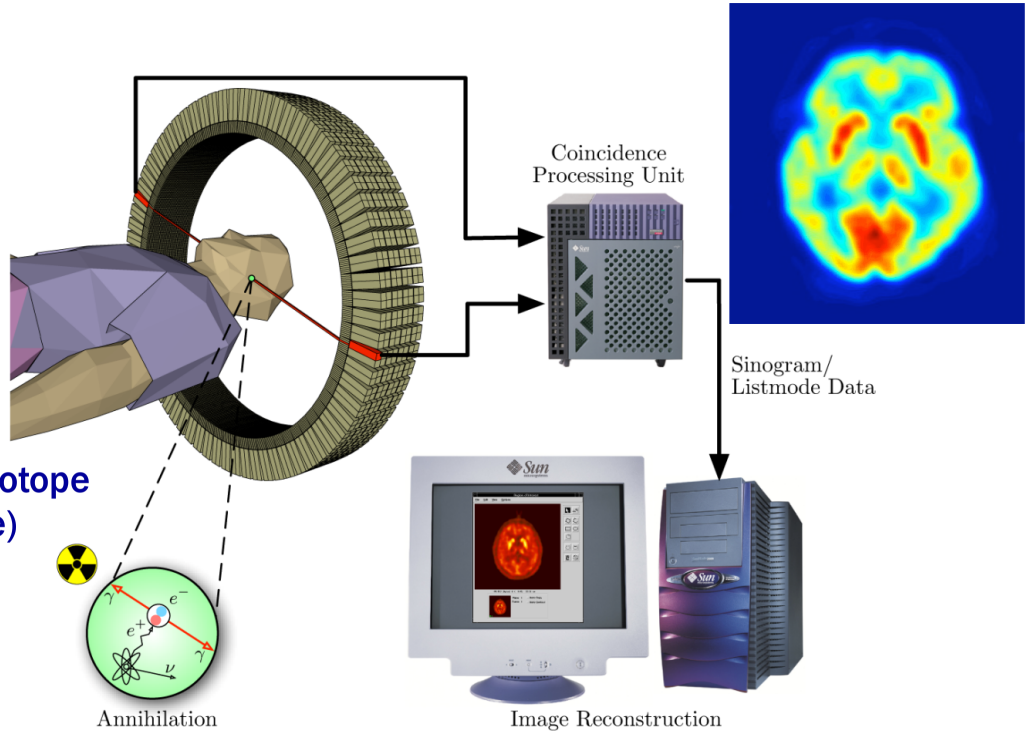
ATOMIC PHYSICS NATURE|Vol 449|13 September 2007

A whiff of antimatter soup

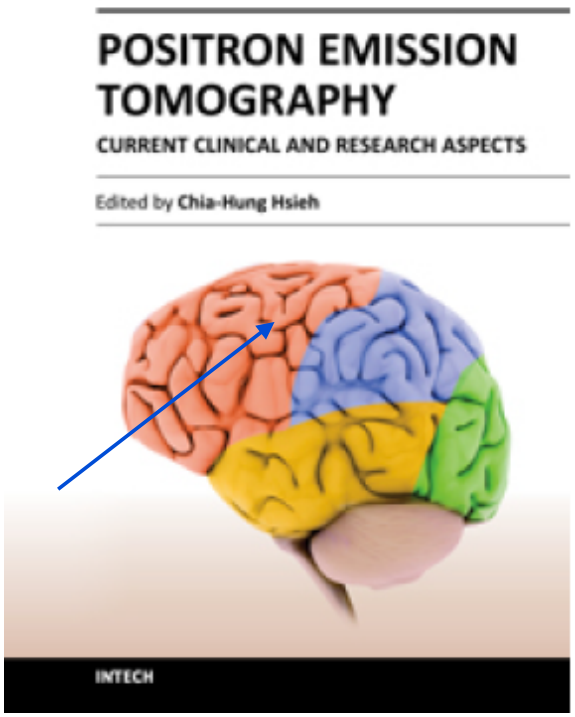
Clifford M. Surko





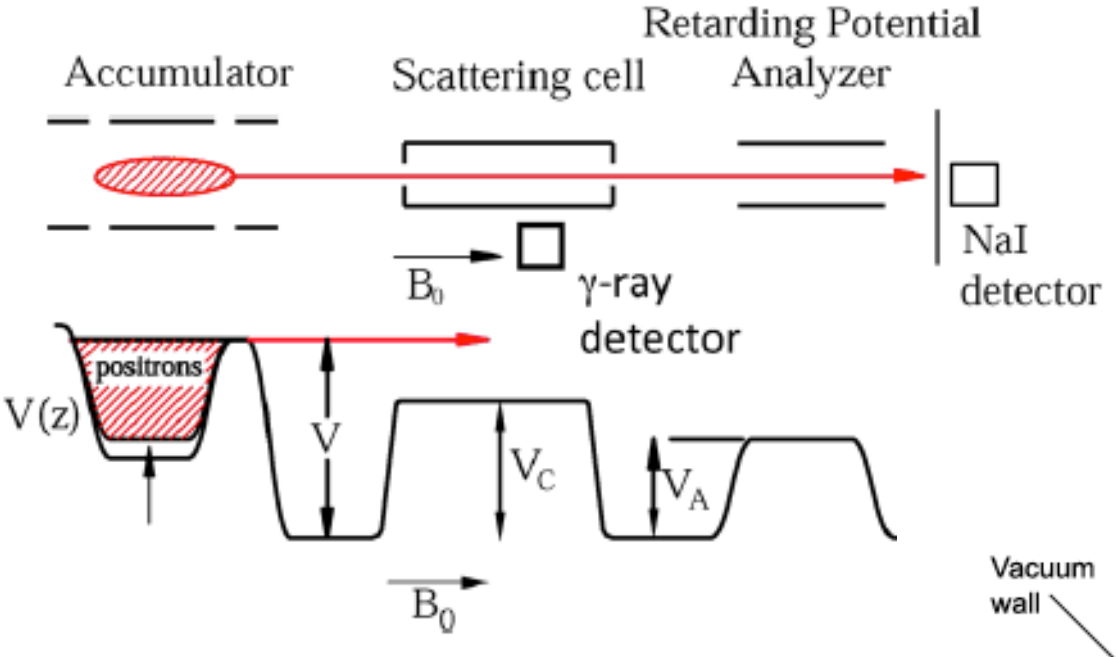


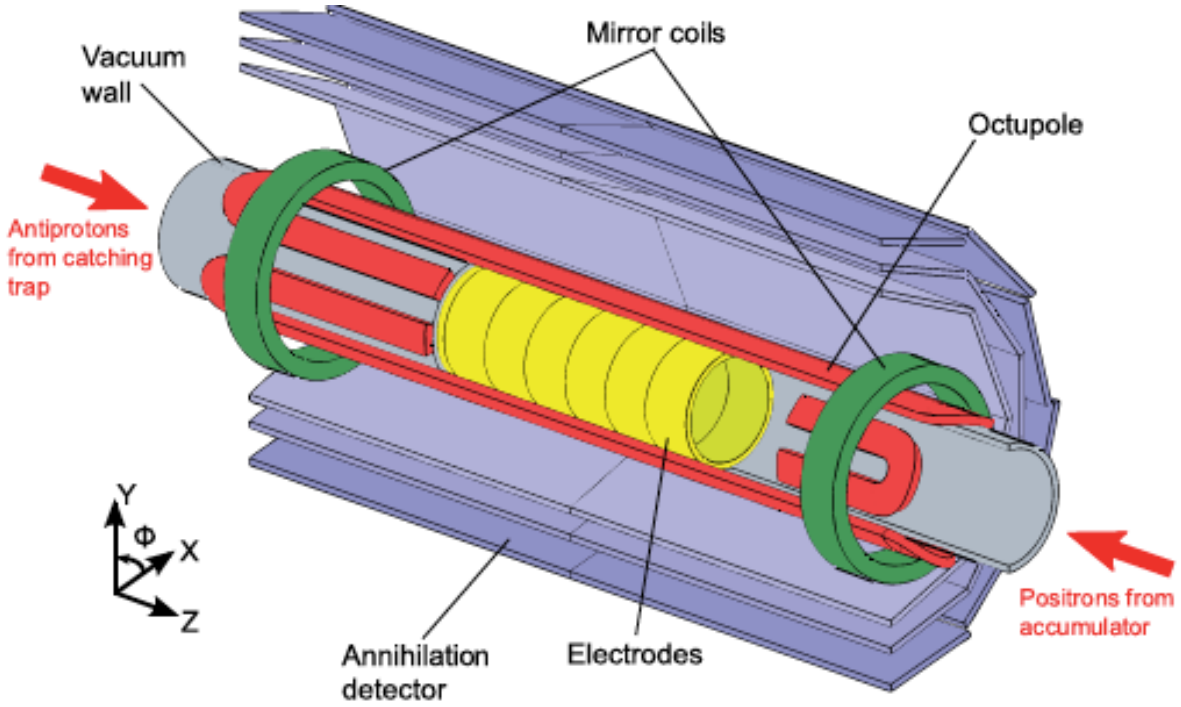
Tracer: FDG with ^{18}F isotope (Fluoro-Desoxi-Glucose)



Plasma and trap-based techniques for science with positrons

Reviews of Modern Physics **87**, 247 (2015)





REVIEWS OF MODERN PHYSICS, VOLUME 82, JULY–SEPTEMBER 2010

Positron-molecule interactions: Resonant attachment, annihilation, and bound states

Molecule	Z	Z_{eff}[a]
H_2O	10	170[b]
NH_3	9	300[b]
CH_3F	18	250[b]
CH_3Br	44	2000[b]
CH_4	10	70[b]
C_2H_6	18	900[c]
C_3H_8	26	10500[c]
C_6H_{14}	50	184000[c]
$C_{12}H_{26}$	98	9800000[c]
CH_3OH	18	750[b]
C_2H_5OH	26	4500[b]
C_6H_6	42	47000[c]
$C_{10}H_8$	68	1240000[c]

Annihilation Rate: $\lambda = \pi r_0^2 c n Z_{\text{eff}}$

$$Z_{\text{eff}}(E) = \frac{\pi}{k_i} \langle \Psi_{k_i}^{(+)} | \sum_{j=1}^{Z} \delta(\mathbf{r}_j - \mathbf{r}_p) | \Psi_{k_i}^{(+)} \rangle$$

