*YITP Workshop*
*"Fundamentals in density functional theory (DFT2022)"*
*Dec. 16th,*
*Yukawa Institute for Theoretical Physics,*
*Kyoto University*

# Local physical quantities based on quantum electrodynamic

Masahiro FUKUDA
*Institute for Solid State physics*
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## Name

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## Education

- 2011-2013: Master
  - Department of Micro Engineering, Graduate School of Engineering, Kyoto University
- 2013-2016: PhD
  - Department of Micro Engineering, Graduate School of Engineering, Kyoto University, Tachibana laboratory

## Research and professional experience

- 2016~2019: Project researcher of the Institute for Solid State Physics, Univ. of Tokyo, Ozaki laboratory
- 2019~present: Assistant professor of the Institute for Solid State Physics, Univ. of Tokyo, Ozaki laboratory, Supercomputer center

# ISSP Supercomputer Center
# （東大物性研スパコン）


**System B, Ohtaka**
**6.881 PFLOPS**
**memory : 420 TB**
**storage : 2.3 PB**

**System C, Kugui**
**0.973 PFLOPS**
**memory : 35.25TB**
**storage : 1.35 PB**


https://mdcl.issp.u-tokyo.ac.jp/scc/

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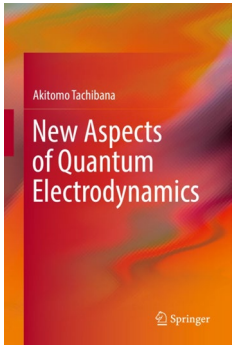
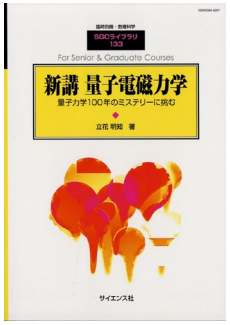
# References

Akitomo TACHIBANA, Emeritus Professor, Kyoto Univ.
Masato SENAMI, Kyoto Univ.
Kazuhide ICHIKAWA, Panasonic




A. Tachibana,
"New Aspects of Quantum Electrodynamics",
Springer (2017)




立花明知,
「新講　量子電磁力学」,
SGCライブラリ, ㈱サイエンス社,
2017年4月

Most of the electronic states are calculated by DFT code OpenMX as an approximation to the quantum field theoretical state vector.


- Software:
  OpenMX
  (http://www.openmx-square.org/)
- Functional:
  GGA-PBE
- Pseudo potential:
  Optimized Pseudo atomic orbitals

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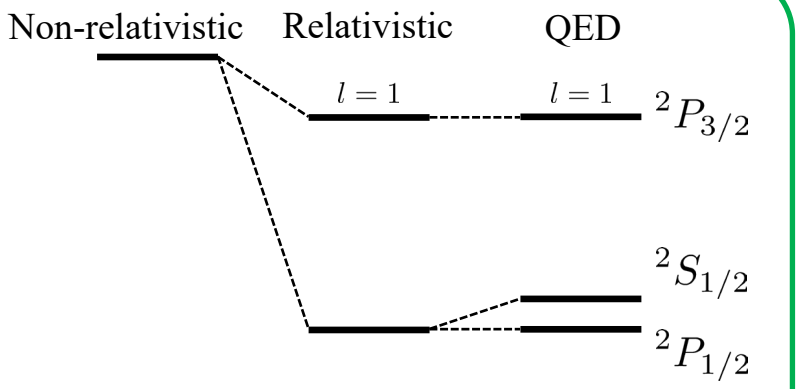
In atomic and molecular scales, it is important to discuss systems which consist of electrons, nuclei and photons on the basis of quantum electrodynamics (QED).

Historically, QED is the first theory where full agreement between quantum mechanics and special relativity is achieved.

The relativistic theory and QED have been regarded as only a slight correction in the field of quantum chemistry.




Lamb's shift:
a subtle structure of the n=2 level in hydrogen

However, the concept of "locality" based on relativistic theory gives novel images to physical phenomena and mechanisms of chemical reactions.

