Influence of $e^+ - e^-$ pair interaction with matter in the vicinity of free volume of condensed medium on the formation of positronium atom

PPC 12.5

Marek Pietrow
(and all co-authors of mentioned papers)

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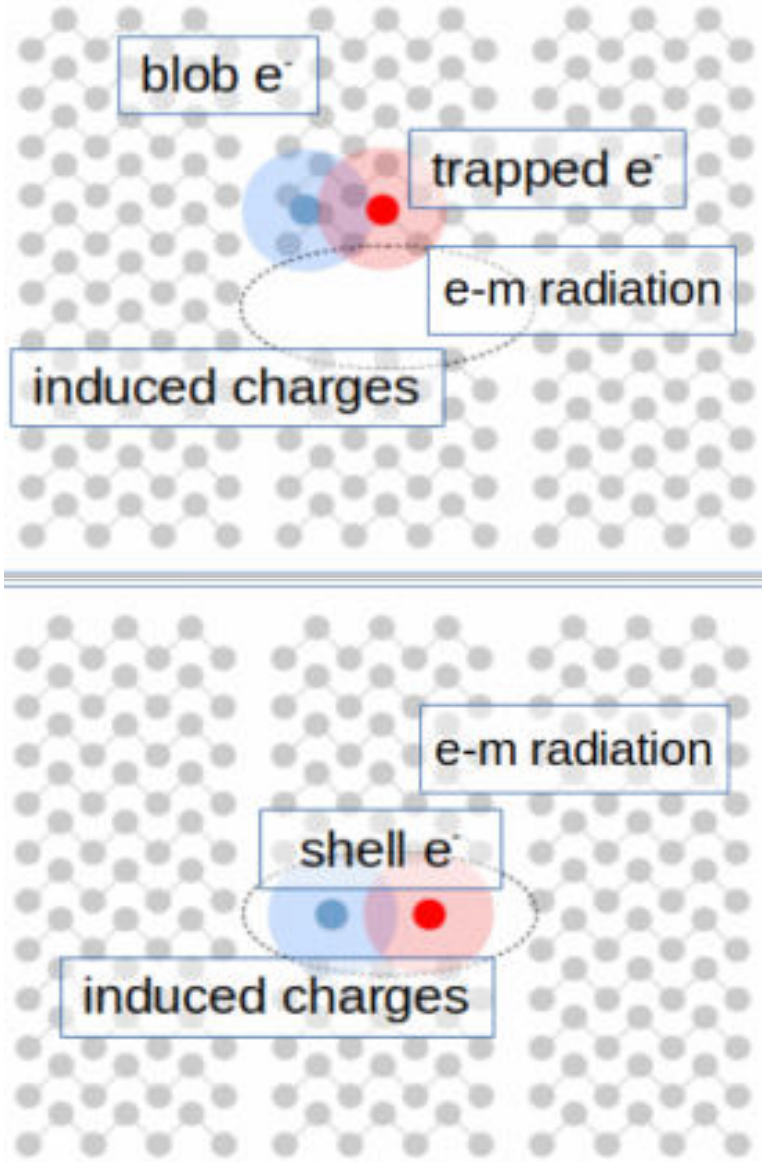
Sept. 3, 2021 10:30-11:00

Abstract

- It is often assumed the single-body model of positronium in the potential well.
- In both the blob and the free volume, the $e^+ - e^-$ distance may be comparable to the distance to other electrons $\longrightarrow$ the strength of the interaction producing the pair formation may be compared in magnitude to the strength of the interaction with surrounding matter.
- In this talk, some selected examples based on my research are indicated where the third body changes the properties of the $e^+ - e^-$ pair and, possibly, influences the results of the experiments.



Purpose of my research. Outline

- Introduction: Alkanes
- Experimental analysis of the properties of electron traps in alkanes
- Numerical model of e^+ and e^- trapping in molecular media
- Ps: Exciton like theory
- Decoherence of the $e^+ - e^-$ pair state

3^{rd} body influence:

- trapped electrons,
- polarized medium surrounding the free volume,
- molecular electrons from free volume walls.

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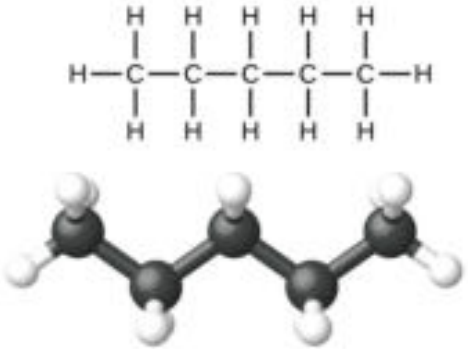
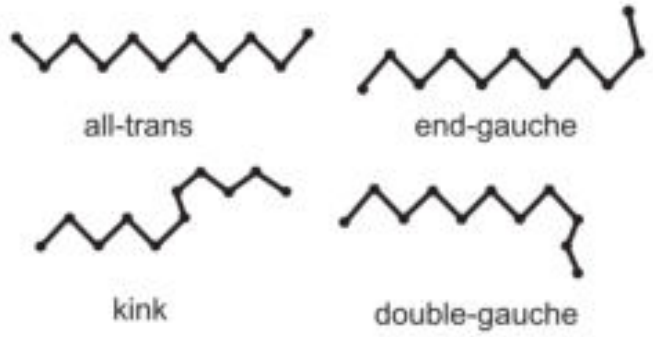
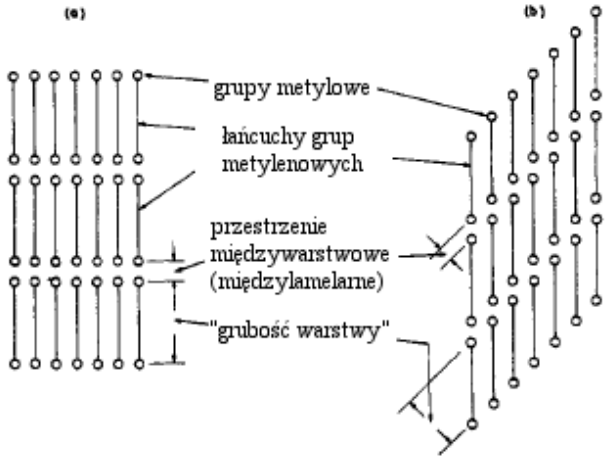
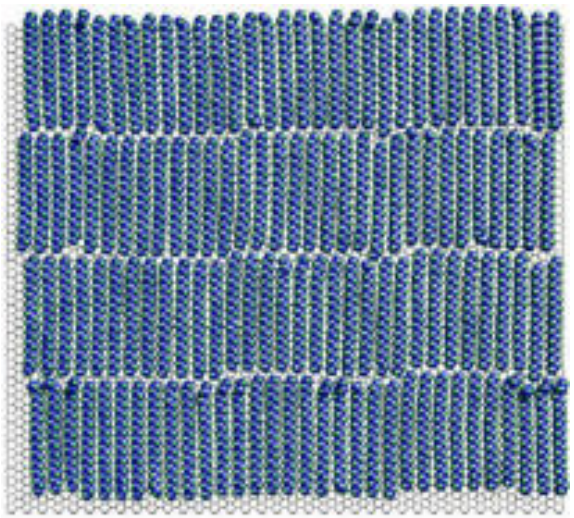
Introduction: molecular medium: n-alkanes