VOLUME 86, NUMBER 8 PHYSICAL REVIEW LETTERS 19 FEBRUARY 2001

Excitation of Molecular Vibrations by Positron Impact

J. P. Sullivan, S. J. Gilbert, and C. M. Surko

VOLUME 87, NUMBER 7 PHYSICAL REVIEW LETTERS 13 AUGUST 2001

Excitation of Electronic States of Ar, H_2, and N_2 by Positron Impact

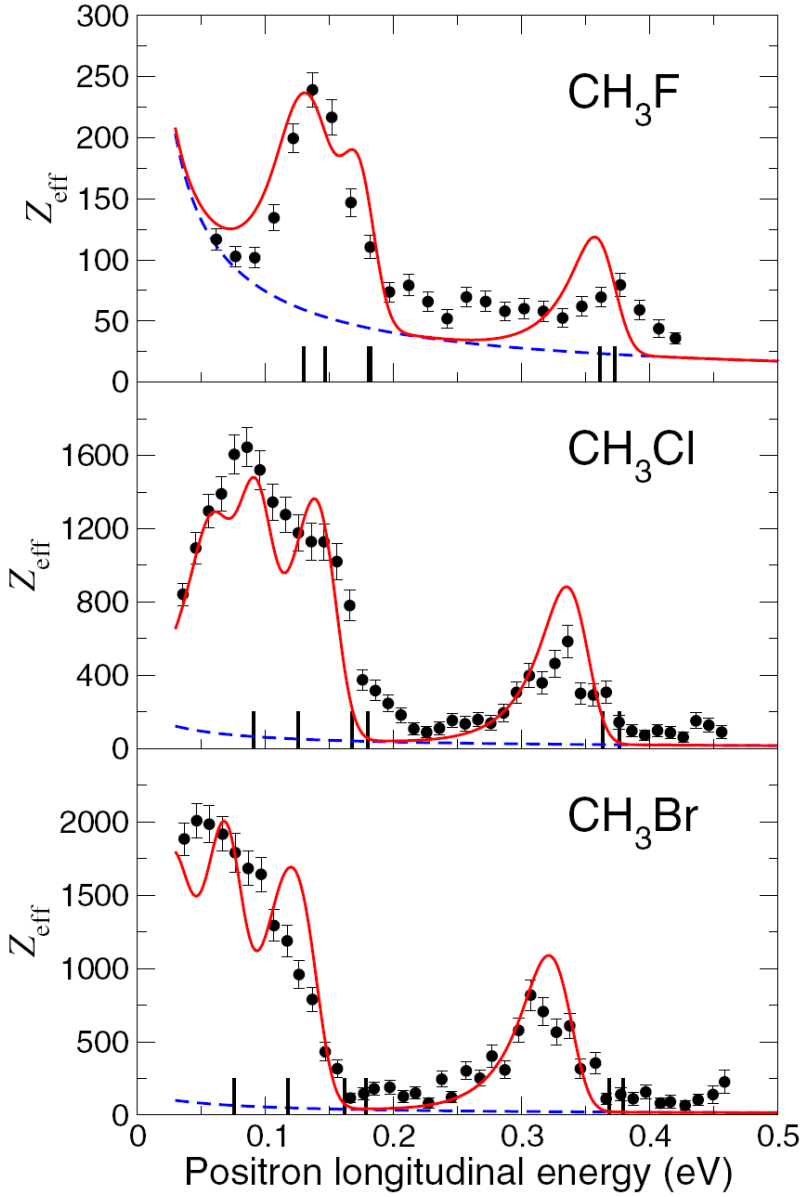
J. P. Sullivan, J. P. Marler, S. J. Gilbert, S. J. Buckman,* and C. M. Surko

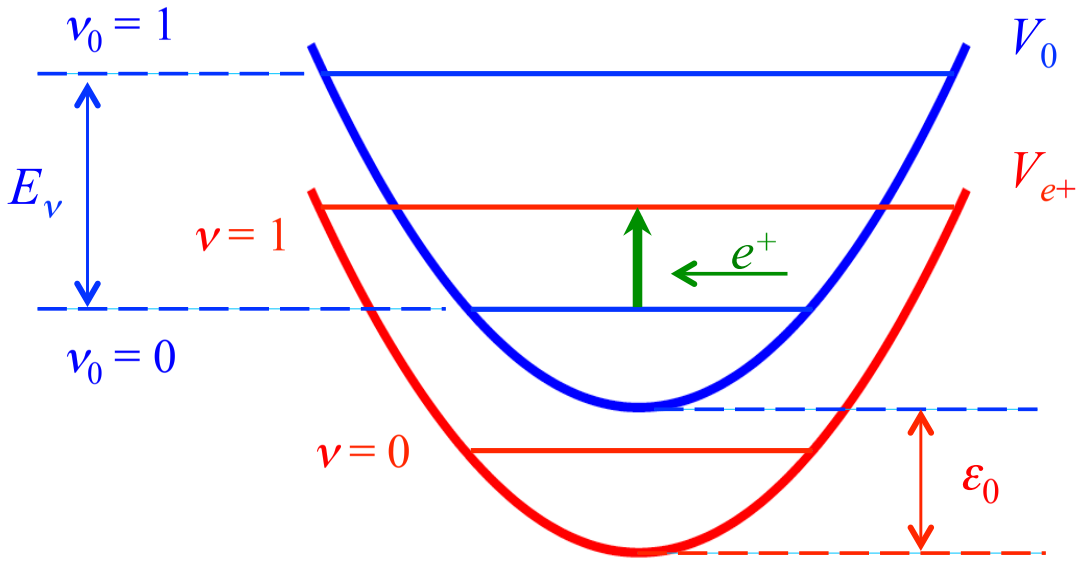
VOLUME 88, NUMBER 4 PHYSICAL REVIEW LETTERS 28 JANUARY 2002

Vibrational-Resonance Enhancement of Positron Annihilation in Molecules

S. J. Gilbert, L. D. Barnes, J. P. Sullivan, and C. M. Surko

IR-Active Vibrations: Gribakin-Lee Model





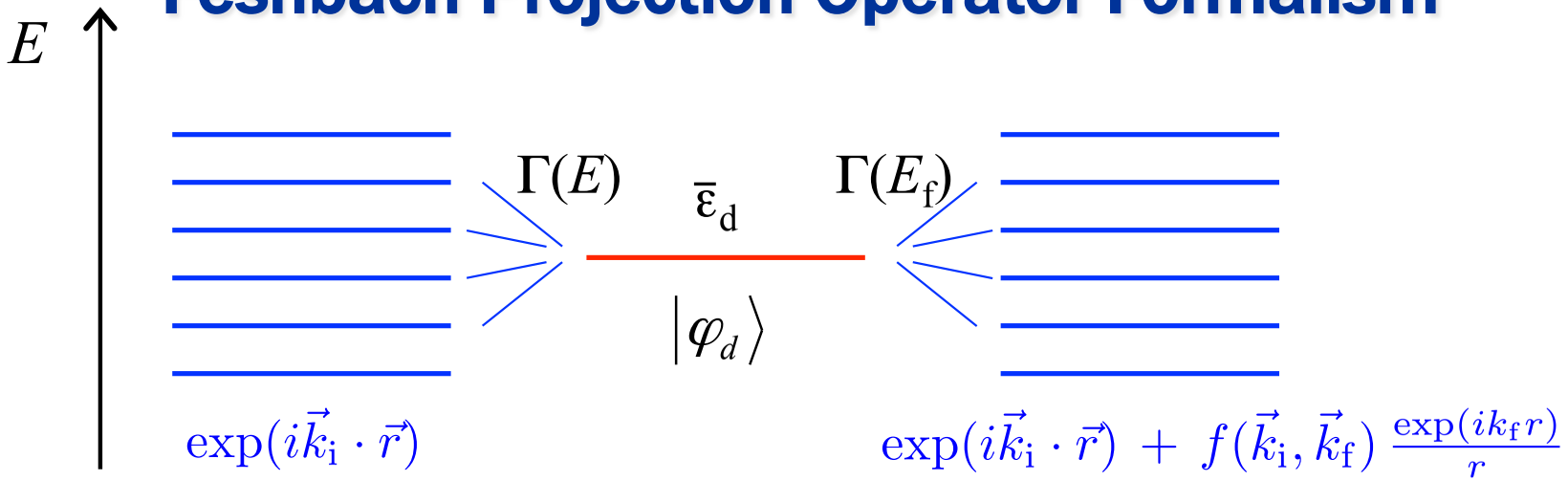
$$\langle \Phi_\nu | V | \Psi_{\mathbf{k}}^{(0)} \rangle = \int \varphi_0(\mathbf{r}) \Phi_\nu^*(\mathbf{R}) \frac{\hat{\mathbf{d}} \cdot \mathbf{r}}{r^3} e^{i\mathbf{k}\cdot\mathbf{r}} \Phi_0(\mathbf{R}) d\mathbf{r} d\mathbf{R}$$

$$Z_{\text{eff}}^{(\text{res})} = \frac{\pi}{k} \rho_{\text{ep}} \sum_\nu \frac{g_\nu \Gamma_\nu^e}{(\varepsilon - E_\nu - \varepsilon_0)^2 + \Gamma_\nu^2/4}$$

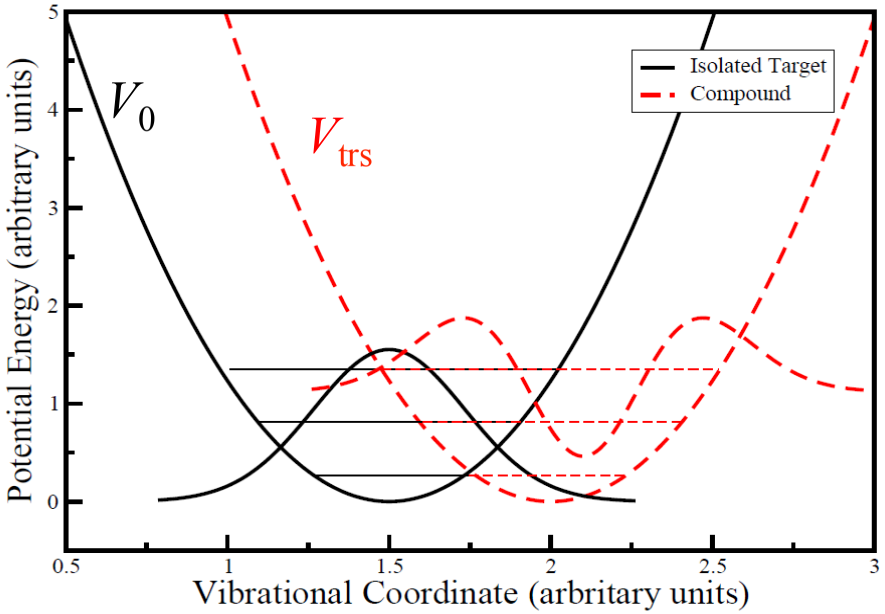
Gribakin & Lee, Phys. Rev. Lett. 97, 193201 (2006)

Reviews of Modern Physics 87, 247 (2015)

Feshbach Projection Operator Formalism



$$V_{\rm opt} = V_0 + \epsilon_{\rm d} + \Delta(E) - \frac{i}{2}\Gamma(E)$$



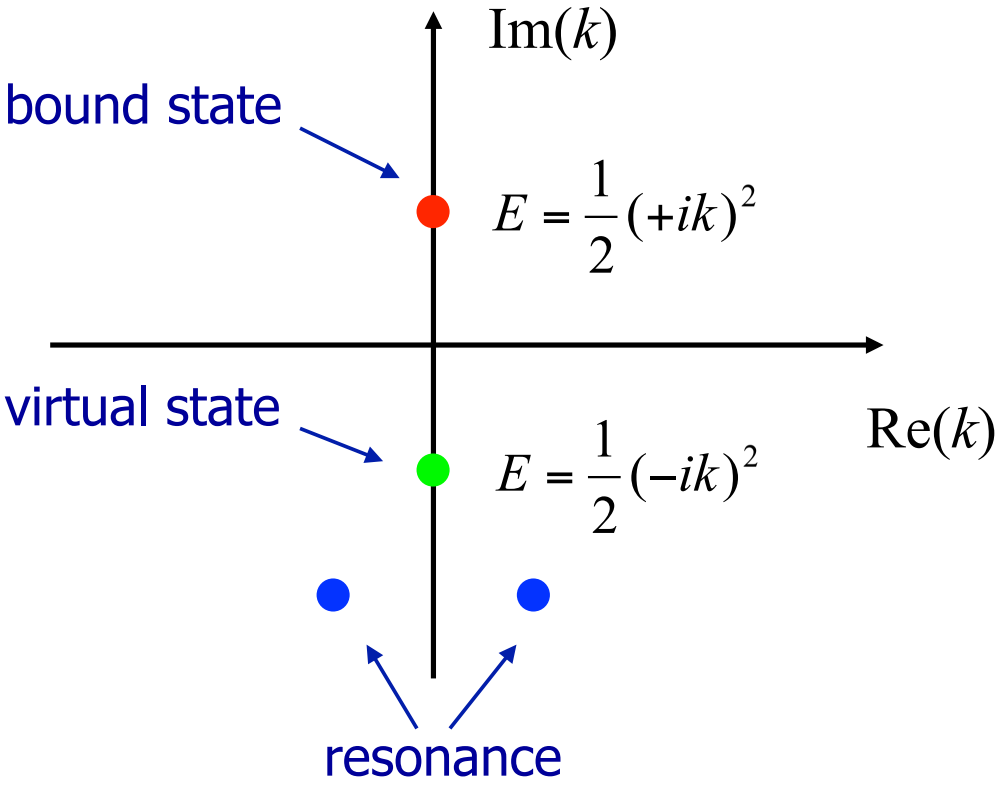
Projection operators

$$\mathcal{Q} = |\phi_{\rm d}\rangle\langle\phi_{\rm d}| \qquad \mathcal{P} = 1 - \mathcal{Q}$$