# ☆Definition of physical quantities in QM and QED

## Electronic momentum in QM

$$\langle\Psi|\left(\sum_i^N \hat{\vec{p}}_i\right)|\Psi\rangle = \int d^3\vec{r}_1,\cdots,d^3\vec{r}_N \Phi_N^\dagger(\vec{r}_1,\cdots,\vec{r}_N)\left(\sum_i^N \hat{\vec{p}}_i\right)\Phi_N(\vec{r}_1,\cdots,\vec{r}_N)$$

$$\approx \int d^3\vec{r}\sum_i^N \psi_i^\dagger(\vec{r})\left(-i\hbar\vec{\nabla}\right)\psi_i(\vec{r})$$

In quantum mechanics, physical quantities are defined after the integration over the whole region.

## Electronic momentum density in QED

$$\langle\Psi|\hat{\vec{p}}(x)|\Psi\rangle = \langle\Psi|\left(\frac{1}{2}\hat{\psi}^\dagger(x)\left(-i\hbar\vec{\nabla}\right)\hat{\psi}(x)+h.c.\right)|\Psi\rangle$$

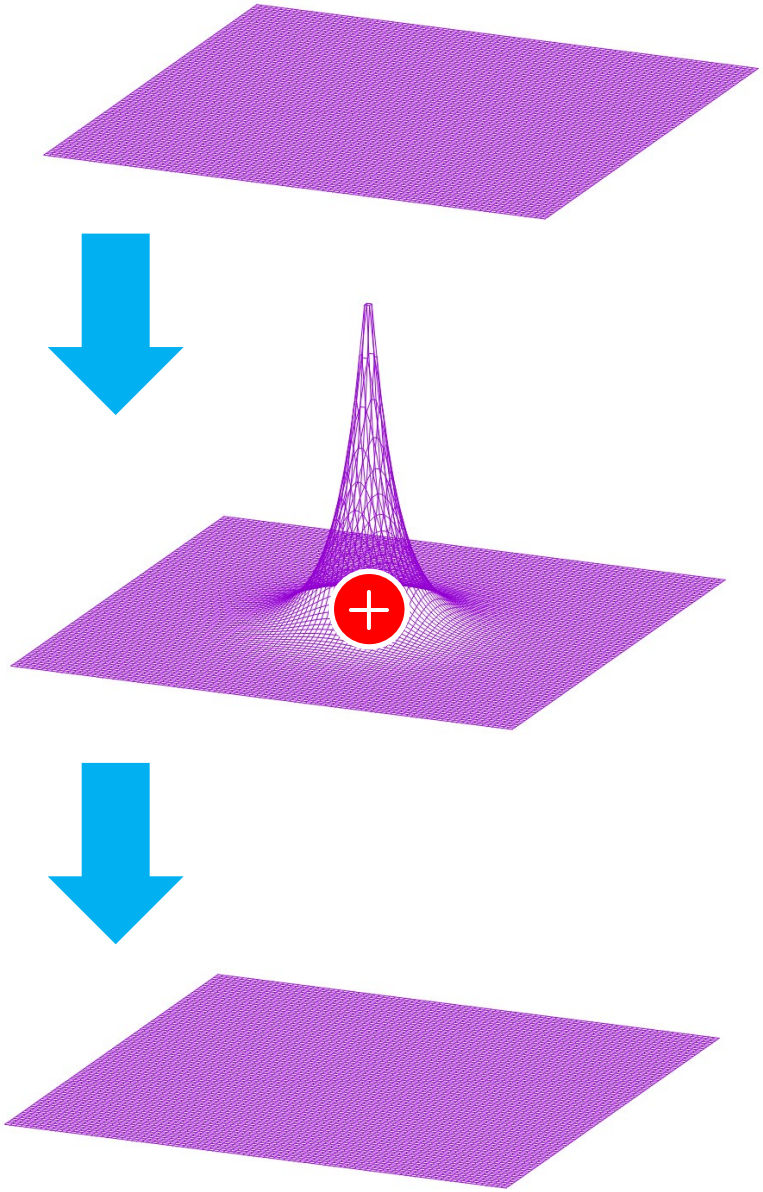
$$x=(ct,\vec{r})$$

- Invariance under the gauge transformation
- Invariance under the general coordinate transformation