Chain lengths: C6-C36 Melting temp. range: -95.3° – +76.5°

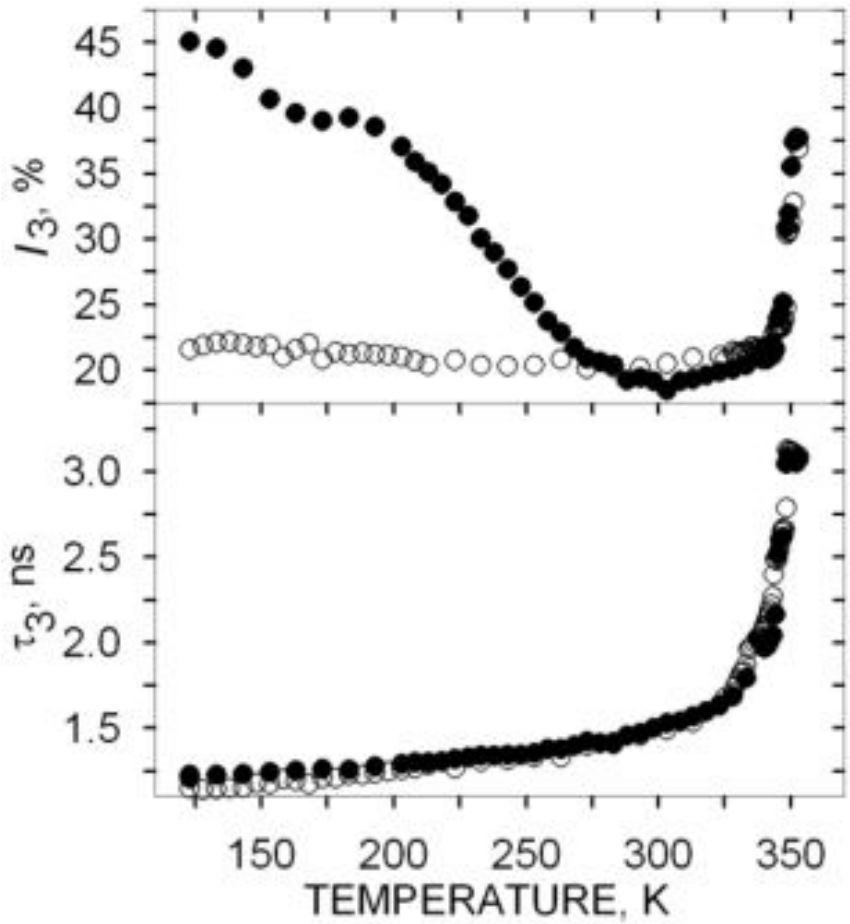








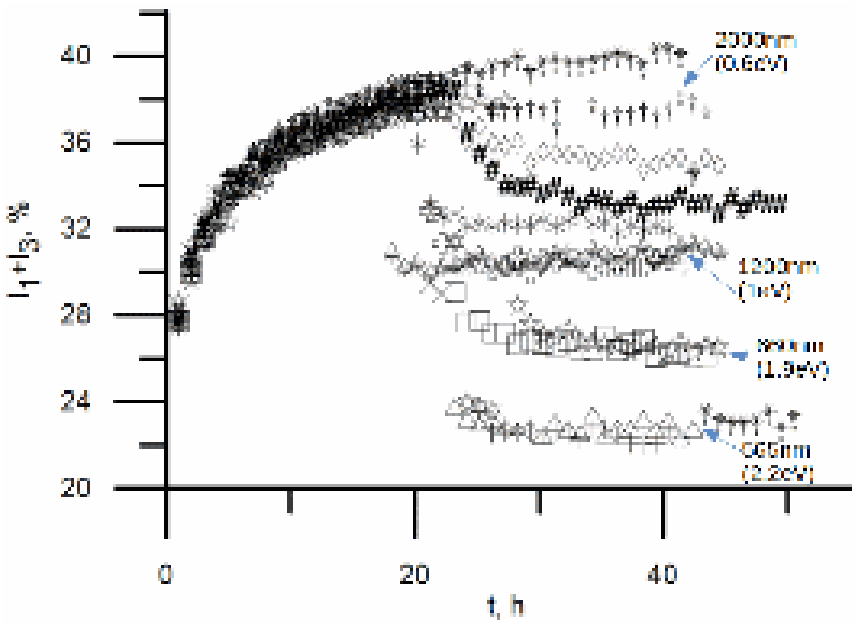
Experimental analysis of electron trapping in alkanes



- Trapped e^- is an example of 3rd body influence on Ps formation
- Trapped electrons have a great contribution in Ps intensity in alkanes
- Energy of their binding determines whether the creation of Ps is profitable or not and what is the energy excess durigng the Ps formation.

Discrete levels of traps energy in alkanes

C7, -140°C

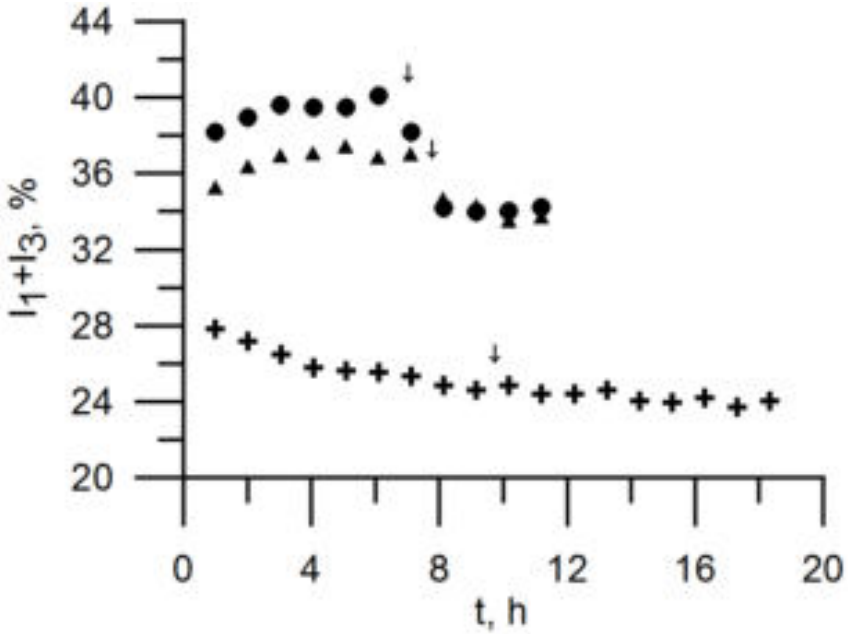


- Discrete energy levels:
  0.6 eV, 1.0 eV, 1.9 eV, 2.2 eV
- Min. quanta energy tested: 0.56 eV (2200nm)
- Max. quanta energy tested: 3.4 eV (370nm)
- Traps depth is temp dependent
- Discrete struct. for even and odd alkanes

Hypothesis: Traps are related to intermolecular spaces (interlamellar gaps) or larger-scale volumes (inter-crystalline damains) but not to particular molecules.

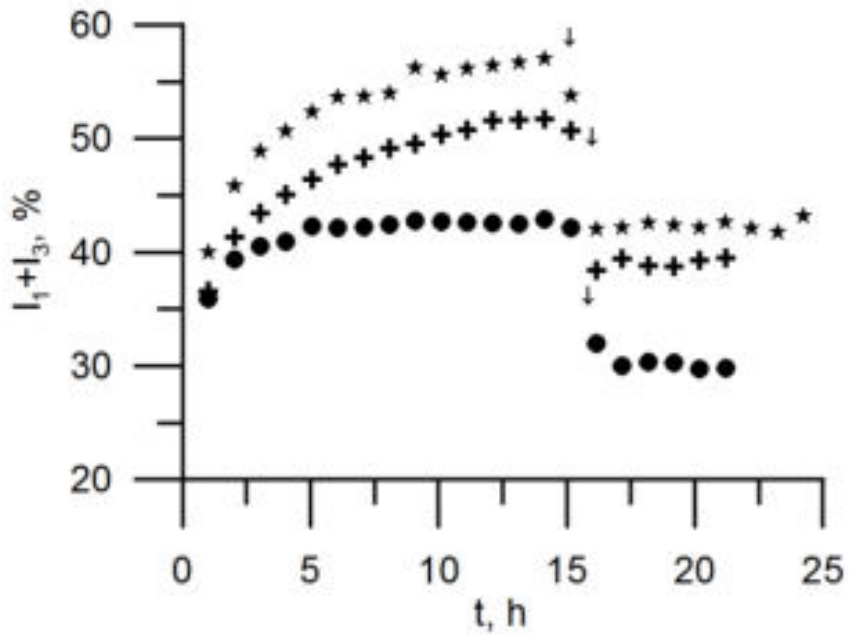
Traps are located mostly in interlamellar spaces

- Trapping depends on the admixture
- if $\frac{\text{chain length of comp. 1}}{\text{chain length of comp. 2}} > 1.22$ they start to crystalize separately



(●) C7,
(▲) C7+10% C8,
(✚) C7+10% C9.

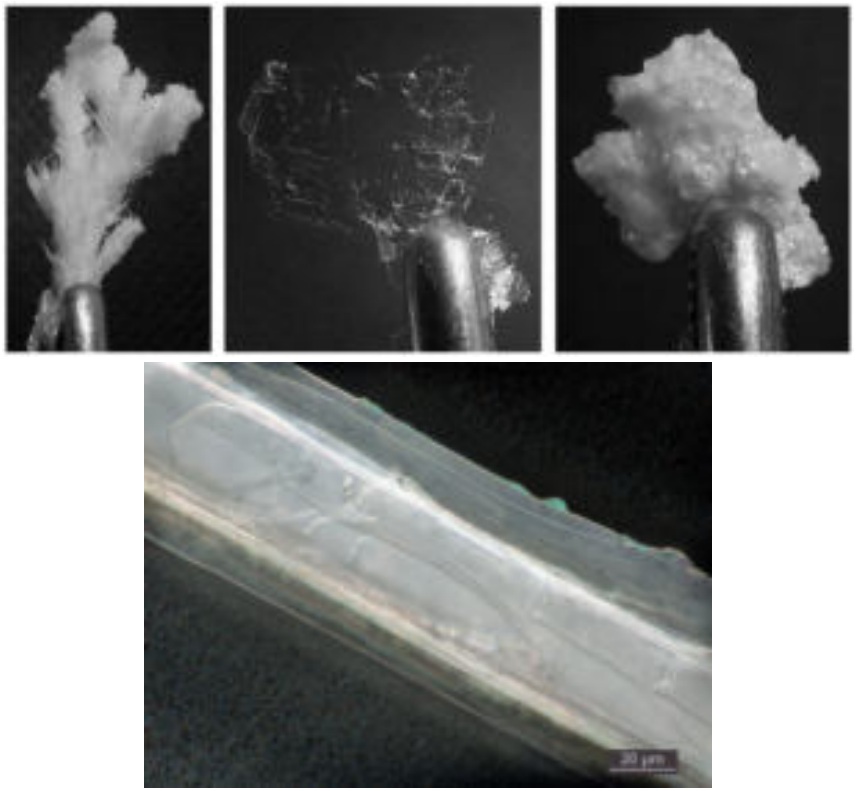
Trapping depends on the concentration of the admixture



(●) C7,
(✚) C7+10% C11,
(★) C7+20% C11.