Collision (*T*) matrix:

$$T_{\nu_f\nu_i} = \langle\nu_f|\, t_{\rm d}(E)\,|\nu_i\rangle$$
$$= \langle\nu_f|U^*_{\mathbf{k}_f}(E)\frac{1}{E - K - V_{\rm opt}}U_{\mathbf{k}_i}(E)|\nu_i\rangle$$

Transient States



S-Matrix Poles

$$E - \varepsilon_d - \Delta(E) + \frac{i}{2}\Gamma(E) = 0$$

Analytical Continuation

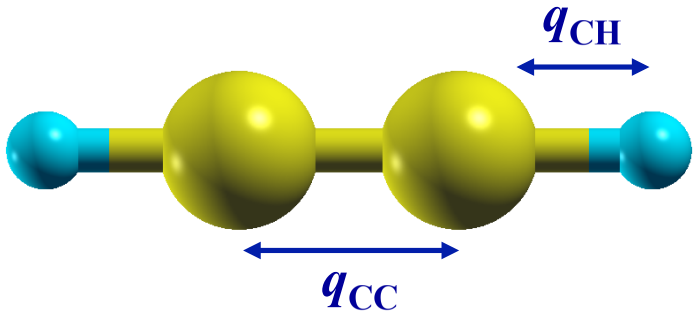
$$F(Z) = \frac{1}{2\pi}\int dE\, \frac{\Gamma(E)}{Z - E}$$

$$\begin{cases} \mathrm{Re}[F(Z \pm i\varepsilon)] = \Delta(E) \\ \mathrm{Im}[F(Z \pm i\varepsilon)] = \mp\Gamma(E) \end{cases}$$

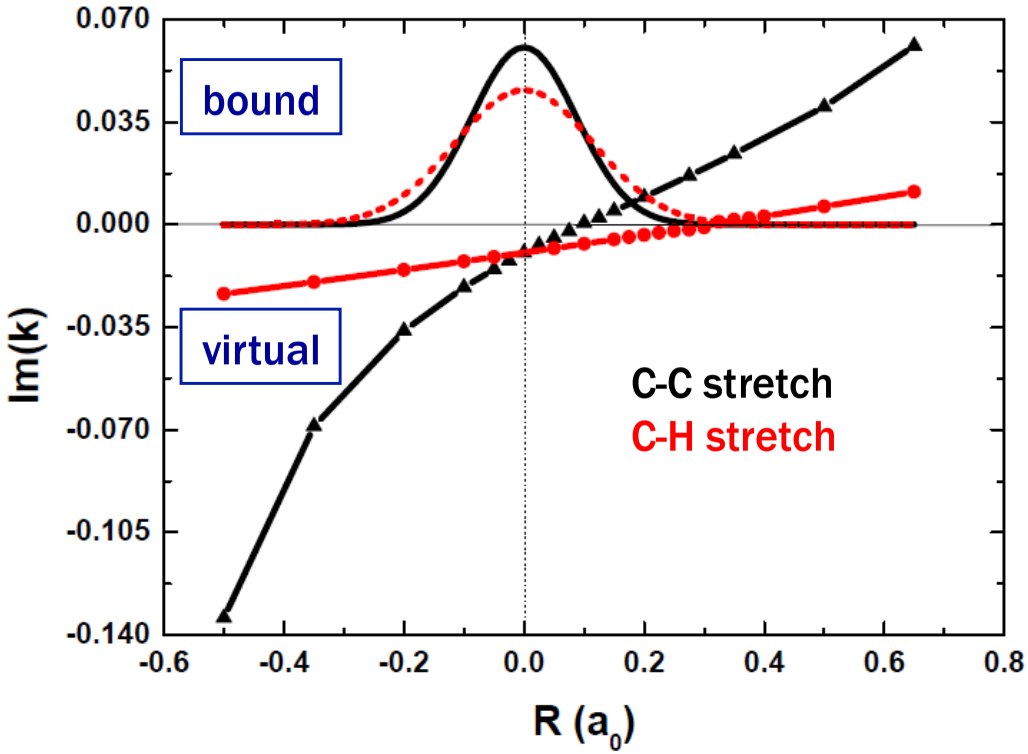
Poles on the Imaginary Axis ($E < 0$)

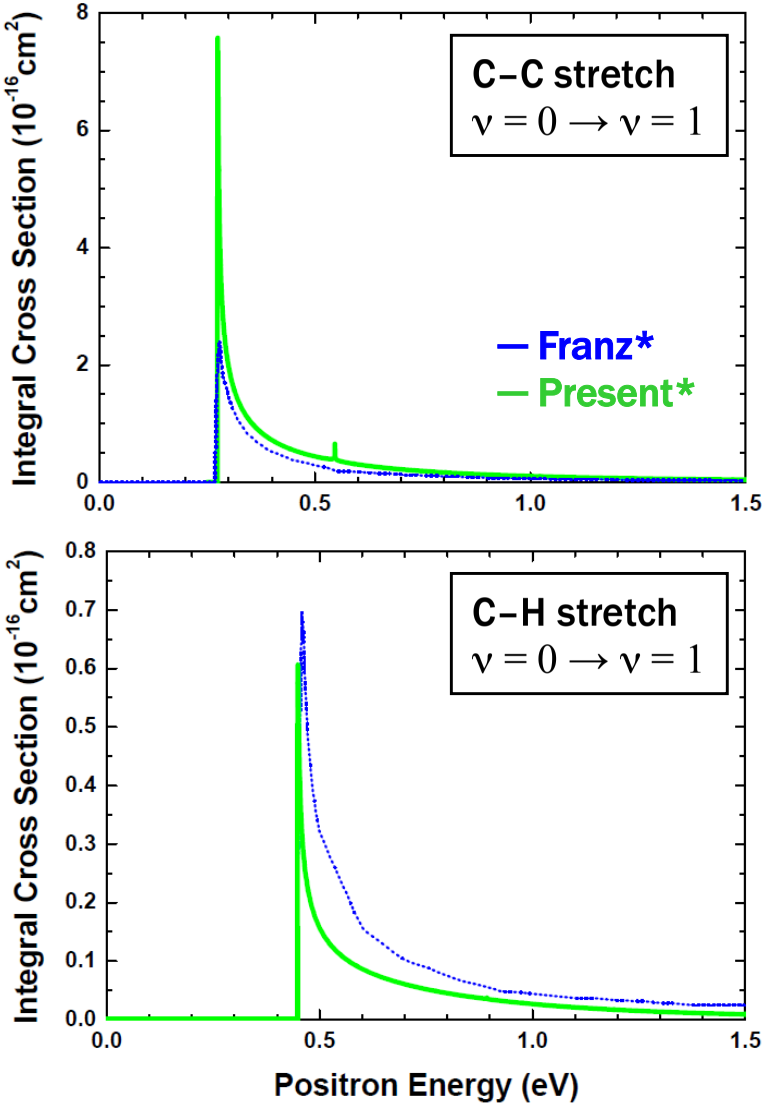
$$F(-|E|) = \Delta(-|E|) = \sum_\alpha \frac{A_\alpha}{2}\left[-\pi^{-1/2} b_\alpha^{-1/2} \pm |E|^{1/2}\, e^{b_\alpha E}\, \mathrm{erfc}(b_\alpha^{1/2}|E|^{1/2})\right]$$

C_2H_2: Symmetric Stretch



Virtual states become bound states upon stretching of C–C and C–H bonds.

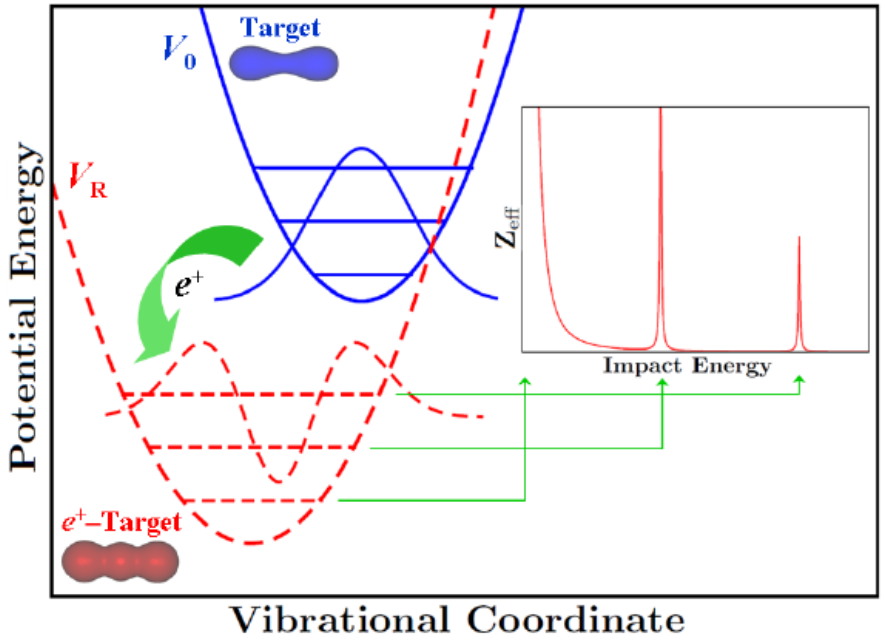




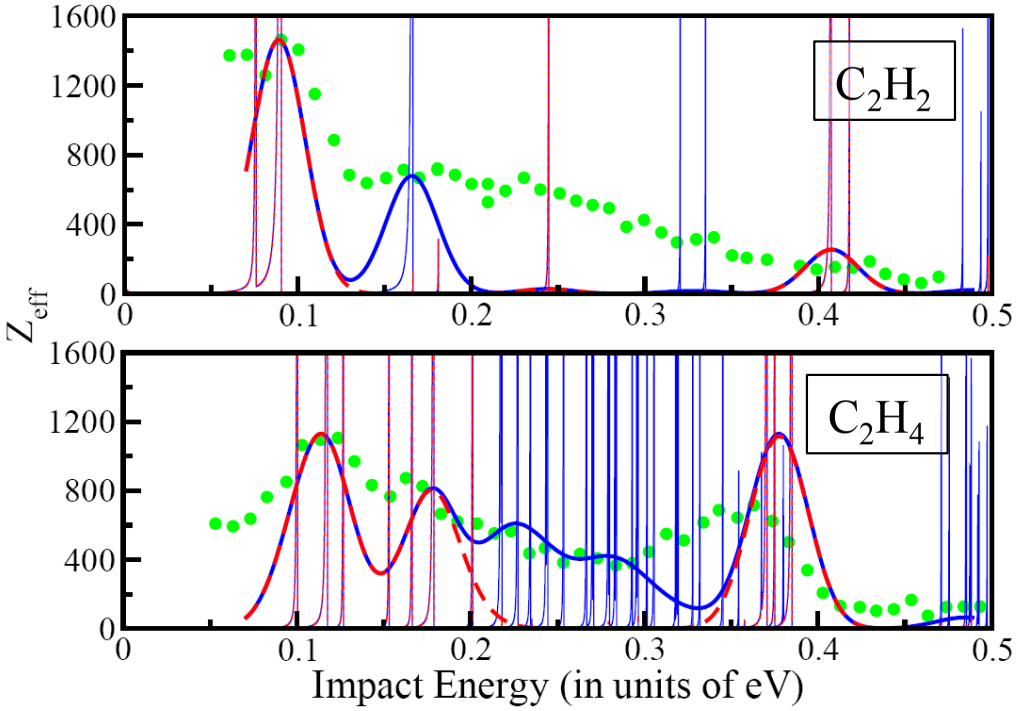
*Franz and Gianturco, Eur. Phys. J. D 39, 407 (2006)
*Oliveira *et al.*

