物質デザインへの展開のための量子多成分系分子理論の高度化

2013年7月9日(火)
@東京大学本郷キャンパス武田先端知ビル
「コンピューティクスによる物質デザイン：
複合相関と非平衡ダイナミクス」

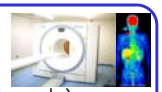
横浜市立大学
大学院生命ナノシステム科学研究科
立川仁典・北幸海

Overview

·Multi-Component (MC) system

- **Electron & Proton**
  - Hydrogen bonding
  - Proton transfer

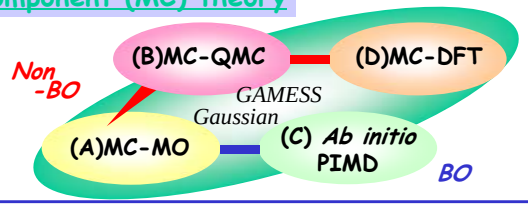
- **Electron & Positron**
  - Positronic compound
  - PET (Positron Emission Tomography) for Cancer diagnosis (http://www.shinyokohama.jp/)



- ***However ...*** *in the conventional first-principles calculation, nuclear quantum effect can not be taken into account directly.*

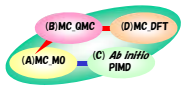
How *can we combine quantum effect of both electrons and nuclei?*

·Multi-Component (MC) theory

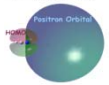


Outline

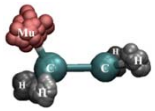
1. **Introduction**
   - エキゾチック分子系



2. 多成分系手法による陽電子化合物への応用
   - ニトリル化合物への陽電子親和力



3. 経路積分法によるミューオン化合物への応用
   - ミュオン化エチルラジカルのHFCC



4. **Summary & 今後の展望**

1. エキゾチック分子系

- エキゾチック粒子

	e^- (電子)	e^+ (陽電子)	μ^+ (ミューオン)	p^+ (プロトン)
Charge	-1	+1	+1	+1
Mass	1	1	207	1836

陽電子化合物
- 電子・陽電子対消滅
- 陽電子親和力(PA)

ミューオン化合物
- ミュオニウム(Mu)：束縛状態(μ^+e^-)
- ^1H 原子の最軽量同位体 $^{0.113}H$

小さな質量 → 量子効果の寄与

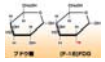
2. Introduction: Positron

Positron (e^+):

- A positron was found by C.D.Anderson in 1932.
- A positron is an antiparticle of an electron (e^-) (charge= +1, mass= 1, spin= 1/2)

Application:

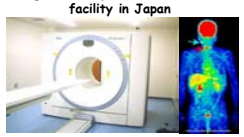
- Material science:
  Band structure and lattice defect of metal and semiconductor
- Medical science:
  Cancer diagnosis by PET
  (Positron Emission Tomography)



^{18}F-FDG :
2-fluoro-2-deoxy-D-glucose ($C_6H_{11}O_5F$)

However, detailed information is still unclear…

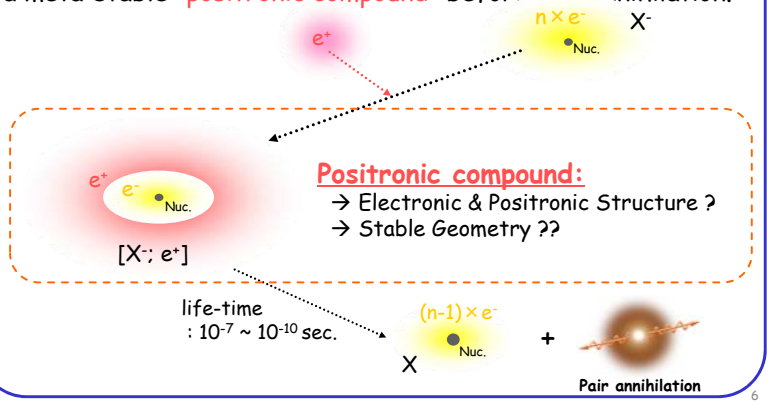
SPring-8; the synchrotron radiation facility in Japan



cite: http://www.shinyokohama.jp/

2. Introduction: Positronic compound

When a positron interacts with atom/molecule, they can form a meta-stable "positronic compound" before pair annihilation.