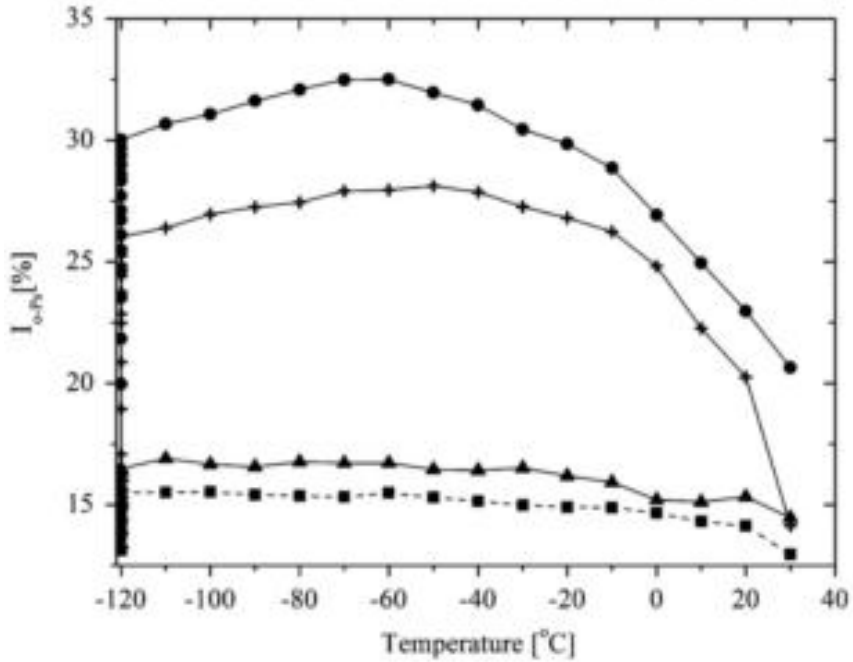
Traps are located in inter-domain spaces

Crystal morphology depends on crystalization conditions

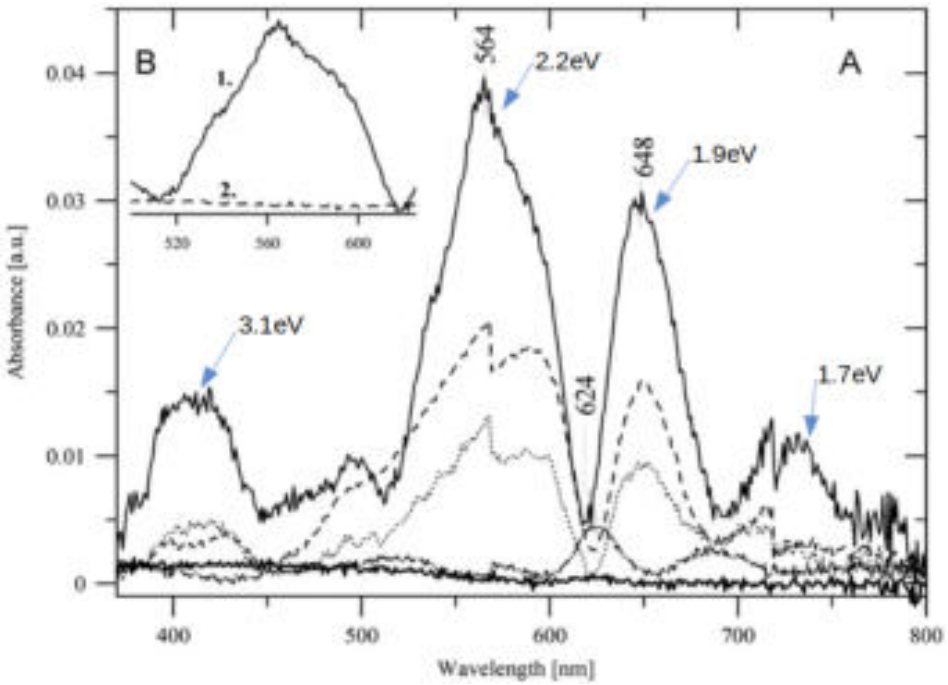


Trapping depends on the crystal morphology (of the same chemical)

No trapping in *powder*!

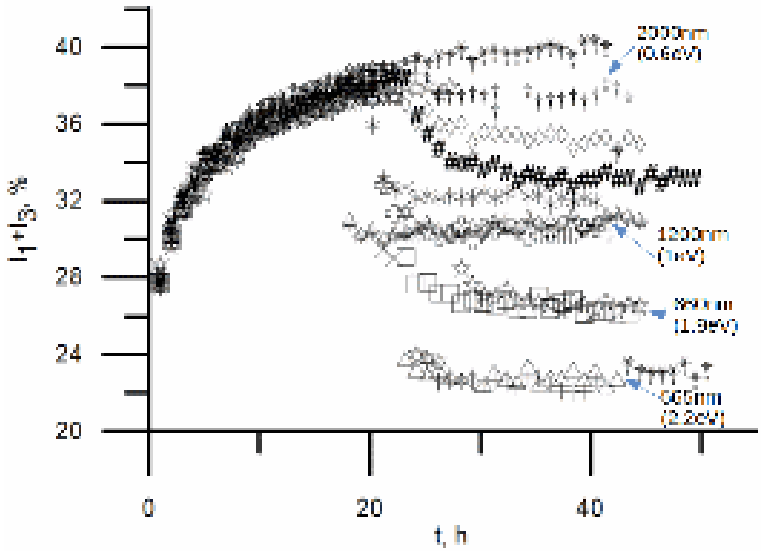


UV-Vis discrete spectrum: related (?) to e^-_{tr}



- UV-Vis spectra have a peaks
- Peaks position depends on both the morphology and temp.
- Peaks remain in a cool liquid
- Energies of peaks are: 1.7 eV, 1.9 eV, 2.2eV, 3.1eV

- Peaks energy coincide with the depth measured by quenching

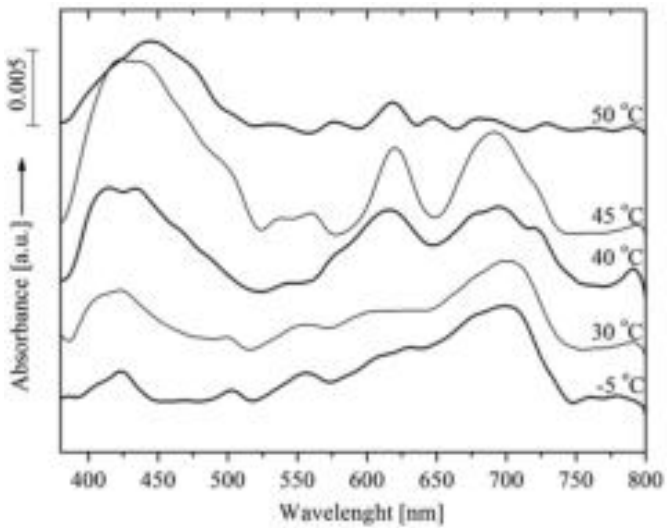


- There is also a more energetic peak not indicated by PALS

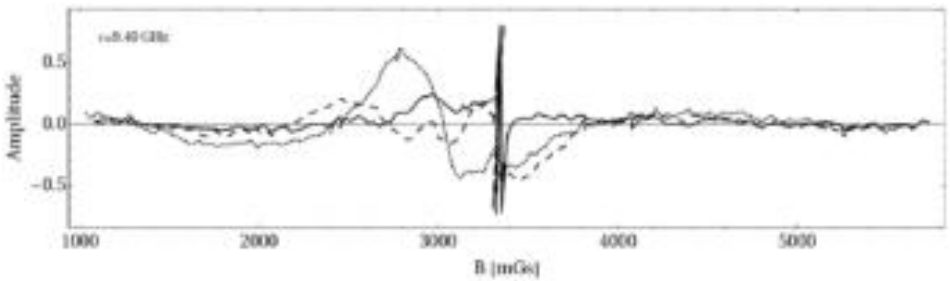
UV-Vis spectra, ESR: related (?) to e^-_{tr}

Peaks change their position and amplitude with:

- temperature,
- irradiation,
- const. magnetic field,
- electric field,
- charging negatively a container.



ESR measurement indicates, that:



- There are unpaired spins in samples,
- Their energy spectrum is smeared,
- The mobility of the spins are limited,
- spatial anisotropy of g-factor (anisotropic space),
- the number of spins is one per 10^5 molecules.