PHYSICAL REVIEW A **81**, 012712 (2010)

Feshbach Projection Operator Approach



Sanchez et al., Phys. Rev. A **80**, 052710 (2009)



Sanchez et al., Phys. Rev. Lett. **107**, 103201 (2011)

Data: S. J. Gilbert, et al.,, Phys. Rev. Lett. 88, 043201 (2002)

$$Z_{\text{eff}}(E) = \frac{\pi}{k_i} \langle \eta_0 | \Gamma^{1/2}(E) \frac{1}{[E - T_N - V_{\text{opt}}]^\dagger} \rho_{\text{d}} \frac{1}{[E - T_N - V_{\text{opt}}]} \Gamma^{1/2}(E) | \eta_0 \rangle$$

$$\bar{\epsilon}(\mathbf{Q}) = \bar{\epsilon}_d(\mathbf{0}) + \nabla \bar{\epsilon}_d(\mathbf{0}) \cdot \mathbf{Q} + \tfrac{1}{2} \mathbf{Q} \cdot \nabla^2 \bar{\epsilon}_d(\mathbf{0}) \cdot \mathbf{Q}$$

Any Particle Molecular Orbital (APMO)

A. Reyes, F. Moncada and J. Charry, *Int. J. Quantum Chem.*, 2019, **119**, e25705.

Prof. Andrés Reyes

(UNAL, Bogota)

LOWDIN Code

R. Flores-Moreno, E. Posada, F. Moncada, J. Romero, J. Charry, M. Díaz-Tinoco, S. A. González, N. F. Aguirre and A. Reyes, *Int. J. Quantum Chem.*, 2014, **114**, 50–56.

The Born-Oppenheimer Hamiltonian:

$$H_T = -\sum_i^{N_{e^-}} \frac{1}{2}\nabla_i^2 - \sum_i^{N_{e^-}}\sum_J^{N_c} \frac{Z_J}{R_{iJ}} + \sum_i^{N_e}\sum_{j>i}^{N_e} \frac{1}{r_{ij}} - \sum_k^{N_{e^+}} \frac{1}{2}\nabla_k^2 + \sum_k^{N_{e^+}}\sum_J^{N_c} \frac{Z_J}{R_{kJ}} + \sum_k^{N_{e^+}}\sum_{l>k}^{N_{e^+}} \frac{1}{r_{kl}} - \sum_i^{N_{e^-}}\sum_k^{N_{e^+}} \frac{1}{r_{ik}}$$

The total wavefunction:

$$\Psi_0 = \Phi^{e^-}\Phi^{e^+}$$

Solving the Fock equations

$$f^\alpha(i)\psi_i^\alpha = \epsilon_i^\alpha \psi_i^\alpha \qquad i = 1, ..., N^\alpha$$

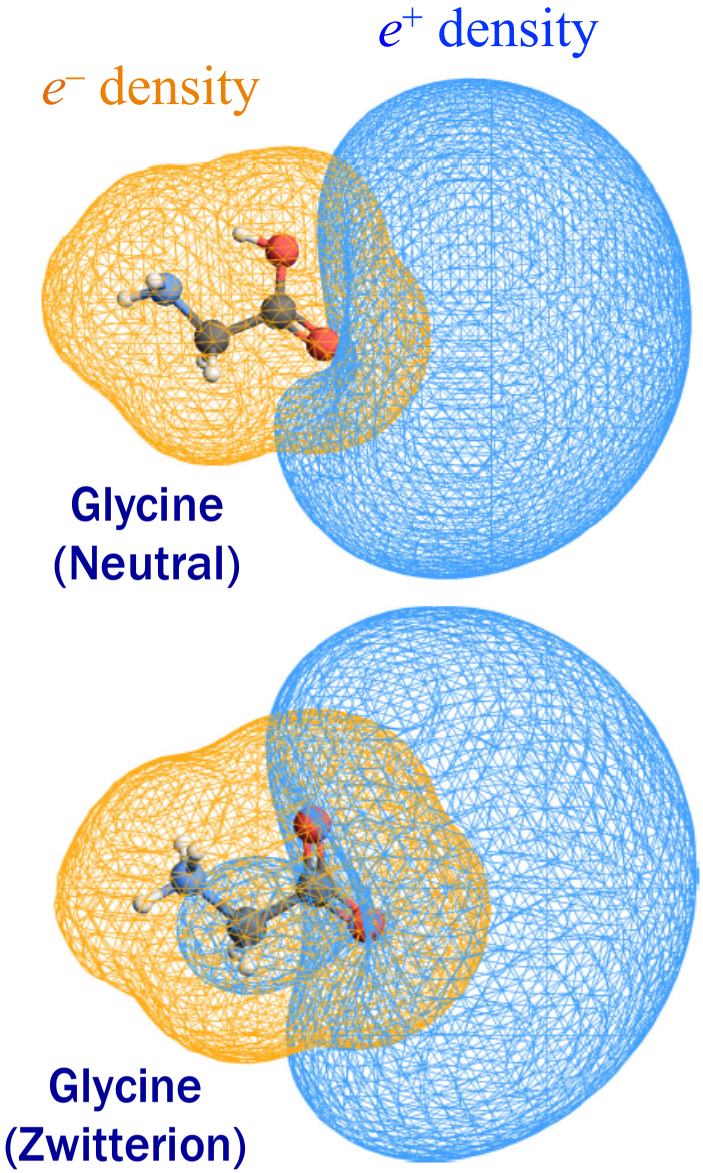
$$\alpha = e^-, e^+$$

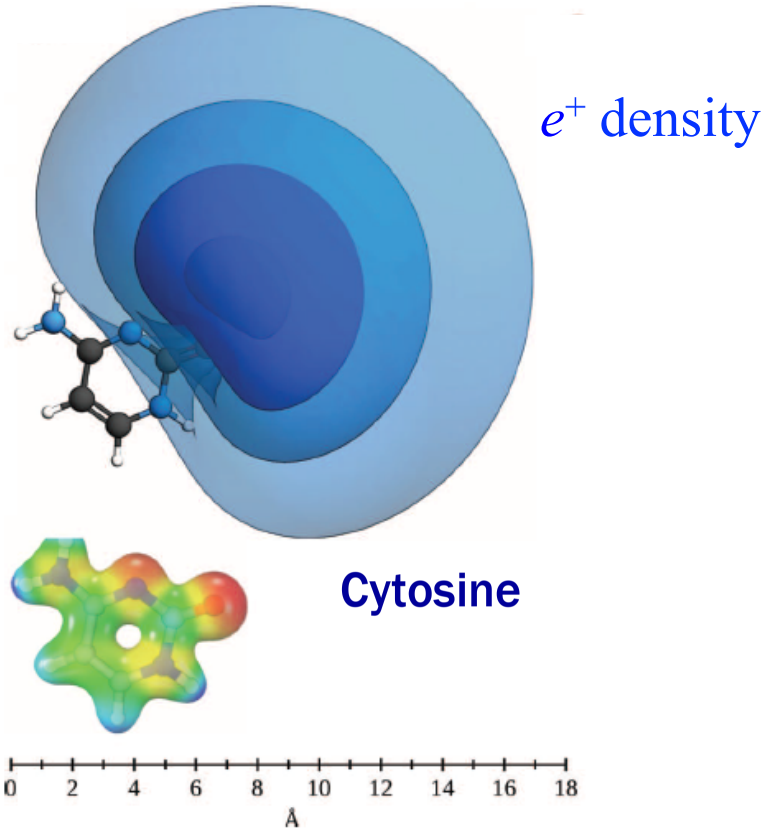
Fock operators

$$f^{e^-}(i) = h^{e^-}(i) + \sum_j^{N_{e^-}}[J_j^{e^-} - K_j^{e^-}] - \sum^{N_{e^+}} J_j^{e^+}$$

$$f^{e^+}(i) = h^{e^+}(i) + \sum_j^{N_{e^+}}[J_j^{e^+} - K_j^{e^+}] - \sum_j^{N_{e^-}} J_j^{e^-}$$

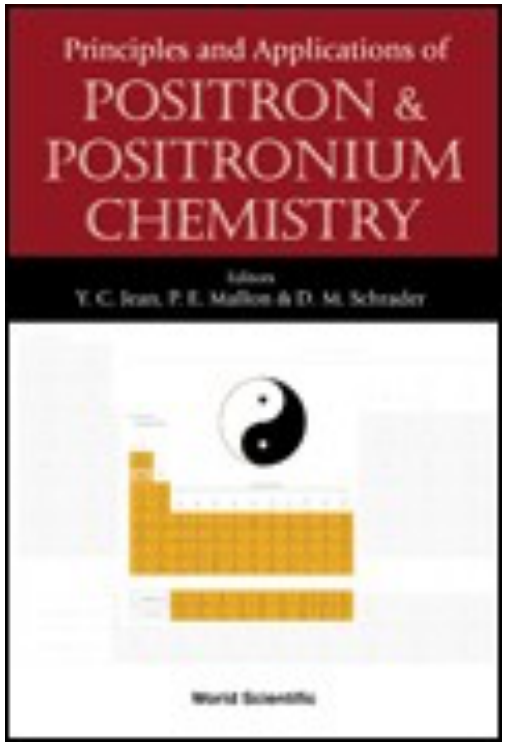
Any-Particle Molecular Orbital Method





Charry *et al.*, Phys. Rev. A **89**, 052709 (2014)

Romero *et al.*, J. Chem. Phys. **141**, 114103 (2014)



Atomic Weights

(Daltons)

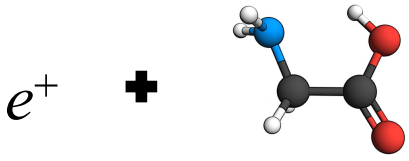
Ps 0.001097								
H 1.008								**He** 4.003
Li 6.94	**Be** 9.01		**B** 10.81	**C** 12.01	**N** 14.01	**O** 16.00	**F** 19.00	**Ne** 20.18
Na 22.99	**Mg** 24.30		**Al** 26.98	**Si** 28.09	**P** 30.97	**S** 32.07	**Cl** 35.45	**Ar** 39.95
K 39.10	**Ca** 40.08	*	**Ga** 69.7	**Ge** 72.6	**As** 74.92	**Se** 79.0	**Br** 79.9	**Kr** 83.8
Rb 85.5	**Sr** 87.6	*	**In** 114.8	**Sn** 118.7	**Sb** 121.8	**Te** 127.6	**I** 126.9	**Xe** 131.3
Cs 132.9	**Ba** 137.3	*	**Tl** 204.4	**Pb** 207.2	**Bi** 209.0			

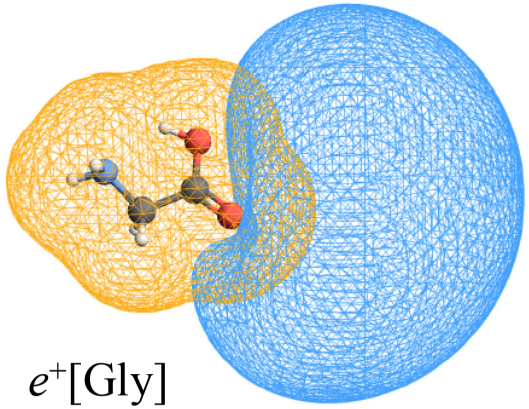
"As an atom, it [Ps] has its rightful place in the peridoc chart."