Physical quantities based on QED do not lose local contribution.
→ Local physical quantities

$$\hat{\vec{P}}_e(x) = \hat{\vec{\Pi}}_e(x) + \frac{1}{2}\mathrm{rot}\hat{\vec{s}}_e(x)$$

Imagine a one electron system



Equation of motion of QM

$$\frac{d\vec{\pi}}{dt} = \frac{1}{i\hbar}[\vec{\pi}, H]$$
$$= Z_e e\left(\vec{E} + \vec{\alpha} \times \vec{B}\right)$$

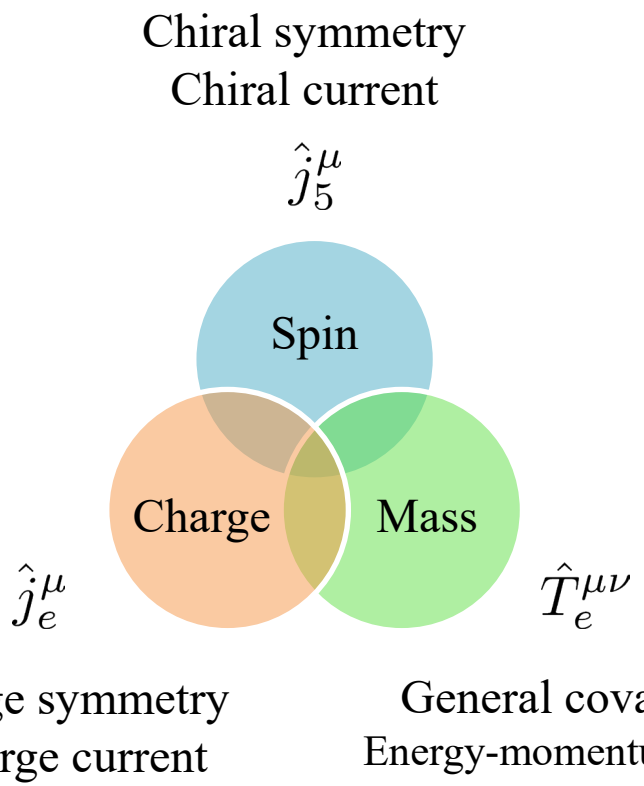
$$\left(\frac{d\vec{p}}{dt} = q\vec{E} + \vec{j} \times \vec{B}\right)$$

In quantum mechanics, the expectation value of the Coulomb force is zero.

In classical electrodynamics,
the Coulomb force is not zero at each point.
However, it cannot explain what is the counter force.

How about in QED?

# What is the "local" physical quantity?




- 4-component charge current density

$$\hat{j}_e^\mu = Z_e e \hat{\psi}^\dagger \gamma^0 \gamma^\mu \hat{\psi} = (\hat{\rho}_e, \hat{\vec{j}}_e)$$

- Chiral current density

$$\hat{j}_5^\mu = Z_e e \hat{\psi}^\dagger \gamma^0 \gamma^\mu \gamma_5 \hat{\psi} = (\hat{j}_5^0, \frac{\hbar}{2Z_e e} \hat{\vec{s}}_e)$$

Spin angular momentum density

- Energy-momentum tensor density

$$\hat{T}_e^{\mu\nu} = \begin{pmatrix} ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \end{pmatrix}$$

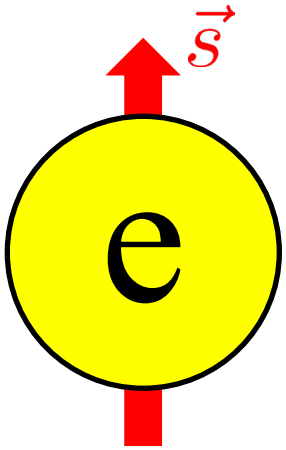
In the framework of QED, the local physical quantities of the electron are mainly derived from three kinds of symmetries.

General covariance is the invariance of the form of physical laws under arbitrary differentiable coordinate transformations.