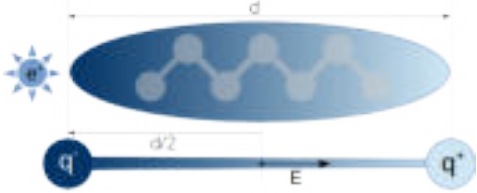
Numerical model of trapping e^+ and e^- in molecular media

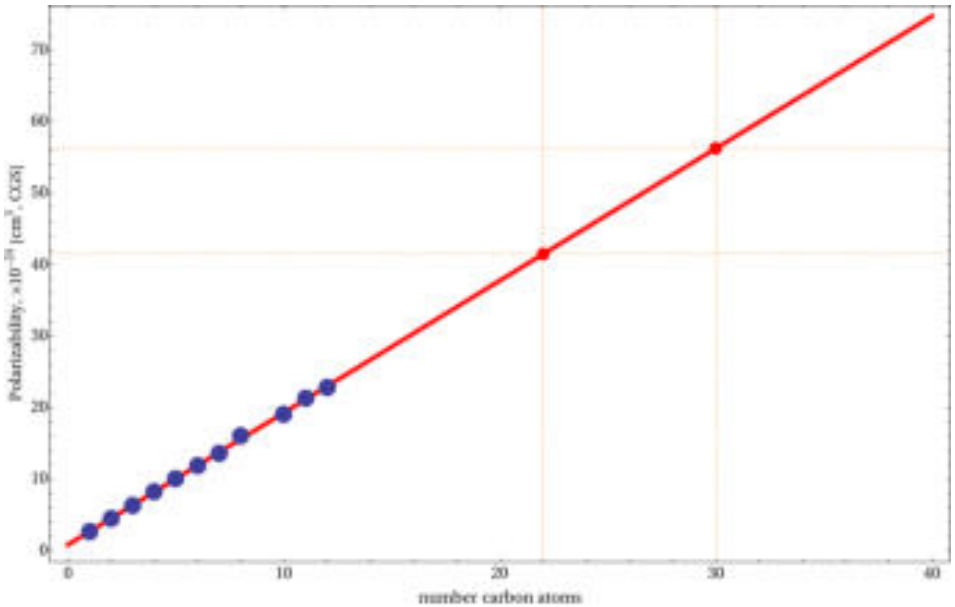
M. Pietrow: *Remarks on energetic conditions for positronium formation in non-polar solids. coupled dipole method application*; Phys. Chem. Chem. Phys. **17** 27726-27733, 2015.

Electron traps can be possibly described theoretically by e-m interactions of e^- with dipole moments of molecules.

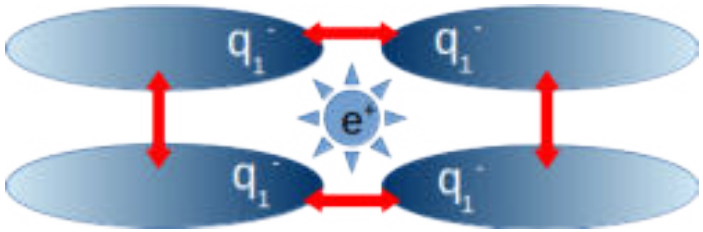
Definition: α

$$\vec{\mu}\ (\text{induced}) = \alpha\ \vec{E}$$



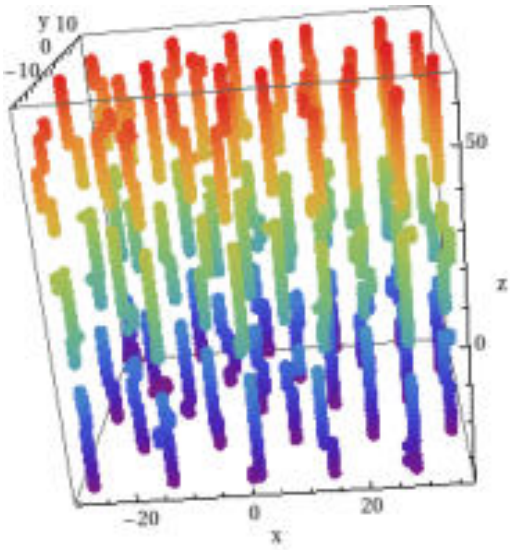


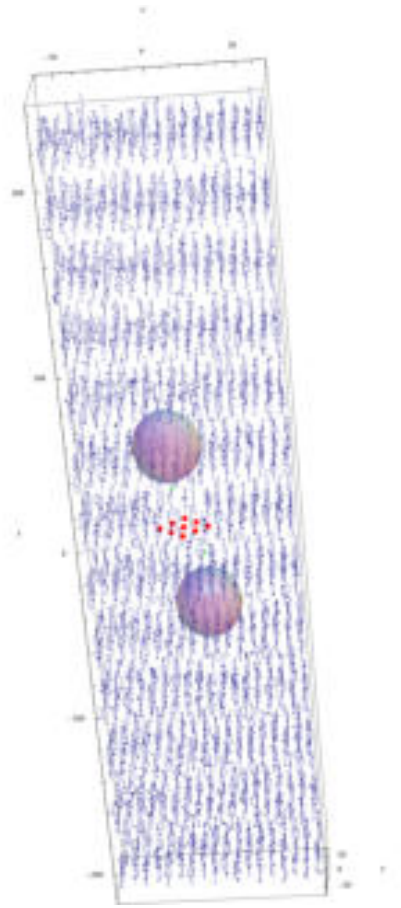
$$\mu = q\,d \quad \vee \quad \mu = \alpha\,E \quad \vee \quad E = \frac{ke}{(d/2)^2}$$
$$\Rightarrow q = \frac{4k\alpha}{d^3}e = 0.05e$$



Simulating docosane crystal

molecules are split into chunks



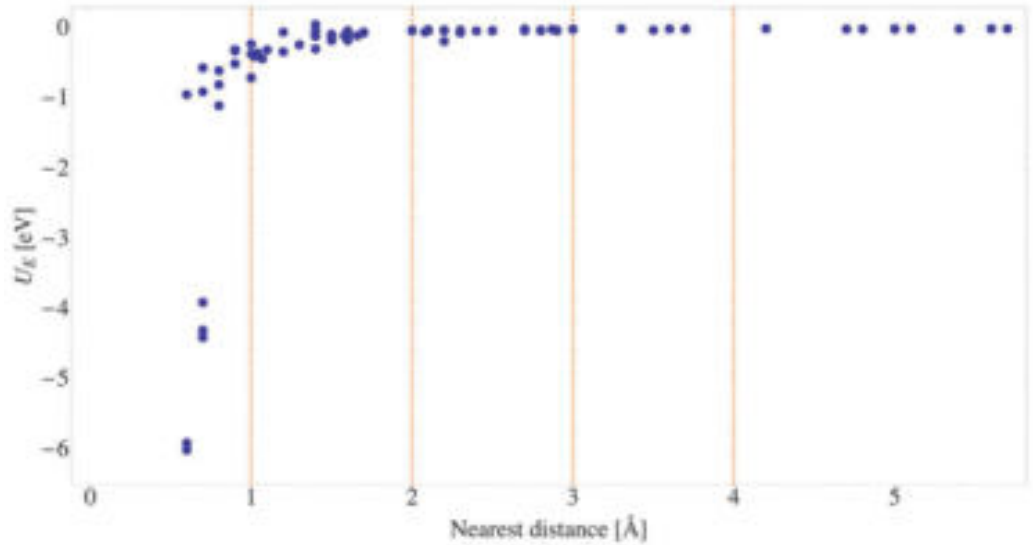


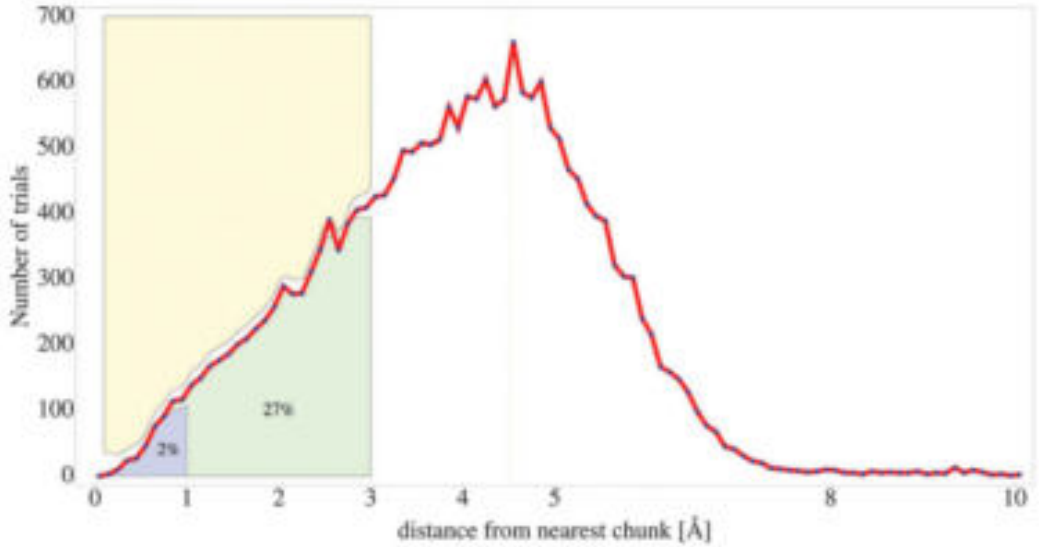
Coupled Dipole Method (CDM) Hamiltonian:

$$H = \frac{1}{2}\sum_{i=1}^{N} \mathbf{k}_i \cdot \mathbf{m}_i^{-1} \cdot \mathbf{k}_i + \frac{1}{2}\sum_{i,j=1}^{N} \mathbf{d}_i \cdot \mathbf{q}_i \cdot (\alpha_i^{-1}\delta_{ij} - \mathbf{T}_{ij}) \cdot \mathbf{q}_j \cdot \mathbf{d}_j - \sum_{i=1}^{N} (\mathbf{q}_i \cdot \mathbf{d}_i) \cdot \mathbf{E}_0$$