2. Experimental PA values !

Dipole enhancement of positron binding to molecules

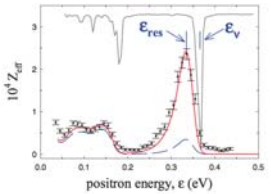
J. R. Danielson, J. J. Gosselin, and C. M. Surko
Department of Physics, University of California at San Diego, La Jolla, CA 92093
(Dated: May 12, 2010)

Measurements of positron-molecule binding energies are made for molecules with large permanent dipole moments (> 2.7 debye), by studying vibrational-Feshbach-mediated annihilation resonances as a function of incident positron energy. The binding energies are relatively large (e.g., ≥ 90 meV) as compared to those for similar sized molecules studied previously and analogous weakly bound electron-molecule (negative ion) states. Comparisons with existing theoretical predictions are discussed.

TABLE I: Measured and predicted positron- and electron-molecule binding energies ϵ_b (meV), permanent dipole moments μ (D) and dipole polarizabilities α (Å^3) for selected molecules. Data for μ and α taken from Ref. [26]. Data from Figs. 1-4 in bold.

Molecule	Formula	μ (D)	α (Å^3)	ϵ_b (meV) positrons meas.	pred.	electrons[g] meas.	pred.
carbon disulf.	CS_2	0	8.7	**75**		0.7	
butane	C_4H_{10}	0	8.2	40[a]			
methanol	CH_3OH	1.7	3.3	2[a]			
meth.-chloride	CH_3Cl	1.9	5.4	25[a]			
formaldehyde	H_2CO	2.3	2.8		19[g]		0.02
acetaldehyde	$(CH_3)HCO$	2.8	4.6	**90**		0.6	0.95
acetone	$(CH_3)_2CO$	2.9	6.4	**173**	4[c]	2.6	1.6
propanal	$(C_2H_5)HCO$	2.7	6.5			1.0	0.6
hydr. cyanide	HCN	3.0	2.5		35[a]	4	3.3
acetonitrile	CH_3CN	3.9	4.4	**180**	135[c]	19	15.5
lith. hydride	LiH	5.9	3.8		1000[f]	342	330

[a]Ref. [11], [b]Ref. [5], [c]Ref. [8], [d]Refs. [6, 7], [e]Ref. [15], [f]Ref. [3], [g]Meas. from Refs. [25, 27–29], pred. from Refs. [25, 30].



振動Feshbach共鳴(VFR)とIRスペクトルからの間接的な陽電子親和力(PA)の測定

2. Experimental PA values !

Dipole enhancement of positron binding to molecules

J. R. Danielson, J. J. Gosselin, and C. M. Surko
Department of Physics, University of California at San Diego, La Jolla, CA 92093
(Dated: May 12, 2010)

Measurements of positron-molecule binding energies are made for molecules with large permanent dipole moments (> 2.7 debye), by studying vibrational-Feshbach-mediated annihilation resonances as a function of incident positron energy. The binding energies are relatively large (e.g., ≥ 90 meV) as compared to those for similar sized molecules studied previously and analogous weakly bound electron-molecule (negative ion) states. Comparisons with existing theoretical predictions are discussed.

TABLE I: Measured and predicted positron- and electron-molecule binding energies ϵ_b (meV), permanent dipole moments μ (D) and dipole polarizabilities α (Å^3) for selected molecules. Data for μ and α taken from Ref. [26]. Data from Figs. 1-4 in bold.