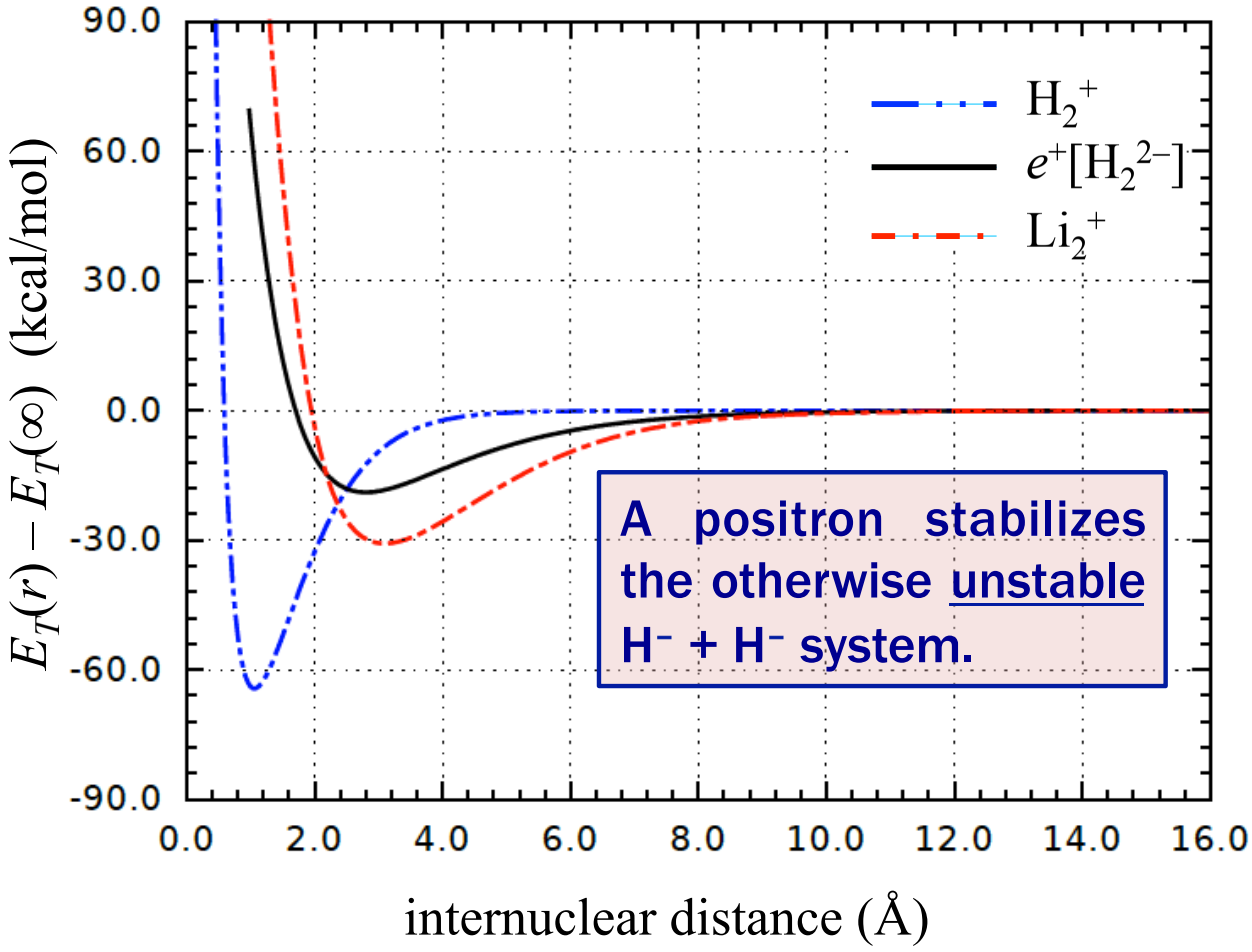
D. M. Schrader, *Compounds of positronium with koino-Atoms and -Molecules*, in: Physics with Many Atom Positron, Eds. A. Dupasquier and A. Mills, Jr., 2010.

Positron-Induced Stabilization

The usual business: positron attachment to stable systems.







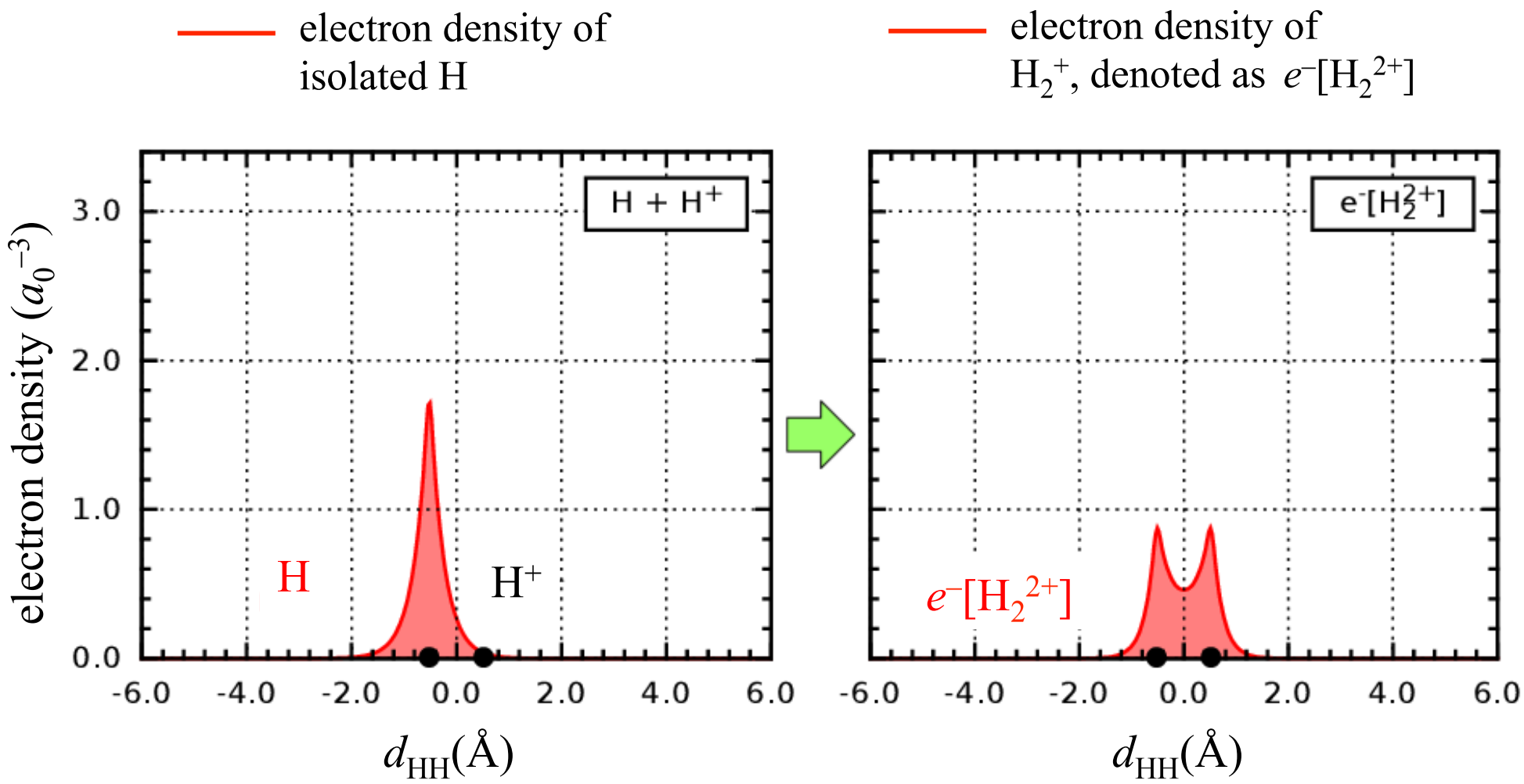
A positron stabilizes the otherwise unstable H^- + H^- system.

10^{-1} ns lifetimes consistent with neglect of annihilation (μeV error).

Bonding in $H + H^+ \rightarrow H_2^+$

a.k.a.

$e^- [H^+] + H^+ \rightarrow e^- [H_2^{2+}]$



Angew. Chem. Int. Ed. **2018**, *57*, 8859–8864

Bonding in $e^+[H^-] + H^- \rightarrow e^+[H_2^{2-}]$

(aka PsH)

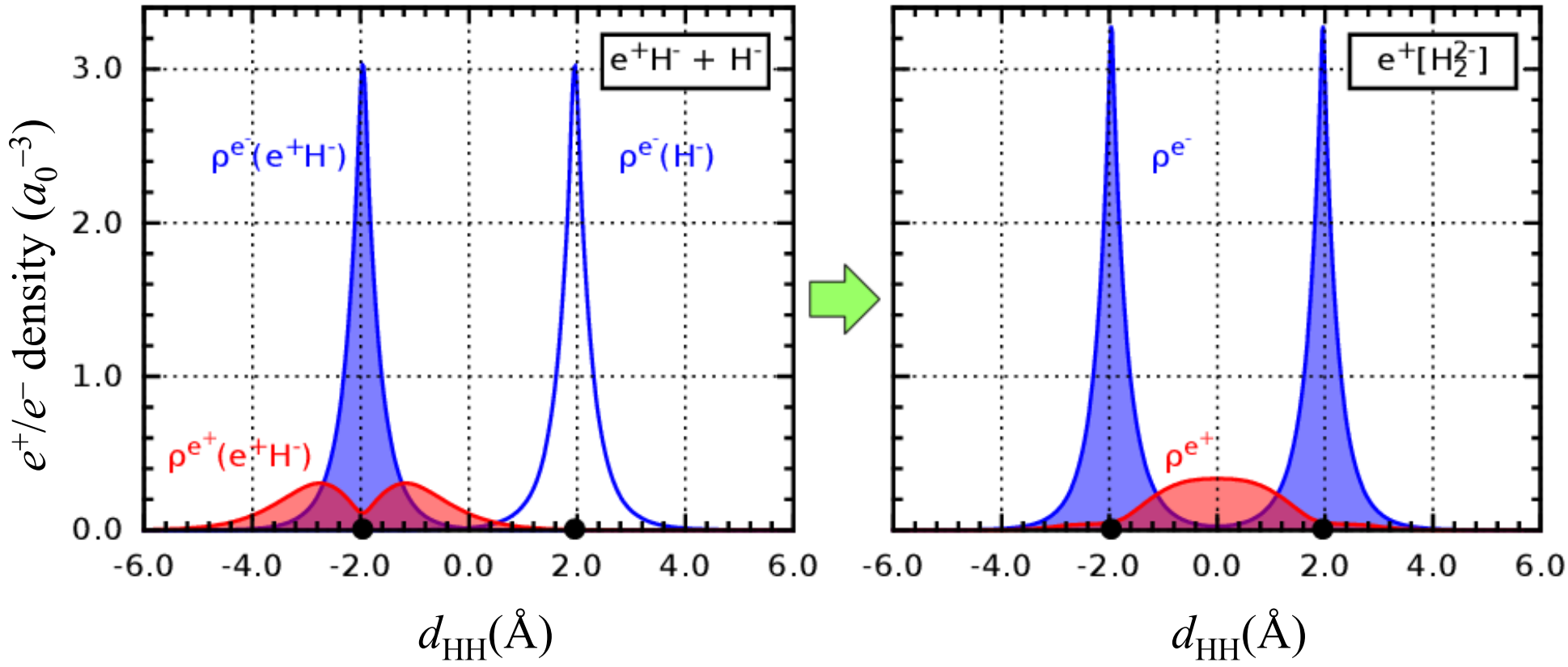
positron density of isolated $e^+[H^-]$

electron density of isolated H^-

electron density of isolated $e^+[H^-]$

positron density of $e^+[H_2^{2-}]$

electron density of $e^+[H_2^{2-}]$



Positron Covalent Bonding

IUPAC definition* of covalent bond:

A region of relatively high **electron** density between nuclei which arises at least partly from sharing of **electrons** and gives rise to an attractive force and characteristic internuclear distance.