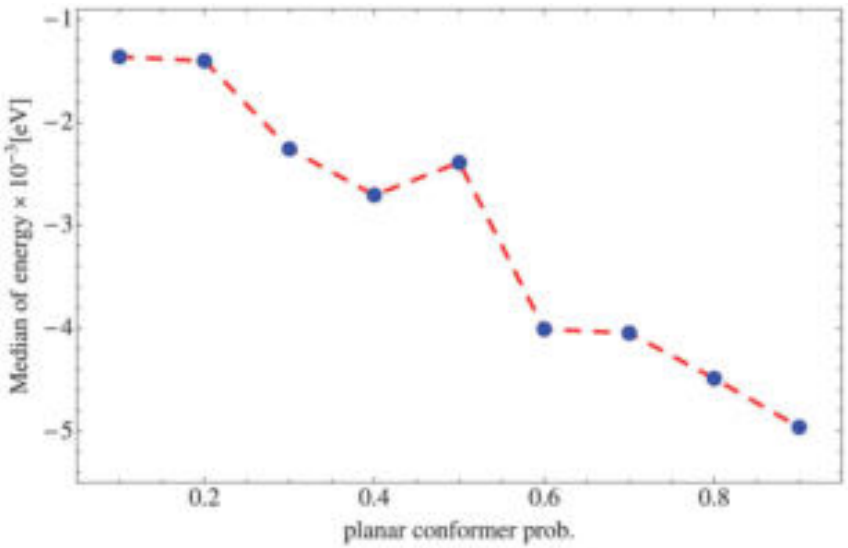
B.W. Kwaadgras, R. van Roij, M. Dijkstra: J. Chem. Phys. **140**, 154901 (2014).

CDM: energy and distance statistics



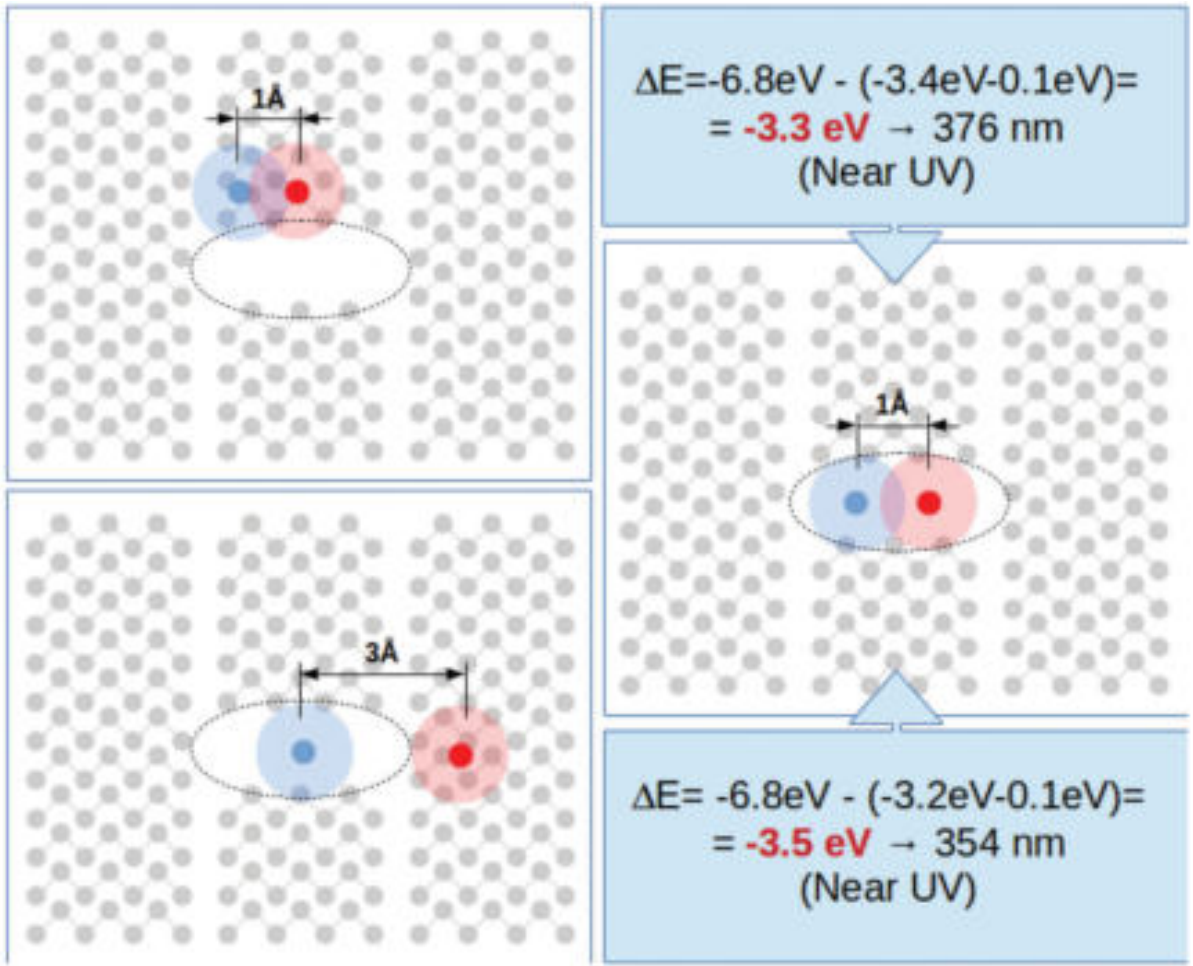


CDM: non-planar conformers



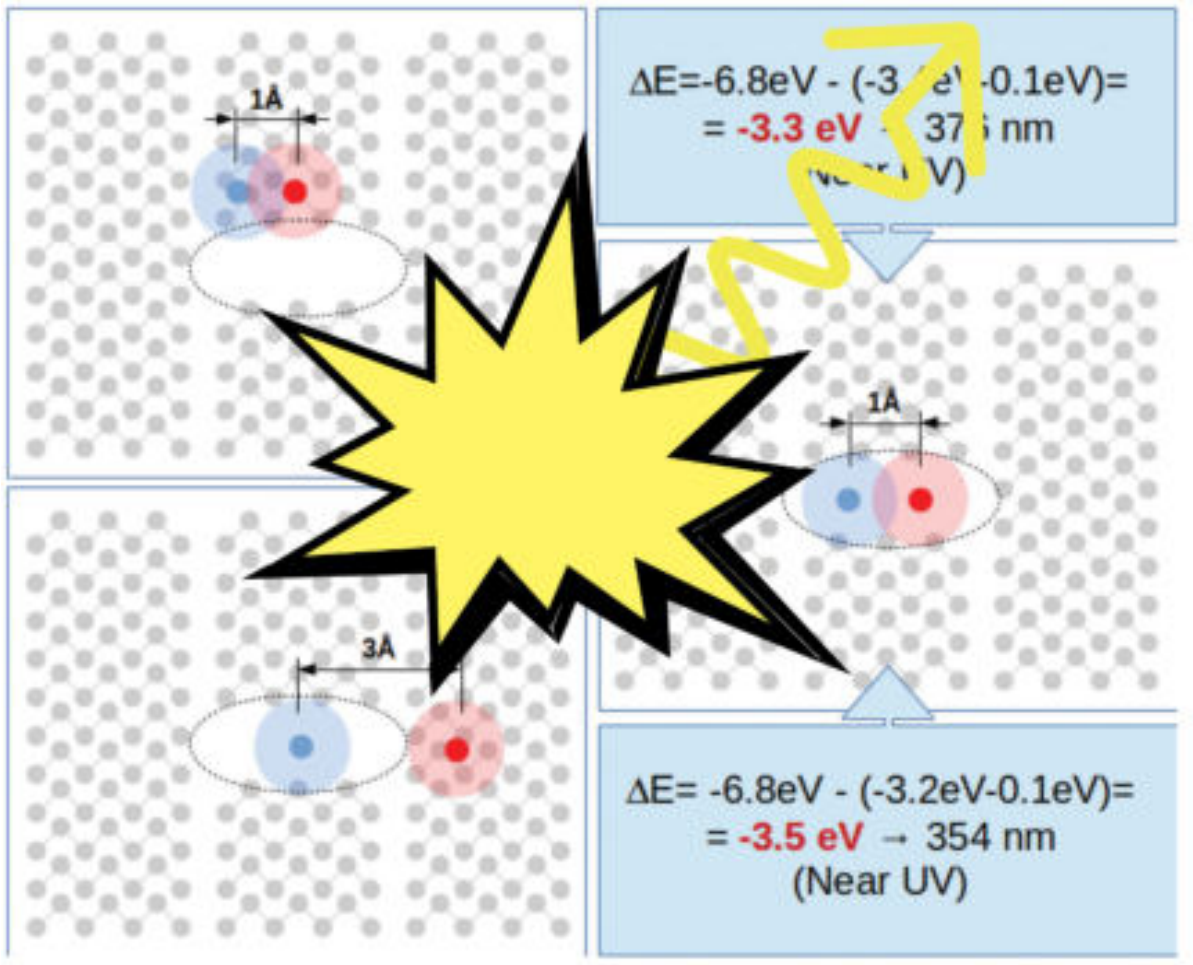
- CDM based on induced dipole idea gives expected eneries of trapping
- it allows to consider many charged particles at the same time
- Indirect relation of traps with conformers: the more non-planar conformers, the lower bound energy $\longrightarrow$ compatibility with experimental fact of dissapearing trapped electrons with temp.