Molecule	Formula	μ (D)	α (Å^3)	ϵ_b (meV) positrons meas.	pred.	electrons[g] meas.	pred.
carbon disulf.	CS_2	0	8.7	**75**		0.7	
butane	C_4H_{10}	0	8.2	40[a]			
methanol	CH_3OH	1.7	3.3	2[a]			
meth.-chloride	CH_3Cl	1.9	5.4	25[a]			
formaldehyde	H_2CO	2.3	2.8		19[g]		0.02
acetaldehyde	$(CH_3)HCO$	2.8	4.6	**90**		0.6	0.95
acetone	$(CH_3)_2CO$	2.9	6.4	**173**	4[c]	2.6	1.6
propanal	$(C_2H_5)HCO$	2.7	6.5			1.0	0.6
hydr. cyanide	HCN	3.0	2.5		35[a]	4	3.3
acetonitrile	CH_3CN	3.9	4.4	**180**	135[c]	19	15.5
lith. hydride	LiH	5.9	3.8		1000[f]	342	330

[a]Ref. [11], [b]Ref. [5], [c]Ref. [8], [d]Refs. [6, 7], [e]Ref. [15], [f]Ref. [3], [g]Meas. from Refs. [25, 27–29], pred. from Refs. [25, 30].

J.R. Danielson, J.J. Gosselin, and C.M. Surko, Phys. Rev. Lett. 104, 233201 (2010).

2. Experimental PA values !

Dipole enhancement of positron binding to molecules

J. R. Danielson, J. J. Gosselin, and C. M. Surko
Department of Physics, University of California at San Diego, La Jolla, CA 92093
(Dated: May 12, 2010)

Measurements of positron-molecule binding energies are made for molecules with large permanent dipole moments (> 2.7 debye), by studying vibrational-Feshbach-mediated annihilation resonances as a function of incident positron energy. The binding energies are relatively large (e.g., ≥ 90 meV) as compared to those for similar sized molecules studied previously and analogous weakly bound electron-molecule (negative ion) states. Comparisons with existing theoretical predictions are discussed.

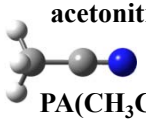
TABLE I: Measured and predicted positron- and electron-molecule binding energies ϵ_b (meV), permanent dipole moments μ (D) and dipole polarizabilities α (Å^3) for selected molecules. Data for μ and α taken from Ref. [26]. Data from Figs. 1-4 in bold.

Molecule	Formula	μ (D)	α (Å^3)	ϵ_b (meV) positrons meas.	pred.	electrons[a] meas.	pred.
carbon disulf.	CS_2	0	8.7	**75**		0.7	
butane	C_4H_{10}	0	8.2	40[a]			
methanol	CH_3OH	1.7	3.3	2[a]			
meth.-chloride	CH_3Cl	1.9	5.4	25[a]			
formaldehyde	H_2CO	2.3	2.8		19[b]		0.02
acetaldehyde	$(CH_3)HCO$	2.8	4.6	**90**		0.6	0.95
acetone	$(CH_3)_2CO$	2.9	6.4	**173**	4[c]	2.6	1.6
propanal	$(C_2H_5)HCO$	2.7	6.5			1.0	0.6
hydr. cyanide	HCN	3.0	2.5		35[d]	4	3.3
acetonitrile	CH_3CN	3.9	4.4	**180**	135[e]	19	15.5
lith. hydride	LiH	5.9	3.8		1000[f]	342	330

[a]Ref. [11], [b]Ref. [5], [c]Ref. [8], [d]Refs. [6, 7], [e]Ref. [15], [f]Ref. [3], [g]Meas. from Refs. [25, 27–29], pred. from Refs. [25, 30].

J.R. Danielson, J.J. Gosselin, and C.M. Surko, Phys. Rev. Lett. 104, 233201 (2010).

acetonitrile



PA(CH_3CN)=180 meV

- *Theoretical reproduction for PA values!*
- *Development of theoretical procedure!*

9

2. Multi-Component MO (MC_MO)

10

- Total Hamiltonian (N electron, 1 positron, M fixed nuclei):

$$H_{tot} = \sum_{i=1}^{N} h^e(i) + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} + h^p(p) - \sum_{i=1}^{N} \frac{1}{r_{pi}}$$

$$h^e(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}}, \qquad h^p(p) = -\frac{1}{2}\nabla_p^2 + \sum_{A=1}^{M} \frac{Z_A}{r_{pA}},$$