We have obtained something like:

A region of relatively high **positron** density between nuclei which arises at least partly from sharing of **positrons** and gives rise to an attractive force and characteristic internuclear distance.

*IUPAC Gold Book, Online Version 2.3.3 (2014). Available at http://goldbook.iupac.org/

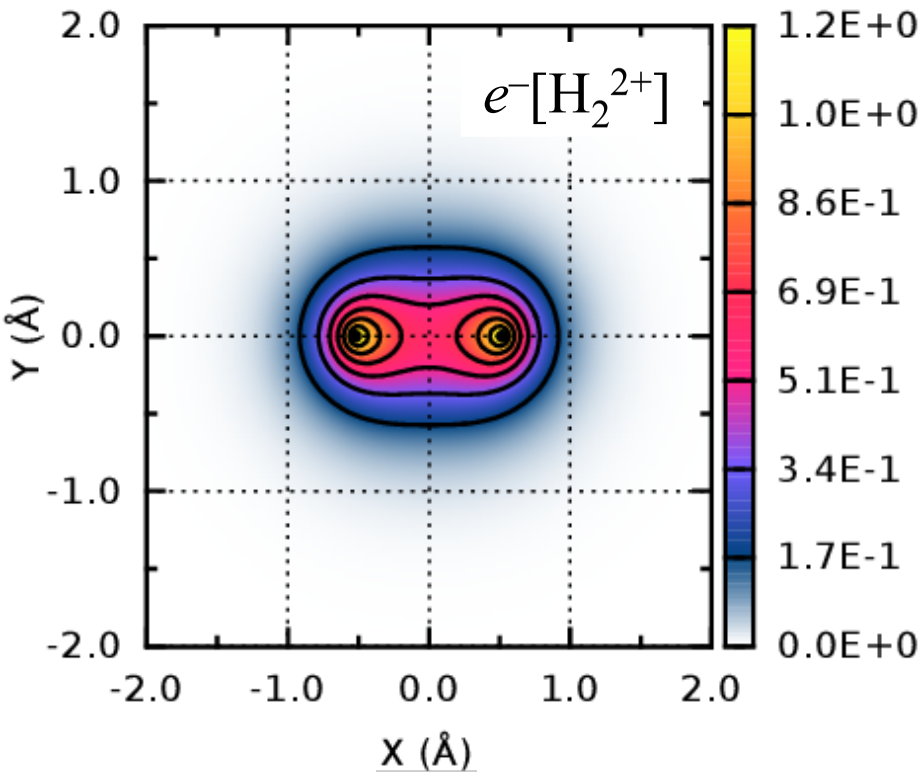
$$e^+[H_2^{2-}] \rightarrow \begin{cases} H^- + PsH \text{ (lowest energy decay channel)} \\ H^- + H^- + e^+ \\ H^- + H + Ps \\ H + H + Ps + e^- \\ H_2^- + Ps \\ H_2 + Ps + e^- \\ H_2^+ + Ps + 2e^- \end{cases}$$

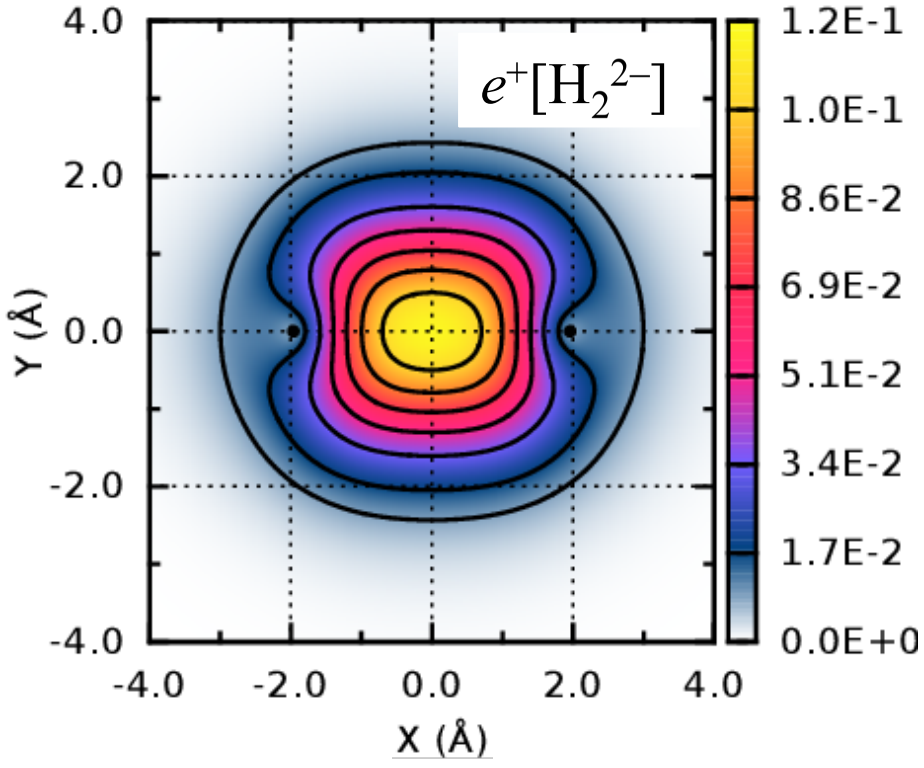
Table 3: CBS extrapolated energies of the positronic molecule and dissociation products.

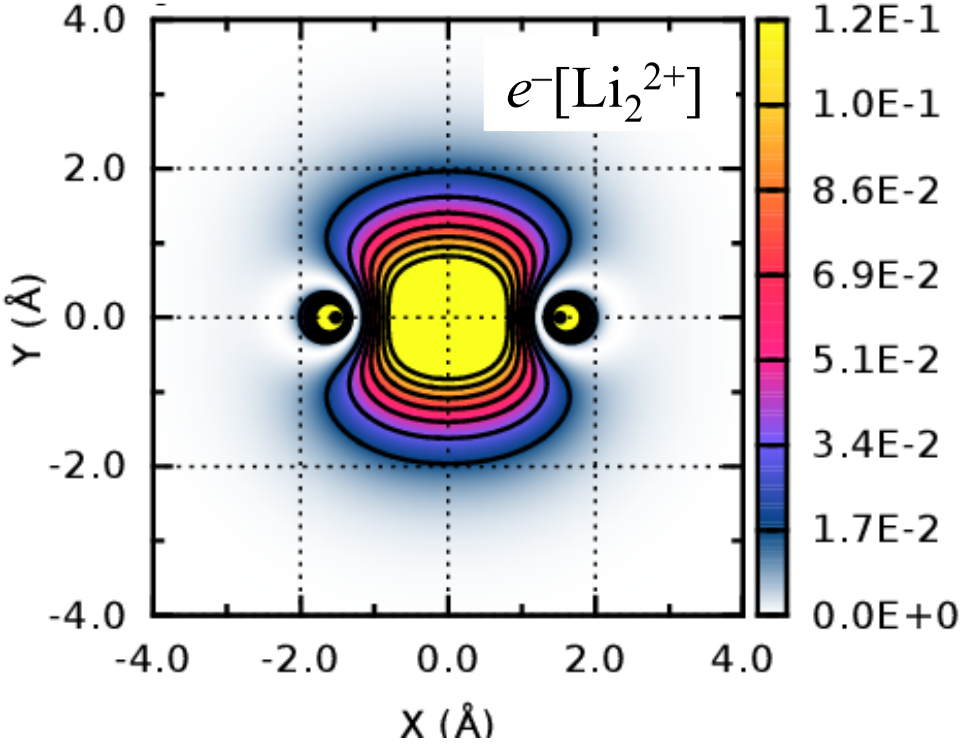
	H^- (a)	PsH (a)	$e^+ \cdot H_2^{2-}$ (a)	BE (b)	BE* (b)
MP2	−0.518455	−0.736369	−1.287855	86.72	−76.38
CISD	−0.527671	−0.780645	−1.326642	48.12	25.45
CISDT	−0.527671	−0.788744	−1.336168	51.86	50.47
CISDTQ	−0.527671	−0.788744	−1.346256	78.35	76.95
Exact	−0.527751	−0.789196	–	–	–

(a) Hartree (b) kJ/mol

Lower bound for energy stability (with vibrational ZPE): 74 kJ/mol (0.77 eV)