CDM: $e^+ - e^-$ pair energy in alkane



$e^+ - e^-$ pair energy in alkane. Photonic deexcitation?

M. Pietrow, R. Zaleski, A. Wagner, P. Słomski, E. Hirschmann, R. Krause-Rehberg, M. Liedke, M. Butterling, and D. Weinberger: *An experimental investigation of light emission produced in the process of positronium formation in matter*; Phys. Chem. Chem. Phys. **23** 11264-11271, 2021.



Ps: Exciton like theory

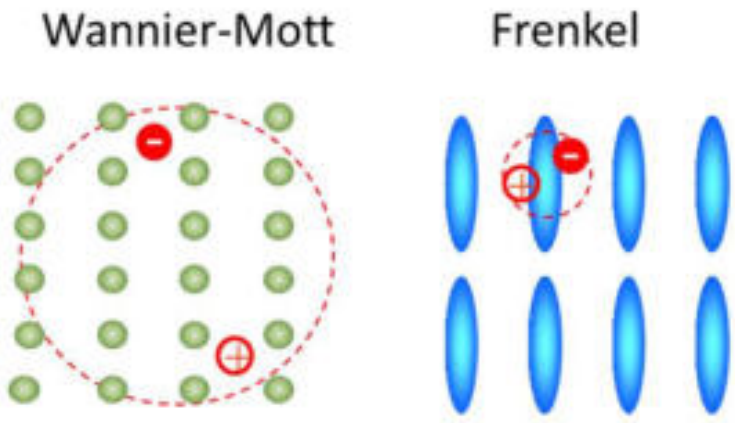
M. Pietrow: *Application of the theory of excitons to study the formation of positronium and optical transition in matter*; J. Phys. Chem. Solids **115** 307-310, 2018.

Many-body approach:

- S.V. Stepanov, D.S. Zvezhinskiy, V.M. Byakov: ***Beyond the Point Ps Approximation***; Mater. Sci. Forum **733** 7-14 (2013).
- G. Tanzi Marlotti, F. Castelli, G. Consolati: ***Numerical Solution of a Two-Particle Model of PositroniumConfined in Small Cavities***; Acta Phys. Polon. A **132** 1575-1578 (2017).
- . . .

Ekscyton Wanniera-Motta i Frenkela

Exciton is a quasi-particle formed by a bound state of an electron and an electron hole which are attracted to each other by the electrostatic Coulomb force.



Electron is attracted by the hole and repelled by other electrons which stabilizes its size and energy. The Wannier-Mott exciton corresponds to large dielectric constant.

Motta-Wannier exciton – hydrogen-like atom

The Wannier-Mott exciton is described by Schrödinger equation assuming:

- effective mass approximation,
- macroscopic dielectric constant.

$$\left[\frac{\mathbf{p}_e^2}{2m_e^*} + \frac{\mathbf{p}_h^2}{2m_h^*} - \frac{e^2}{4\pi\epsilon_0\epsilon_r|\mathbf{r}_e - \mathbf{r}_h|}\right]\Psi = E\,\Psi$$

which allows for variable separation $\rightarrow$ $\boxed{E = \Lambda(K) + E_n}$

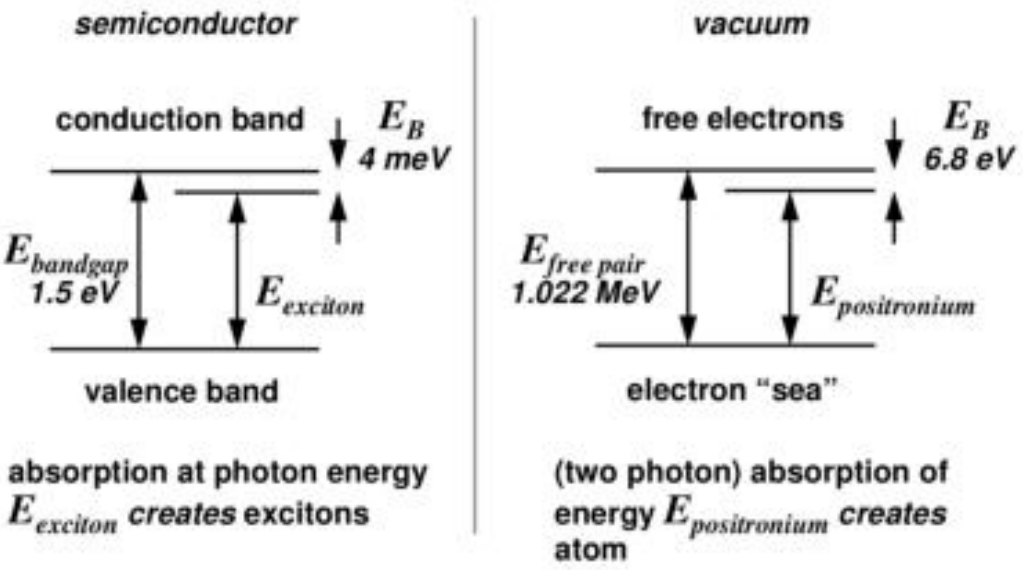
Elliott, Phys. Rev. 108, 1384 (1957)

Si	14.7 meV	KCl	400
Ge	4.15	BaO	56
CdSe	15	LiF	1000

$E > kT \rightarrow$ quasi-free quasi-particle.

Exciton vs. Ps

Analogy:



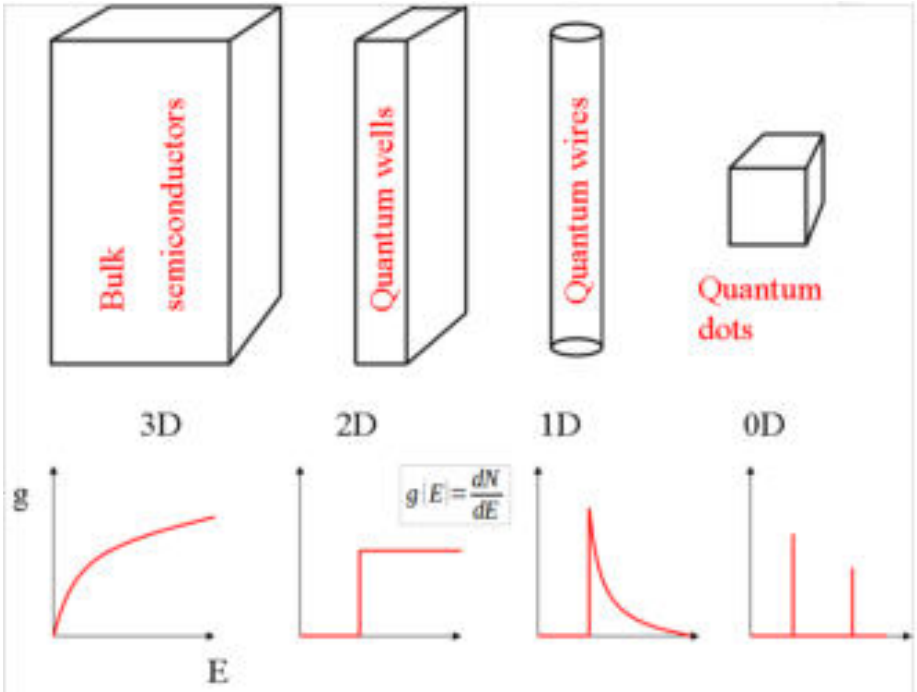
Both Ps and Wannier-Mott exciton have:

- spherical symmetry,
- similar size,
- may have either parallel or anti-parallel spins,
- are unstable.