- Total wavefunction:

$$|\Psi_{tot}\rangle = C_{00}|\Phi_0^e\rangle|\Phi_0^p\rangle + \sum_{IJ}{}' C_{IJ}|\Phi_I^e\rangle|\Phi_J^p\rangle \qquad |\Phi_0^e\rangle|\Phi_0^p\rangle \longrightarrow \text{Hartree-Fock}$$

$$\sum_{IJ}{}' C_{IJ}|\Phi_I^e\rangle|\Phi_J^p\rangle \longrightarrow \text{Configuration Interaction}$$

1. Hartree-Fock (HF) equations:

Electrons: $f^e\varphi_i^e = \varepsilon_i^e\varphi_i^e \qquad f^e = h^e + \sum_i^N (J_i - K_i) - J_p$

Positron : $f^p\varphi_p^p = \varepsilon_p^p\varphi_p^p \qquad f^p = h^p - \sum_i^N J_i$

2. Multi-Component MO (MC_MO)

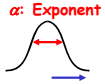
11

2. LCAO expansion → HF Roothaan equations:

Electrons: $\varphi_i^e = \sum_\mu \chi_\mu^e C_{\mu i}^e \qquad \mathbf{F}^e\mathbf{C}^e = \mathbf{S}^e\mathbf{C}^e\boldsymbol{\varepsilon}^e$

Positron: $\varphi_p^p = \sum_\mu \chi_\mu^p C_{\mu p}^p \qquad \mathbf{F}^p\mathbf{C}^p = \mathbf{S}^p\mathbf{C}^p\boldsymbol{\varepsilon}^p$

α: Exponent



R: Center

[*] STF: I. L. Thomas, PR (1969). ECG: L. Adamowicz, PRL (2002). GTF: H. Nagao, IJQC (1996), Y. Shigeta, JCP (1999), H. Nakai, JCP (2003), S. Hammes-Schiffer, JCP (2005), C.D.Sherrill, MP (2004). DFT: E. K. U. Gross, PRL (2001).

3. Correlation: Configuration Interaction (CI)

$$H_{tot} = \sum_{i=1}^{N} h^e(i) + \underbrace{\sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}}}_{E_{ee}} + h^p(p) - \underbrace{\sum_{i=1}^{N} \frac{1}{r_{pi}}}_{E_{ep}}$$

$$|\Psi_{tot}\rangle = C_{00}|\Phi_0^e\rangle|\Phi_0^p\rangle + \sum_{IJ}{}' C_{IJ}|\Phi_I^e\rangle|\Phi_J^p\rangle$$

|mn> : m-electron excitation [m0]; n-positron excitation [0n]; m-elec & n-pos excitation [mn]

[*] MP2: M. Tachikawa, K. Iguchi, and K. Suzuki, J. Chem. Phys. 101, 5925 (1995). Gradient: M. Tachikawa, K. Mori, H. Nakai, and K. Iguchi, Chem. Phys. Lett. 290, 437 (1998). CI: M. Tachikawa, Chem. Phys. Lett. 350, 269 (2001), Chem. Phys. Lett. 360, 494 (2002). MRCI: R. J. Buenker, M. Tachikawa, M. Kimura, et al., Phys. Rev. A73, 022705 (2006).

2. Multi Component QMC (MC_QMC)

12

試行関数Ψ_T： $\Phi = \Psi_{trial} = e^{J(R)}\Psi_{HF}(R)$

(A)多成分系MO法

$$f^e = h^e + \sum_i^{Ne}(J_i - K_i) - \sum_p^{Np} J_p$$

$$f^p = h^p + \sum_p^{Np}(J_p - K_p) - \sum_i^{Ne} J_i$$

(B)多成分系QMC法 (Jastrow因子)

$$J(R) = J(R_e, R_I, r_p) = \sum_i^N\sum_{j(>i)}^N \underbrace{u_{ij}(r_{ij})}_{e^- \text{-} e^-} + \sum_i^N\sum_I^M \underbrace{\chi_I(r_{iI})}_{e^- \text{-Nuc.}} + \sum_i^N\sum_{j(>i)}^N\sum_I^M \underbrace{f_{ijI}(r_{iI}, r_{jI}, r_{ij})}_{e^- \text{-} e^- \text{-Nuc.}} + \sum_i^N \underbrace{u_p(r_{ip})}_{e^- \text{-} e^+} + \sum_i^M \underbrace{\chi_p(r_{pI})}_{e^+ \text{-Nuc.}}$$