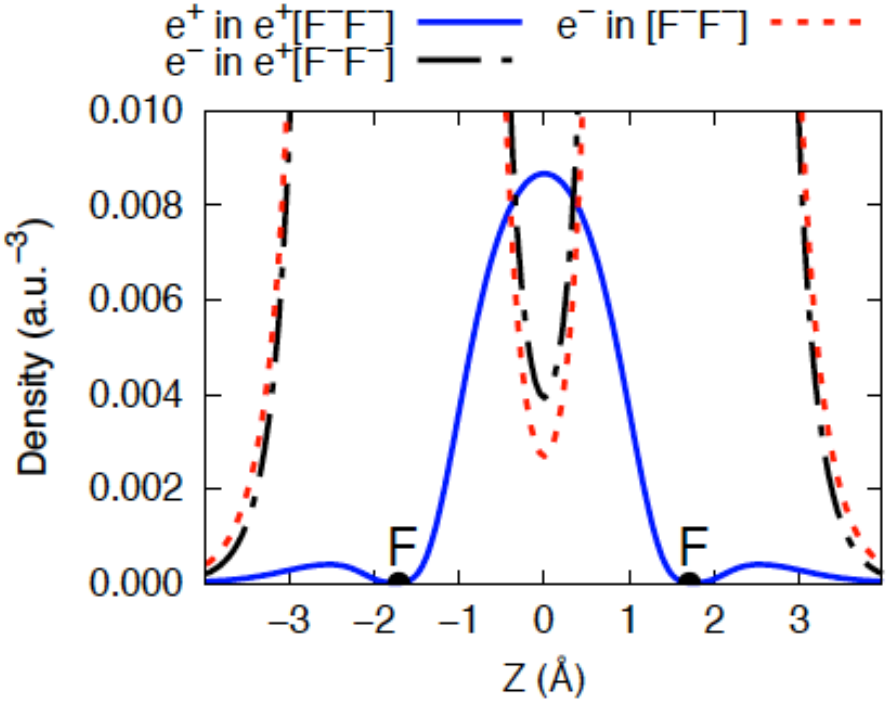


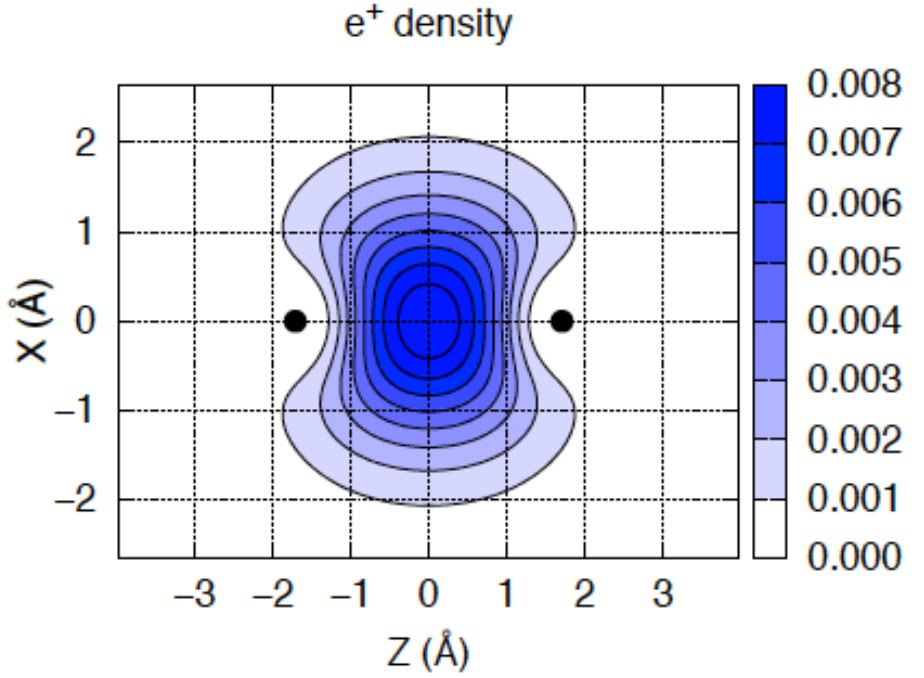


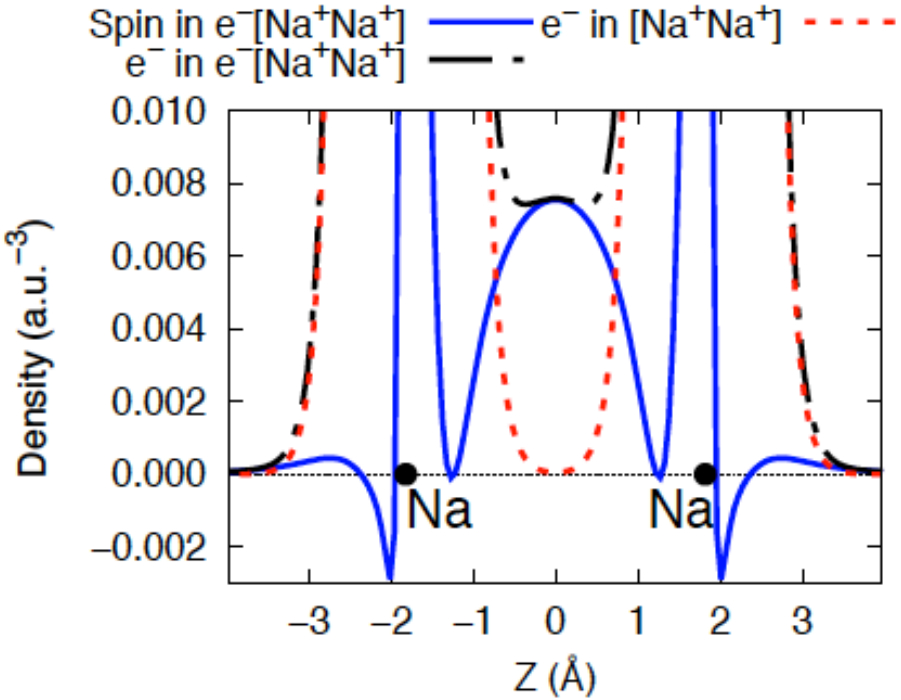


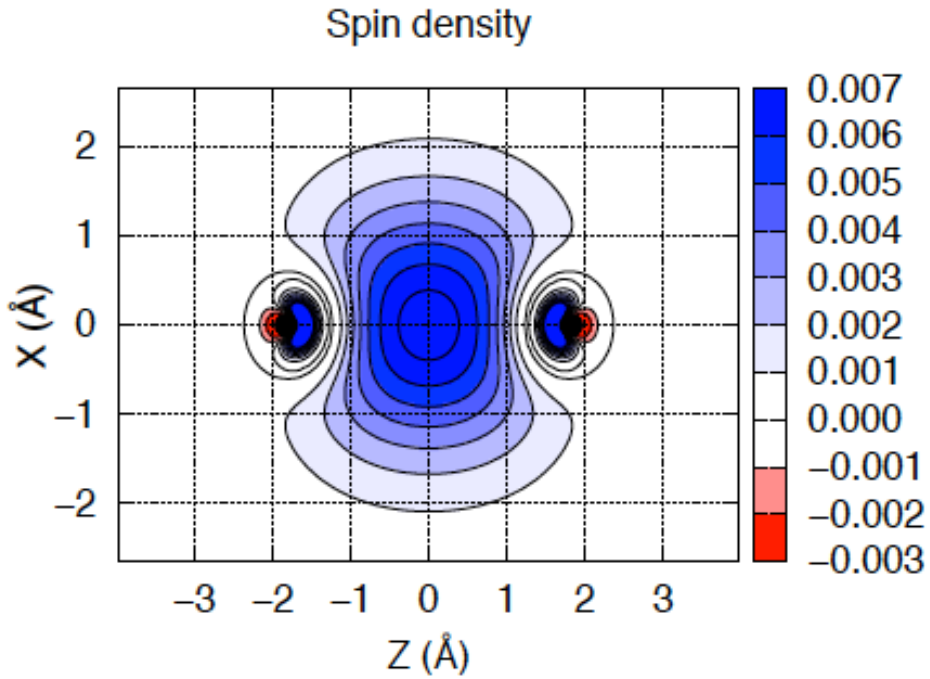
Positron density is similar to the valence density of $e^{-}[Li_2^{2+}]$ (aka Li_2^{+}), having the same number o core electrons.

Covalent bonds in positron di-halides (submitted)

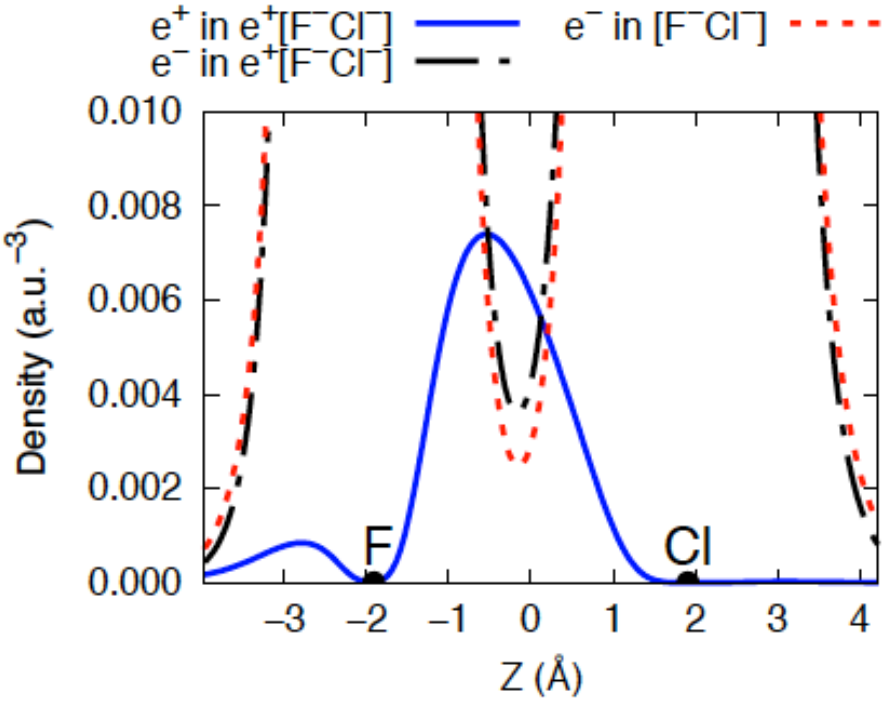


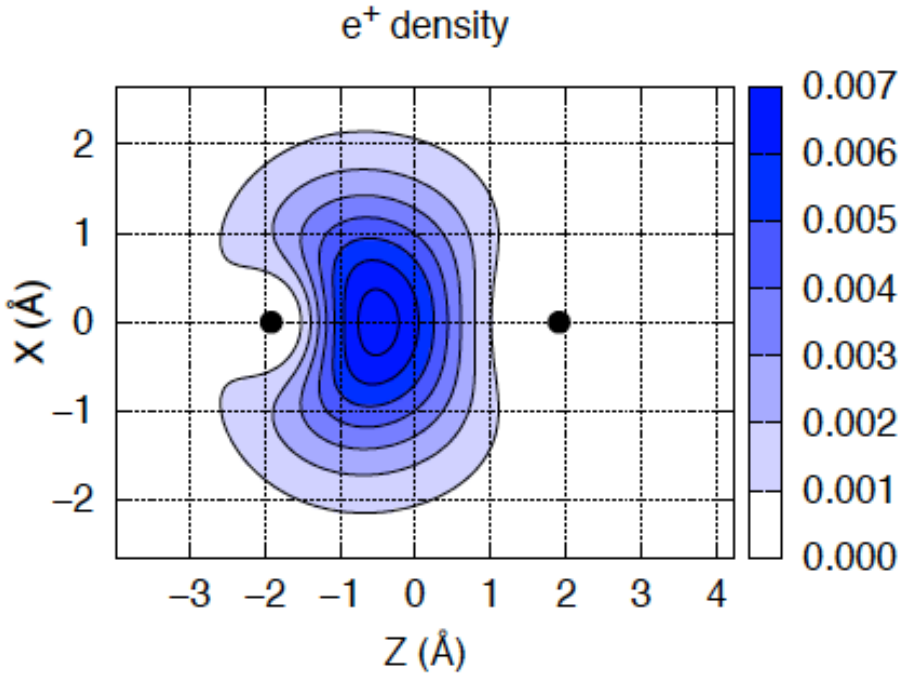


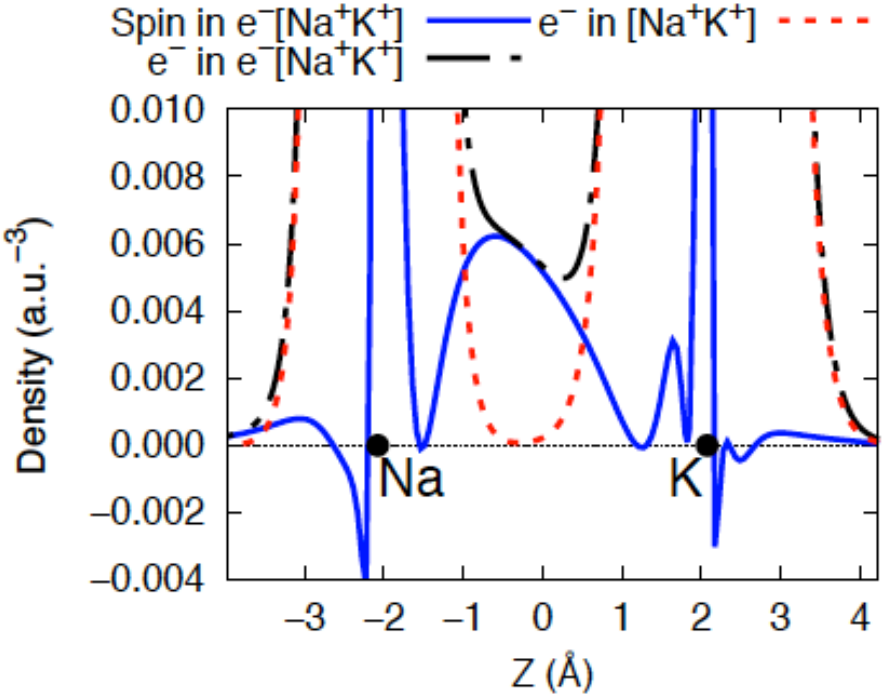


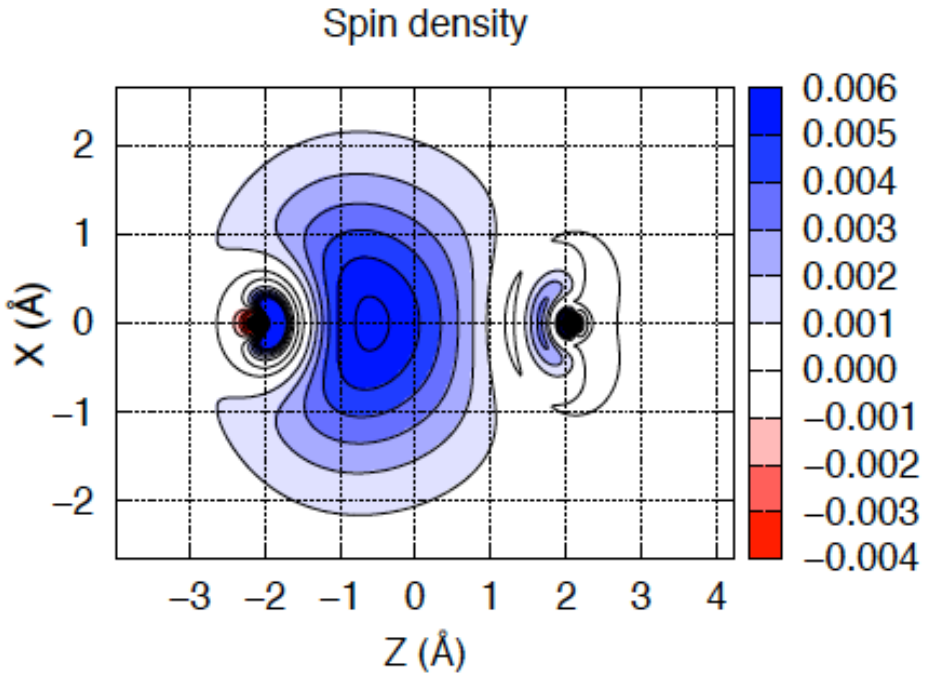


Covalent bonds in positron di-halides (submitted)