# Spin

$$\hat{\vec{s}}(\vec{r}) = \hat{\psi}^{\dagger}(\vec{r})\frac{\hbar}{2}\vec{\Sigma}\hat{\psi}(\vec{r}) = \frac{\hbar}{2Z_e ec}\hat{\vec{j}}_5(\vec{r})$$

## Quantum mechanics

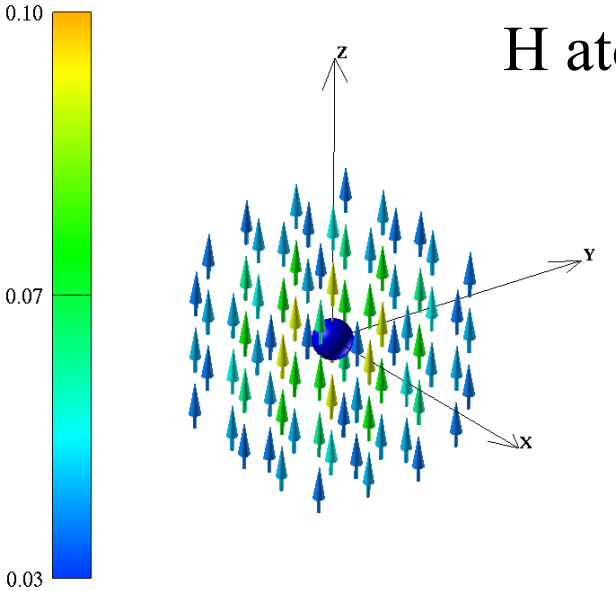



Spin angular momentum $\vec{s}$

$$\vec{s} = \int \langle \hat{\vec{s}}(\vec{r}) \rangle d^3\vec{r}$$

In quantum mechanics, the image of spin is a single vector because physical quantities are defined after the integration over the whole region.

## Quantum field theory (QED)



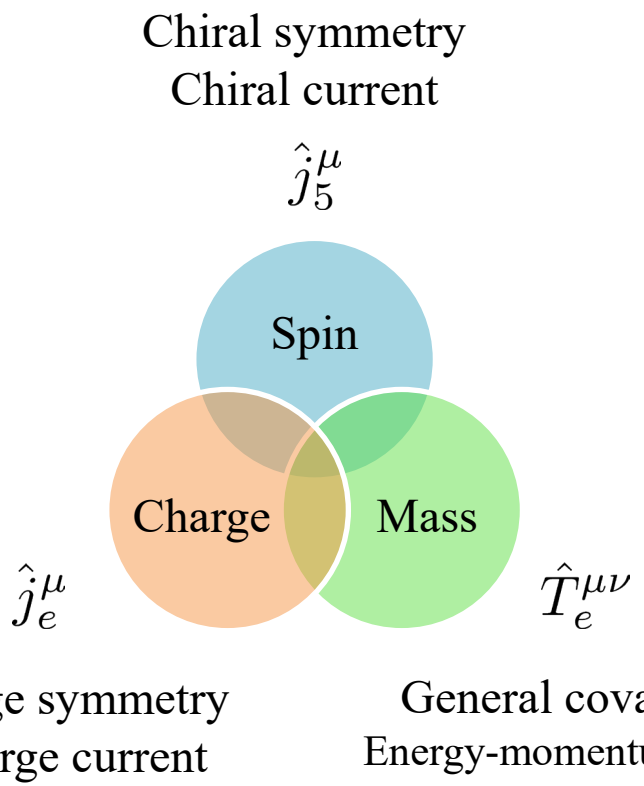

H atom

Spin angular momentum density $\vec{s}(\vec{r})$

$$\vec{s}(\vec{r}) = \langle \hat{\vec{s}}(\vec{r}) \rangle$$

In quantum field theory, spin is distributed as a density, because physical quantities based on quantum field theory do not lose local contribution.

# What is the "local" physical quantity?




- 4-component charge current density

$$\hat{j}_e^\mu = Z_e e \hat{\psi}^\dagger \gamma^0 \gamma^\mu \hat{\psi} = (\hat{\rho}_e, \hat{\vec{j}}_e)$$

- Chiral current density

$$\hat{j}_5^\mu = Z_e e \hat{\psi}^\dagger \gamma^0 \gamma^\mu \gamma_5 \hat{\psi} = (\hat{j}_5^0, \frac{\hbar}{2Z_e e} \hat{\vec{s}}_e)$$

Spin angular momentum density

- Energy-momentum tensor density

$$\hat{T}_e^{\mu\nu} = \begin{pmatrix} ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \end{pmatrix}$$

In the framework of QED, the local physical quantities of the electron are mainly derived from three kinds of symmetries.