Quantum dot

Confined volume induces dicretization of momentum and energy

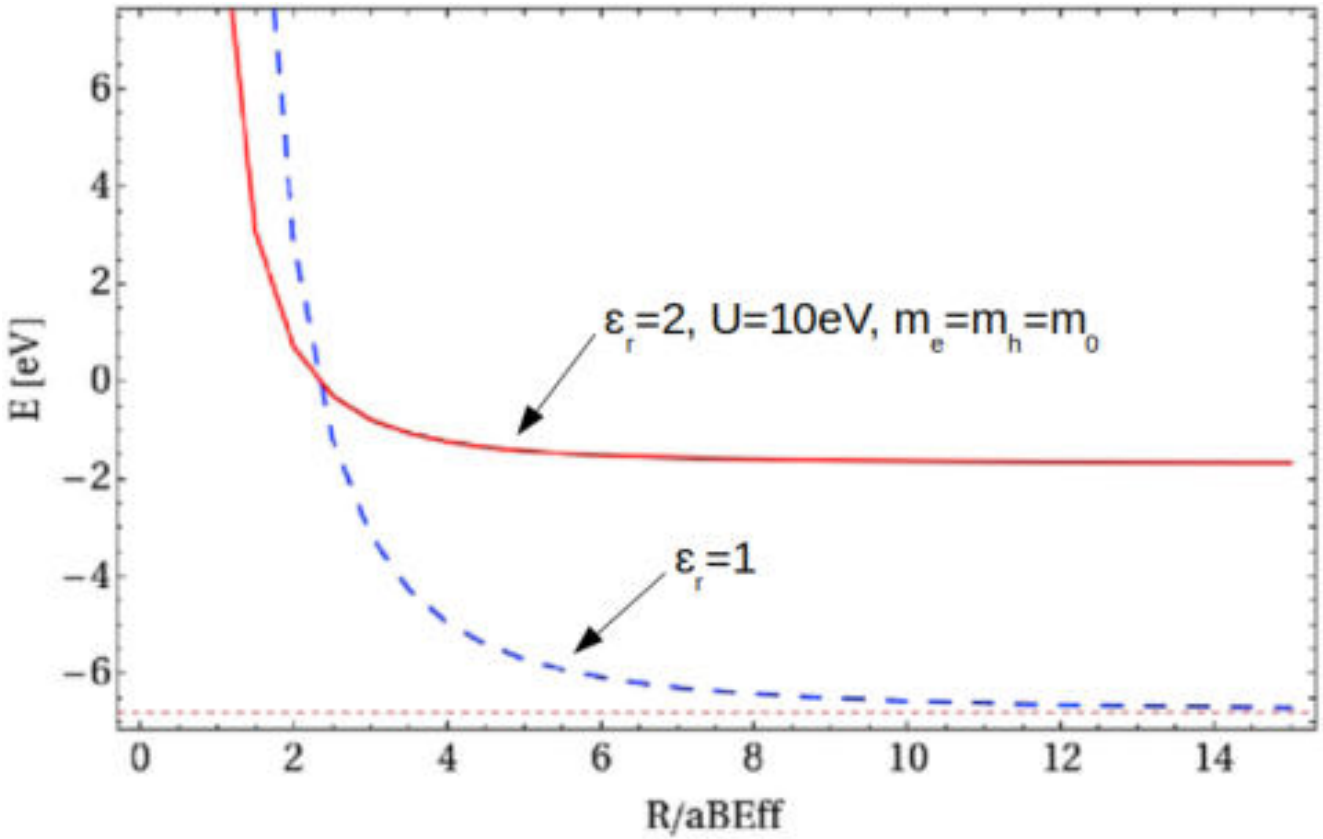
- Quantum dot – 3D confined space,
- Quantum wire – 2D confined space,
- Quantum well – 1D confined space.



Finite potential well, variational method: application to Ps

For confined states, the infinite potential wells give unrealistic results

Y. Kayanuma, H. Momiji: Phys. Rev. B 41, 10261 (1990)

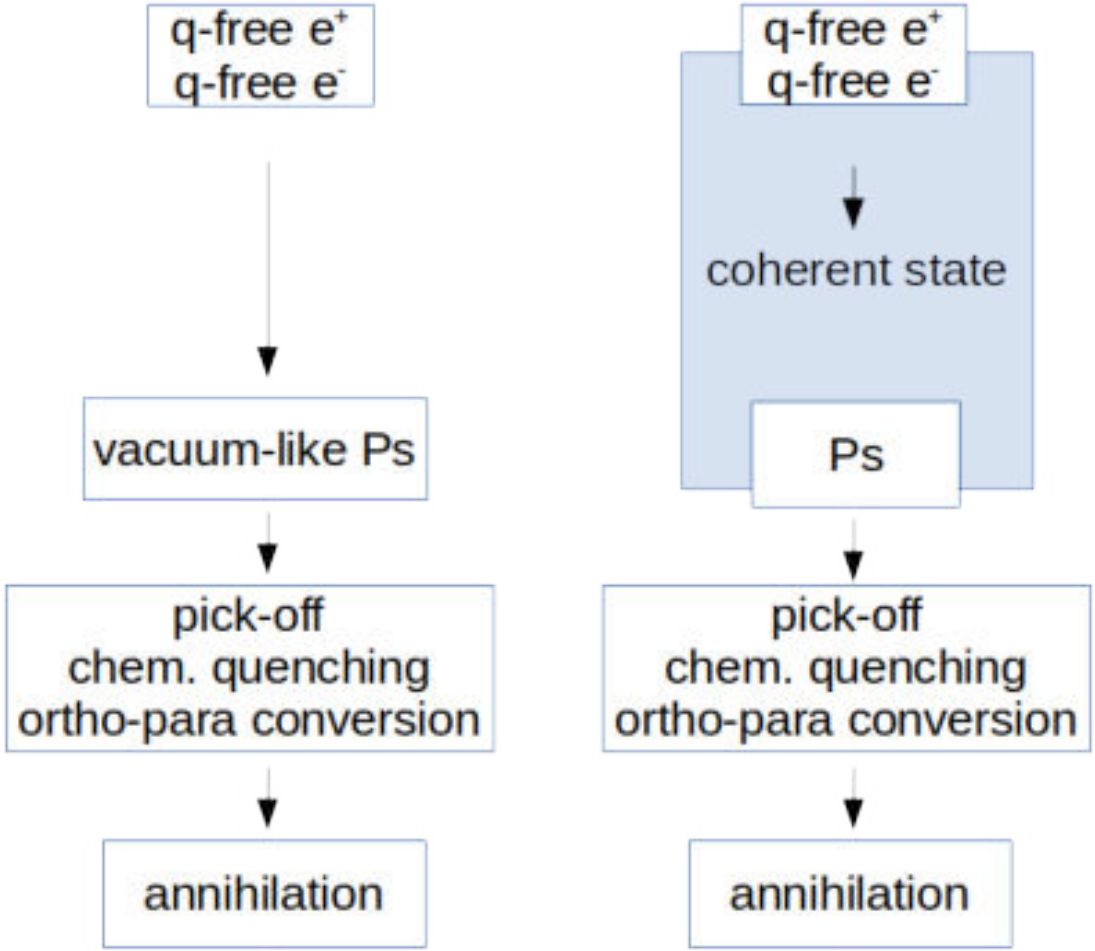


Typical ϵ_r for alkanes is 2 whereas for alcohols $\epsilon_r \simeq$10.

Decoherence

M. Pietrow and P. Słomski: *The role of positronium decoherence in positron annihilation in matter*; Phys. Lett. A **375** 3872-3876, 2011.

As long as there exists a definite phase relation between different (spin) states, the system is said to be coherent.



Decoherence of the $e^+ - e^-$ pair state

QED processes are PC – invariant. It leads to a selection rule for Ps decay

$$(-1)^{L+S} = (-1)^n$$

Some facts:

- Energy difference between p-Ps and o-Ps is $8.4 \cdot 10^{-4}$ eV ($kT \simeq 2.5 \cdot 10^{-2}$eV). Ps can exist in the cohered state of spins.
- $e^+ - e^-$ interactions with paired orbital electrons do not prefer p-Ps, o-Ps basis and can change the spin.

Does it lead to the p-Ps and o-Ps?

How long does it take?