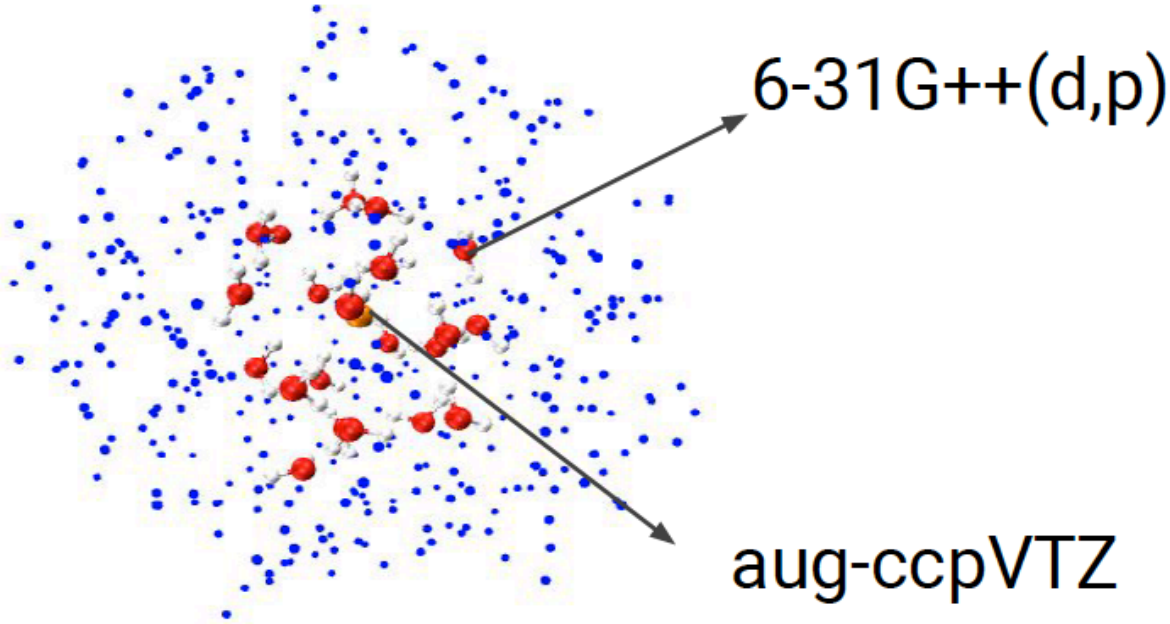


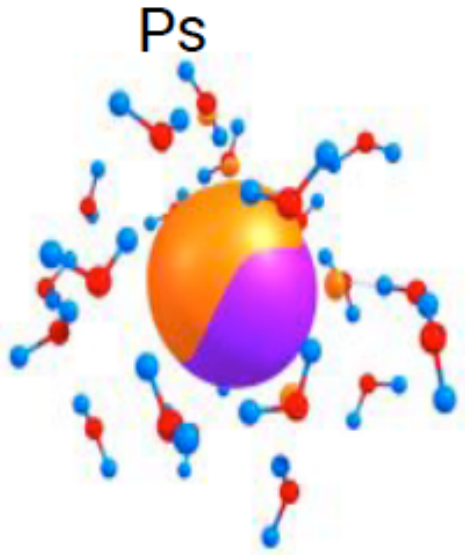




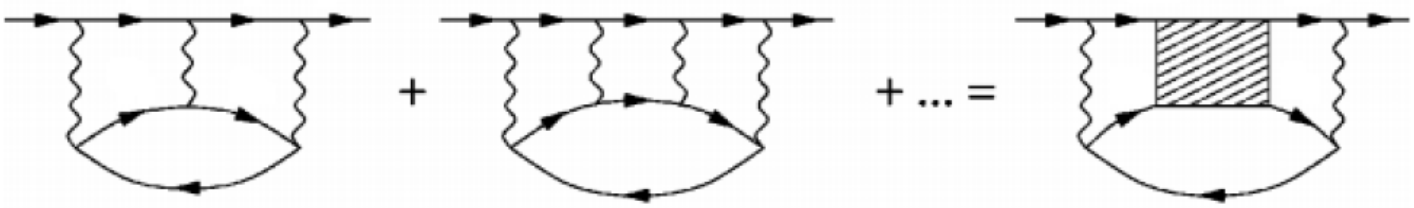


QM/MM approach to solvated Ps

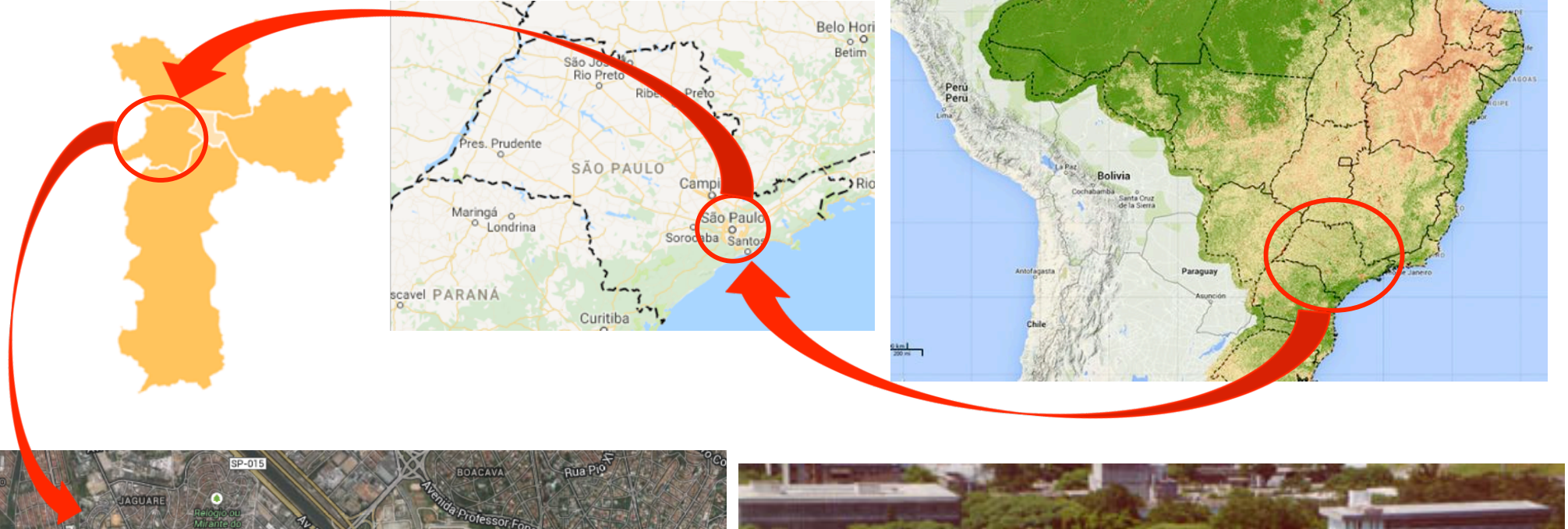


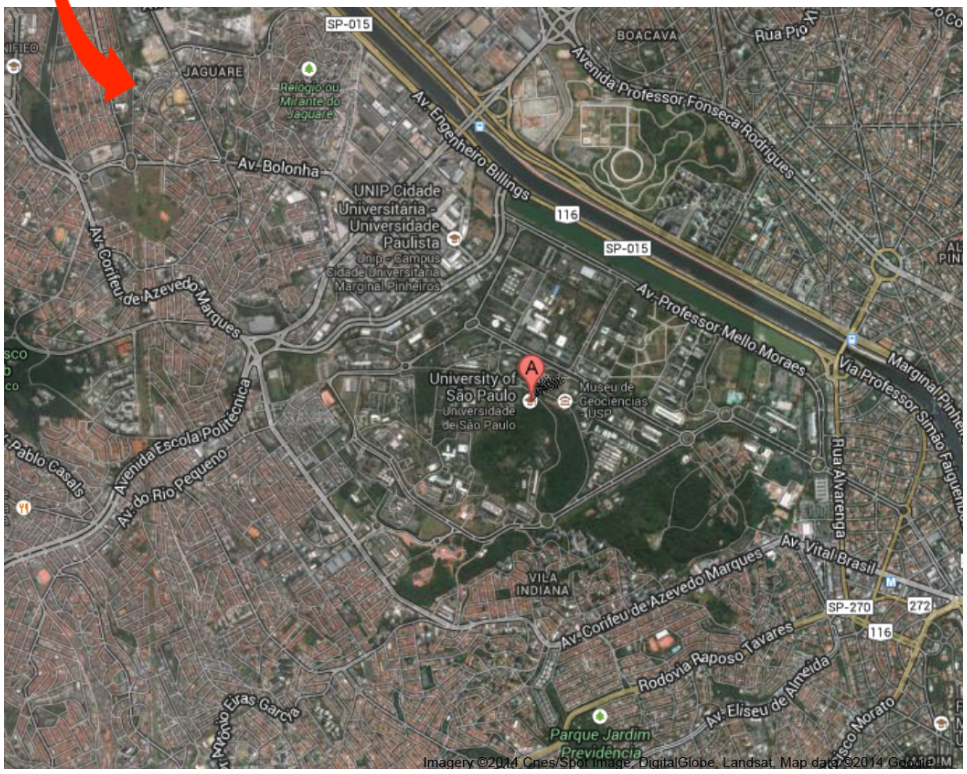


Improved electron-positron propagators in the APMO/LOWDIN framework:



$$\Sigma_{pp}(E) \approx \Sigma_{pp}^{(2)}(E) + (1+F)^{-1}(\bar{\Sigma}_{pp}^{(3)}(E) + \Sigma_{pp}^{(Ps)}(E))$$





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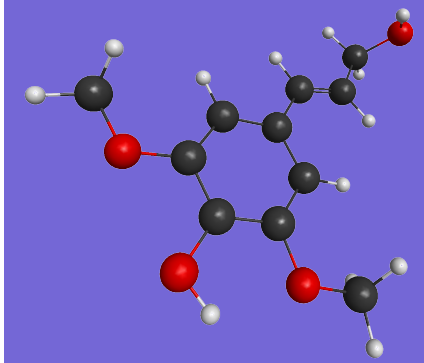
Support

FAPESP
CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico
CAPES
USP PRÓ-REITORIA DE PESQUISA

Tanks for your attention!



Molecular Physics and Modelling Group

Interactions with electrons, positrons and photons

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