General covariance is the invariance of the form of physical laws under arbitrary differentiable coordinate transformations.

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*The Quantum Theory of the Electron.*

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received January 2, 1928.)

The new quantum mechanics, when applied to the problem of the structure of the atom with point-charge electrons, does not give results in agreement with experiment. The discrepancies consist of "duplexity" phenomena, the observed number of stationary states for an electron in an atom being twice the number given by the theory. To meet the difficulty, Goudsmit and Uhlenbeck have introduced the idea of an electron with a spin angular momentum of half a quantum and a magnetic moment of one Bohr magneton. This model for the electron has been fitted into the new mechanics by Pauli,* and Darwin,† working with an equivalent theory, has shown that it gives results in agreement with experiment for hydrogen-like spectra to the first order of accuracy.

The question remains as to why Nature should have chosen this particular model for the electron instead of being satisfied with the point-charge. One would like to find some incompleteness in the previous methods of applying quantum mechanics to the point-charge electron such that, when removed, the whole of the duplexity phenomena follow without arbitrary assumptions. In the present paper it is shown that this is the case, the incompleteness of the previous theories lying in their disagreement with relativity, or, alternatively, with the general transformation theory of quantum mechanics. It appears that the simplest Hamiltonian for a point-charge electron satisfying the requirements of both relativity and the general transformation theory leads to an explanation of all duplexity phenomena without further assumption. All the same there is a great deal of truth in the spinning electron model, at least as a first approximation. The most important failure of the model seems to be that the magnitude of the resultant orbital angular momentum of an electron moving in an orbit in a central field of force is not a constant, as the model leads one to expect.

* Pauli, 'Z. f. Physik,' vol. 43, p. 601 (1927).
† Darwin, 'Roy. Soc. Proc.,' A, vol. 116, p. 227 (1927).

Quantum mechanics
+ relativity
+ general transformation theory

→ **Dirac equation**

(equation of Dirac field)

Note1:
Dirac tried to construct relativistic quantum mechanics of a point-charge electron, but he failed. Instead, he paved the way to construct quantum field theory.

Note2:
Weinberg said "relativistically invariant quantum theories always do turn out to be quantum field theories"[*].
In this sense, "relativistic quantum mechanics" does not exist.

Note3:
Weinberg said "Although this is often talked about as second quantization, I would like to urge that this description should be banned from physics, because a quantum field is not a quantized wave function"[*].

[*] S. Wienberg http://arxiv.org/abs/hep-th/9702027

"In fact, it was quite soon after the Born–Heisenberg–Jordan paper of 1926 that the idea came along that in fact one could use quantum field theory for everything, not just for electromagnetism. This was the work of many theorists during the period 1928–1934, including Jordan, Wigner, Heisenberg, Pauli, Weisskopf, Furry, and Oppenheimer.

Although this is often talked about as second quantization, I would like to urge that this description should be banned from physics, because a quantum field is not a quantized wave function. Certainly the Maxwell field is not the wavefunction of the photon, and for reasons that Dirac himself pointed out, the Klein–Gordon fields that we use for pions and Higgs bosons could not be the wave functions of the bosons. In its mature form, the idea of quantum field theory is that quantum fields are the basic ingredients of the universe, and particles are just bundles of energy and momentum of the fields. In a relativistic theory the wave function is a functional of these fields, not a function of particle coordinates. Quantum field theory hence led to a more unified view of nature than the old dualistic interpretation in terms of both fields and particles."