1.変分モンテカルロ[VMC]法：

・パラメータを含む試行関数を仮定し、変分原理に基づいて最適化。

2.拡散モンテカルロ[DMC]法：

・時間依存Schrödinger方程式の虚時間発展により、基底状態へ射影。

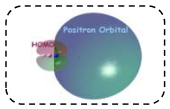
$$\lim_{\tau\to\infty} \Phi(R, \tau{=}it) \to \Psi_{Exact}(R)$$

公立大学法人 横浜市立大学 13

2. Multi Component QMC (MC_QMC)

- MC_QMC法による高精度計算:

[HCN;e⁺]



PA (Positron Affinity)
=E(X)-E([X;e⁺])

MC_MO(HF) -92.90074 (hartree)

[e⁻/e⁺= 6-311++G(2d,2p) /15s 15p 6d 2f]

-92.901915

CISD [*]

[e⁻: 6-311++G(2d,2p)
e⁺: 6-311++G(2d,2p)
+ 10s GTF (off-atom)]

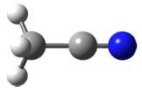
VMC
-93.2591(5)

DMC
-93.39830(8)[1]

PA(meV)	
HF	: +1.8
DMC	: +38(5)
CISD	: +36

- PAの実験値：
振動Feshbach共鳴を利用[**]

acetonitrile



PA(CH_3CN)=180 meV

[**] J. R. Danielson, J. J. Gosselin, and C. M. Surko, Phys. Rev. Lett. 104, 233201 (2010).

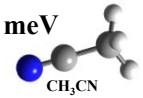
[*] H. Chojnacki and K. Strasburger, Mol. Phys. **104** 2273 (2006)
[1] Y. Kita, R. Maezono, M. Tachikawa, M. Towler, and R. J. Needs, J. Chem. Phys. **131** 134310 (2009)

公立大学法人 横浜市立大学

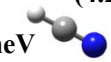
2. PAs of nitrile species

PA=135 meV
(4.23D)

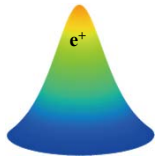
PA_{exptl}= 180 meV



PA=36 meV
(3.29D)



•Electronic 6-31++G(2df,2pd)
•Positronic [15s15p3d2f1g]
•CI ([10], [01], and [11])



Positron (e^+) adsorption

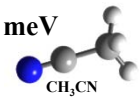
About 75% of the experimental PA value of 180 meV
by Danielson et al. [Phys. Rev. Lett. 104, 233201 (2010)].

公立大学法人 横浜市立大学

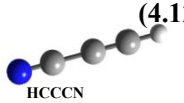
2. PAs of nitrile species

PA=135 meV
(4.23D)

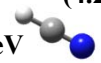
PA_{exptl}= 180 meV



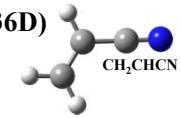
PA=87 meV
(4.12D)



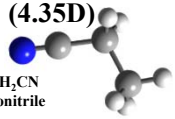
PA=36 meV
(3.29D)

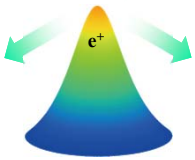


PA=155 meV
(4.36D)



PA=164 meV
(4.35D)





PA_{exptl}=225 meV

Positron (e^+) adsorption

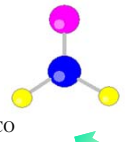
The PA values are strongly correlated with the dipole moments.

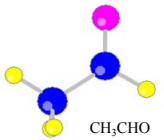
M. Tachikawa, Y. Kita, and R. J. Buenker, Phys. Chem. Chem. Phys., *13*, 2701 (2011).

YOKOHAMA CITY UNIVERSITY

2. PAs of CO species

PA=15 meV
(2.76D)

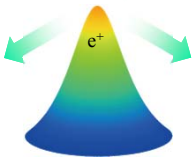




PA=52 meV
(3.13D)

PA_{exptl}=90 meV

PA=58 meV
(3.27D)



Positron (e^+) adsorption

PA=92 meV
(3.01D)

PA_{exptl}=173 meV

The PA values are strongly correlated with the dipole moments.