Decoherence of the e^+ – e^- pair state

Assume permanent interaction of e^+ – e^- with N electron spins

$$H_{int} = J\frac{\hbar^2}{4}\sum_{i=3}^{N+2}\bar{\sigma}^{(2)}\circ\bar{\sigma}^{(i)},$$

$\rho_0 \equiv |\Psi_0\rangle\langle\Psi_0|$

$|\Psi_0\rangle = |Ps\rangle_0 \prod_{i=3}^{N+2}|s_i\rangle \equiv |Ps\rangle_0|S\rangle$

$|Ps\rangle_0 = \frac{1}{2}(|0,0\rangle + |1,-1\rangle + |1,0\rangle + |1,+1\rangle)$

$\rho(t) = |\Psi_t\rangle\langle\Psi_t|$

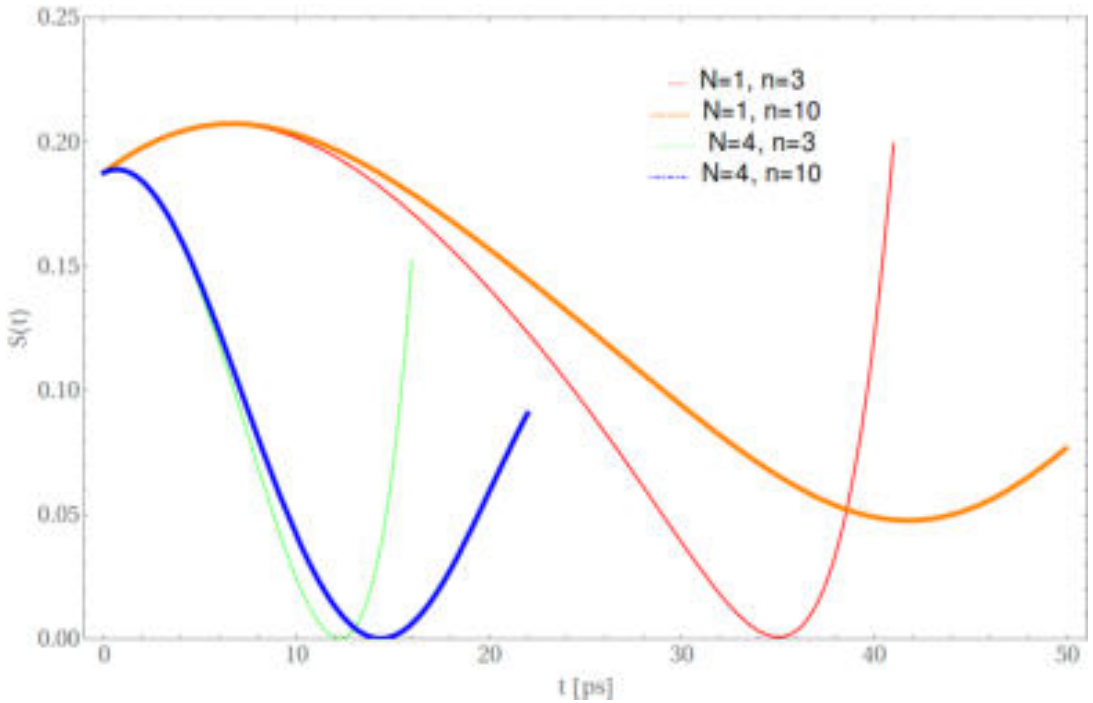
$|\Psi_t\rangle = e^{-iHt/\hbar}|\Psi_0\rangle \simeq \sum_{j=0}^{n}\frac{1}{j!}(-\frac{itH}{\hbar})^j\ |\Psi_0\rangle$

$\rho_{Ps}(t) = Tr_{env}[\rho(t)]$

Decoherence of the $e^+ - e^-$ pair state: Results

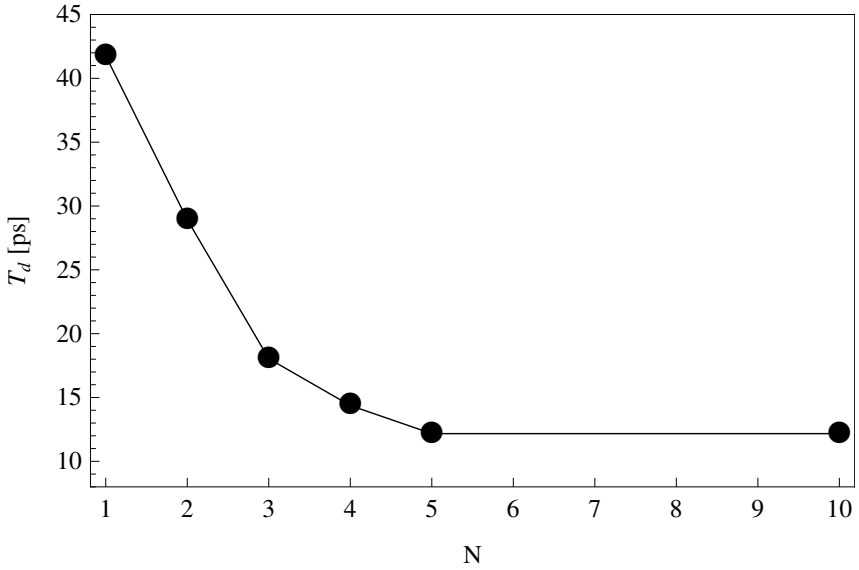
The measure of nondiagonality

$$S(t) = \sum_{s_z=-1}^{+1} |\langle s=0|\rho_{Ps}(t)|s=1,s_z\rangle|^2$$



Decoherence of the $e^+ - e^-$ pair state

T_d decreases with N

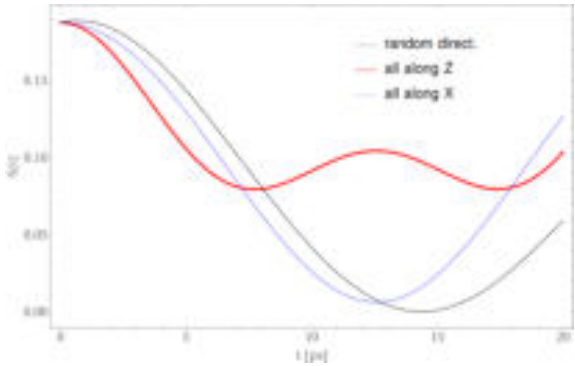


Here, J in H_{int} is set as 10^{-4} eV (ortho-para conversion energy).

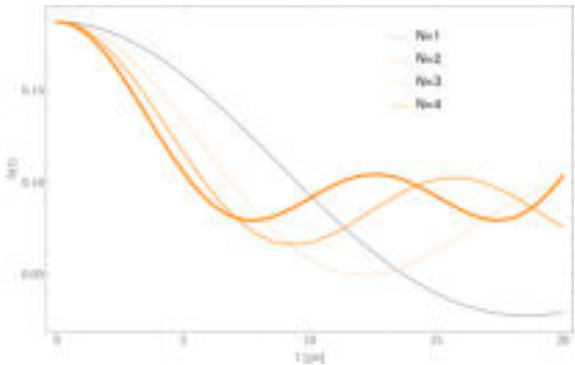
However, if J=10^{-5} eV and $N = 3$

$\Longrightarrow$ $T_d \simeq$ 150 ps.

In a magnetic field (depending on its direction), the Ps maintains the coherence of *p*-Ps and *o*-Ps.



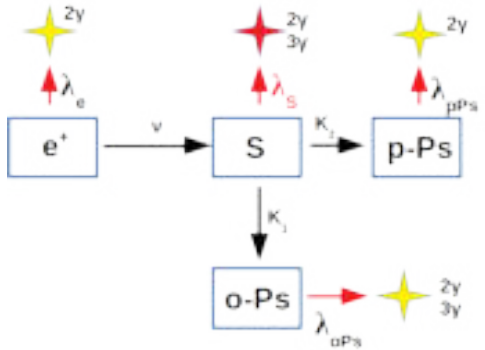
Magnetic field along the z-axis: oscillation freq. and amplitude dependes on the number of interacting particles



Decoherence of the $e^+ - e^-$ pair: Decay rate, PALS

Now, the dynamics of positron population is given by

$$\begin{cases} dP_e(t) = -(\lambda_e + \nu)P_e(t)dt, & P_e(0) = 1, \\ dS(t) = \nu P_e(t)dt - (\lambda_S + K)S(t)dt, & S(0) = 0, \\ d(oPs)(t) = K_1\ S(t)dt - \lambda_{oPs}(oPs)(t)dt, & (oPs)(0) = 0, \\ d(pPs)(t) = K_2\ S(t)dt - \lambda_{pPs}(pPs)(t)dt, & (pPs)(0) = 0 \end{cases}$$



where $K_1 + K_2 = K$.

Now in PALS, the gamma spectra are modified

$$dN_\gamma \sim -dP_e^{(\lambda_e)} - dS^{(\lambda_S)} - d(pPs)^{(\lambda_{pPs})} - d(oPs)^{(\lambda_{oPs})}.$$

Summary

- Considerable account of trapped electron in Ps formation in alkanes was shown
  - Traps have discrete spectrum of energies,
  - Traps are located in intermolecular spaces and inter-domain regions of crystals,
  - Both the pre-existing traps and the dynamically-made traps are possible,
  - Trapped e^- give UV-Vis absorbance and the ESR signal.
- Non-quantum numerical modelling of traps based on induced dipoles was elaborated
  - Increasing number of non-planar conformers produce shallower traps and explains decreasing Ps intensity preceding the melting temps.,
  - Excess energy during the Ps formation is estimated including the influence of medium polarization,
- Quantum model of $e^+ - e^-$ interaction with a medium was shown. Ps in a free volume can be undersood as exciton in quantum dot. Polarization of a medium can greatly distort a vacuum-like Ps state
- Time scale of decoherence of Ps state caused by interaction with orbital electrons is estimated■