M. Tachikawa, Y. Kita, and R. J. Buenker, New J. Phys., 14, 035004 (10pages) (2012).

YOKOHAMA CITY UNIVERSITY

2. Future plan

J. R. Danielson, J. J. Gosselin, and C. M. Surko, Phys. Rev. Lett. 104, 233201 (2010).

TABLE I: Measured and predicted positron- and electron-molecule binding energies ϵ_b (meV), permanent dipole moments μ (D) and dipole polarizabilities α (Å^3) for selected molecules. Data for μ and α taken from Ref. [26]. Data from Figs. 1-4 in bold.

Molecule	Formula	μ (D)	α (Å^3)	ϵ_b (meV) positrons meas.	pred.	electrons[g] meas.	pred.
carbon disulf.	CS_2	0	8.7	75		0.7	
benzene	C_6H_6	0	8.2	40[a]			
methanol	CH_3OH	1.7	3.3	2[a]			
meth.-chloride	CH_3Cl	1.9	5.4	25[a]			
formaldehyde	H_2CO	2.3	2.6		19[b]		0.02
acetaldehyde	$(CH_3)HCO$	2.8	4.6	**90**		0.6	0.95
acetone	$(CH_3)_2CO$	2.9	6.4	**173**	4[c]	2.6	1.6
propanal	$(C_2H_5)HCO$	2.7	6.5			1.0	0.6
hydr. cyanide	HCN	3.0	2.5		35[d]	4	3.3
acetonitrile	CH_3CN	3.9	4.4	**180**	135[e]	19	15.5
lith. hydride	LiH	5.9	3.8		1000[f]	342	330

[a]Ref. [11], [b]Ref. [5], [c]Ref. [8], [d]Refs. [6, 7], [e]Ref. [15], [f]Ref. [3], [g]Meas. from Refs. [25, 27–29], pred. from Refs. [25, 30].

How is the non-polar molecule?
→ Multi-mode vibrational effect

J. R. Danielson, A. C. L. Jones, M. R. Natisin, and C. M. Surko, Phys. Rev. Lett. (2012)

TABLE I: Positron and electron molecule binding energies ϵ_b (meV), permanent dipole moments μ (D) and dipole polarizabilities α (Å^3) for selected molecules. Positron data for ϵ_b are from Ref. [11, 12], and electron data from Ref. [8]; and values for μ and α are from Ref. [13].

Molecule	μ	α	$\epsilon_b(e^+)$	$\epsilon_b(e^-)$
Aldehydes				
acetaldehyde C_2H_4O	2.8	4.6	90	0.6
propanal C_3H_6O	2.5	6.5	120	1.0
butanal C_4H_8O	2.7	8.2	152	1.2
Ketones				
acetone C_3H_6O	2.9	6.4	173	2.6
2-butanone C_4H_8O	2.8	8.1	205	1.8
cyclopentanone C_5H_8O	3.3	9.3	235	2.8
Nitriles				
acetonitrile CH_3CN	3.9	4.4	180	19
propionitrile C_2H_5CN	4.1	6.5	225	15
2-methylpropionitrile C_3H_7CN	4.3	8.1	275	12

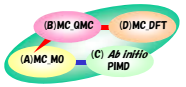
17

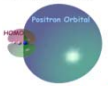
公立大学法人 横浜市立大学

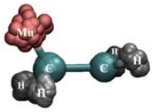
Outline

18

1. **Introduction**
   - エキゾチック分子系
2. 多成分系手法による陽電子化合物への応用
   - ニトリル化合物への陽電子親和力
3. 経路積分法によるミューオン化合物への応用
   - ミュオン化エチルラジカルのHFCC
4. **Summary & 今後の展望**





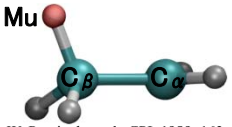


公立大学法人 横浜市立大学

3. ミュオン化エチルラジカルへの応用

19

【実験】超微細結合定数(HFCC)の気相での実験[1] FT-μSR



Temp. [℃]	A_μ [MHz]
10.7	333.5
25.3	329.8
37.2	327.2

[1] P. W. Percival, *et al.*, CPL **1989**, 163.
E. Roduner, *et al.*, *Hyperfine Interaction* **1986**, 733.

【計算】経路積分＋Tight-binding(TB)法を使った研究[2]

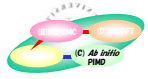
591.5 MHz

[2] R. Ramírez, *et al.*, *CPL*, **2005**, 402. M. C. Böhm, *et al.*, *Mol. Phys.* **2005**, 103.

【目的】ミュオン化エチルラジカルのHFCCを精度よく評価
1. ミュオンの量子的振る舞いの記述
2. HFCCに大きく関与する不対電子の的確な記述

公立大学法人 横浜市立大学

3. *ab initio* 経路積分(PIMD)法



·**Path Integral procedure**

- ·Marx and Parrinello (1994)
- ·Cheng, Barnett, and Landman (1995)
- ·Schulte, Bohm, and Ramirez (1996)
- · Kitamura, Tsuneyuki, Ogitsu, and Miyake (2000)

-(*N*)-body **quantum** problem

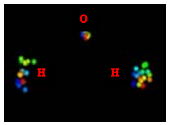
$$\hat{H} = \sum_{I=1}^{N} \frac{\hat{P}_I^2}{2M_I} + V_0(R_1 \cdots R_N), \qquad V_0 : Potential$$

-(*N* × *P*)-body **classical** problem

$$Z = Tr\left(e^{-\beta\hat{H}}\right) = Tr\left(e^{-\beta\hat{H}/P}\right)^P \quad \leftarrow \textbf{Partition function}$$

$$\propto \lim_{P\to\infty} \int \left[\prod_{I=1}^{N} dR_I^{(1)} dR_I^{(2)} \cdots dR_I^{(P)}\right] \exp\left(-\beta V_{eff}\right)$$

$$V_{eff} = \sum_{s=1}^{P}\left[\sum_{I=1}^{N} \frac{\kappa_I}{2}(R_I^{(s)} - R_I^{(s+1)})^2 + \frac{1}{P} V_0\left(R_1^{(s)} \cdots R_N^{(s)}\right)\right], \qquad \kappa_I = M_I\left(\frac{\sqrt{P}}{\beta\hbar}\right)^2$$



N=2 → *N*(=2) × *P*(=8)

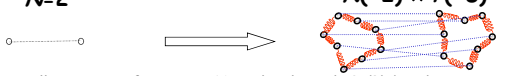
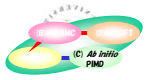


Figure 2. Schematic illustration of quantum H_2 molecule with 8 (P) beads.

公立大学法人 横浜市立大学

3. *ab initio* 経路積分(PIMD)法



·Path Integral procedure

- (*N*)-body **quantum** problem

$$\hat{H} = \sum_{I=1}^{N} \frac{\hat{P}_I^2}{2M_I} + V_0(R_1 \cdots R_N), \quad V_0 : Potential$$

- (*N* × *P*)-body **classical** problem

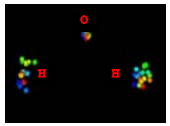
$$Z = Tr\left(e^{-\beta \hat{H}}\right) = Tr\left(e^{-\beta \hat{H}/P}\right)^P \quad \leftarrow \text{Partition function}$$

$$\propto \lim_{P\to\infty} \int \left[\prod_{I=1}^{N} dR_I^{(1)} dR_I^{(2)} \cdots dR_I^{(P)}\right] \exp(-\beta V_{eff})$$

$$V_{eff} = \sum_{s=1}^{P} \left[\sum_{I=1}^{N} \frac{\kappa_I}{2} (R_I^{(s)} - R_I^{(s+1)})^2 + \frac{1}{P} V_0(R_1^{(s)} \cdots R_N^{(s)})\right], \quad \kappa_I = M_I \left(\frac{\sqrt{P}}{\beta\hbar}\right)^2$$

·Marx and Parrinello (1994)
·Cheng, Barnett, and Landman (1995)
·Schulte, Bohm, and Ramirez (1996)
· Kitamura, Tsuneyuki, Ogitsu, and Miyake (2000)

·Potential
***ab initio* MO**



Full quantum treatment !! ⇒ **Path integral** for nucleus
***Ab initio* MO** for electron

·M. Shiga, M. Tachikawa, and S. Miura, **J. Chem. Phys.** *115*, 9149 (2001).
·M. Tachikawa and M. Shiga, **J. Am. Chem. Soc.** *127*, 11908 (2005).

公立大学法人 横浜市立大学

3. ミュオン化エチルラジカルへの応用

1. On-the-fly PIMD計算
2. 原子間相互作用の計算：O3LYP/6-31G(d,p)
   - UCCSD(T)/aug-cc-pVTZ//UMP2/aug-cc-VDZ の結果との比較から採用

	温度	ビーズ数	虚時間刻み
ミュオン化エチルラジカル ($C_\beta MuH_2$–$\dot{C}_\alpha H_2$) →Mu体	300 K	64	40 asec
エチルラジカル ($C_\beta H_3$–$\dot{C}_\alpha H_2$) →H体	300 K	16	0.1 fsec

公立大学法人 横浜市立大学

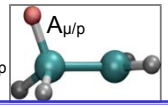
3. ミュオン化エチルラジカルへの応用

Isotropic HFCCの評価

	DFT最適化構造	本研究(量子核) Mu体	本研究(量子核) H体	先行研究[2] Mu体	先行研究[2] H体	Exptl.[1] Mu体	Exptl.[1] H体
$A_{\mu/p}$	478.7	374.2	70.8	591.5	-	329.8	-
A_p	36.9	66.8	81.0	77.6	-	66.8	-
$\bar{A}$ a)	74.7	83.8	77.6	113.8	101.2	79.1	75.1

a) $\bar{A} = (A'_\mu + A_p)/3$

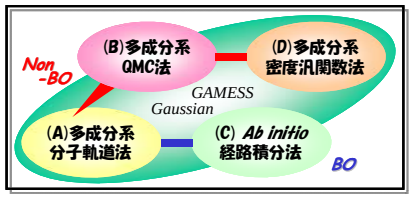
DFT構造：過大or過小評価
量子核　：reasonableに再現



公立大学法人 横浜市立大学

4. Summary

·量子多成分系分子理論の開発：

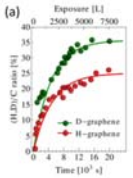


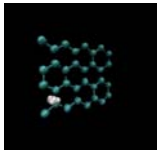
·量子多成分系分子理論の応用：

- 水素結合系への応用：　重水素化に伴う電子状態・骨格構造変化
  → 低障壁水素結合系、水素吸蔵金属、生体分子
- 陽電子化合物系への応用：　数値的な厳密エネルギーの算出
  → 陽電子化合物、陽電子分光法への応用
- ミューオン化合物系への応用：　精密なHFCCの算出

4. Near future work!

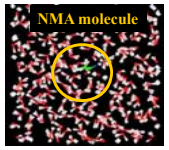
- **H-Chemisorption on graphene**

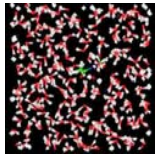




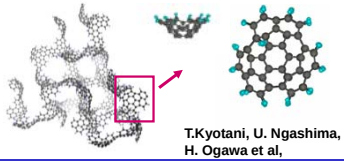
[*] T. Zecho, J. Kuppers *et al*, J. Chem. Phys. *117*, 8486 (2002).

- **Aqueous solution of NMA (methylacetamide)**



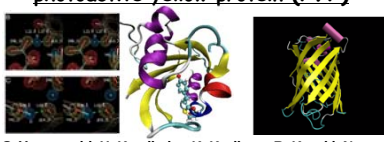


- **Hydrogen storage in Zeolite-Templated Carbon (ZTC)**



T.Kyotani, U. Ngashima, H. Ogawa et al,

- **Low-barrier hydrogen bond in photoactive yellow protein (PYP)**



S. Yamaguchi, H. Kamikubo, K. Kurihara, R. Kuroki, N. Niimura, N. Shimizu, Y. Yamazaki, and M. Kataoka, PNAS, 106, 440-444 (2009).