[*] S. Wienberg http://arxiv.org/abs/hep-th/9702027

- Classical field theory
  - Maxwell field
  - Dirac field
  - (Schrödinger field)
  - Gravitational field
  - etc

→

- Quantum field theory
  - Maxwell field
  - Dirac field
  - (Schrödinger field)
  - etc

---

- Quantum Electrodynamics (QED)
  - Maxwell field (photon)
  - Dirac field (electron)

non-relativistic limit →

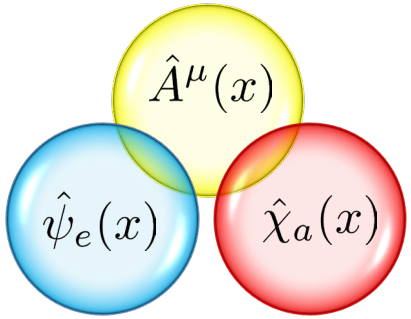
- Non-Relativistic QED (NRQED)
  - Maxwell field (photon)
  - Schrödinger field (electron)

↓ Add freedom of nuclei

- Rigged QED
  - Maxwell field (photon)
  - Dirac field (electron)
  - Schrödinger field (nuclei)

non-relativistic limit →

- Primary Rigged QED (PRQED)
  - Maxwell field (photon)
  - Schrödinger field (electron)
  - Schrödinger field (nuclei)




$$|\hat{\psi}, \hat{\chi}_a, \hat{A}\rangle$$

# Classical field theory

- Lagrangian density
  - Lorentz invariance
  - Gauge invariance

$$I = \int L\sqrt{-g}d^4x$$

- Variation principle for $I_S$ (+ $I_G$) respect to
  - Maxwell field → Maxwell equation
  - Dirac field → equation of motion of Dirac field
  - Vierbein (tetrad) field → Einstein equation, the symmetric energy-momentum tensor and the conservation law

# Dirac field and U(1) gauge field

- Lagrangian density of free electron

$$L_e = \frac{1}{2}\left(i\hbar\bar{\psi}\gamma^\mu\partial_\mu\psi - m_e c\bar{\psi}\psi + h.c.\right)$$

$$\partial_\mu = \left(\frac{1}{c}\frac{\partial}{\partial t}, \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

local phase transformation

$$\psi \to e^{i\theta(x)}\psi$$

$$\partial_\mu\psi \to e^{i\theta(x)}\left(\partial_\mu + i\partial_\mu\theta(x)\right)\psi$$

- Lagrangian density of free photon

$$L_{\mathrm{EM}} = -\frac{1}{16\pi}F_{\mu\nu}F^{\mu\nu}$$

$$F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu$$

gauge transformation

$$A_\mu \to A_\mu + \partial_\mu\Lambda(x)$$

$$\underbrace{\left(\partial_\mu + i\frac{q}{\hbar c}A_\mu\right)}_{\equiv D_{e\mu}}\psi \to e^{i\theta(x)}\left(\partial_\mu + i\frac{q}{\hbar c}A_\mu + \underbrace{i\partial_\mu\theta(x) + i\frac{q}{\hbar c}\partial_\mu\Lambda(x)}_{=0}\right)\psi$$

$$D_{e\mu}\psi \to e^{i\theta(x)}D_{e\mu}\psi$$

Gauge invariant !

# Dirac field and U(1) gauge field

- Lagrangian density of electron

Gauge invariant !

$$L_e = \frac{1}{2}\left(\underbrace{i\hbar\bar{\psi}\gamma^\mu D_{e\mu}\psi}_{\text{kinetic term}} \underbrace{- mc\bar{\psi}\psi}_{\text{mass term}} + h.c.\right)$$

local phase transformation

$$\psi \to e^{i\theta(x)}\psi$$

$$D_{e\mu}\psi \to e^{i\theta(x)} D_{e\mu}\psi$$

- Lagrangian density of photon

Gauge invariant !

$$L_{\text{EM}} = -\frac{1}{16\pi} F_{\mu\nu}F^{\mu\nu}$$

$$F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu$$

$$= [D_{e\mu}, D_{e\nu}]$$

gauge transformation

$$A_\mu \to A_\mu + \partial_\mu \Lambda$$

$$\partial_\mu \theta(x) = -\frac{q}{\hbar c}\partial_\mu \Lambda(x)$$

$$L_{\text{QED}} = L_e + L_{\text{EM}}$$

$$= \frac{1}{2}\left(i\hbar\bar{\psi}\gamma^\mu D_{e\mu}\psi - mc\bar{\psi}\psi + h.c.\right) - \frac{1}{16\pi}F_{\mu\nu}F^{\mu\nu}$$

$$= \frac{1}{2}\left(i\hbar\bar{\psi}\gamma^\mu \partial_\mu\psi - mc\bar{\psi}\psi + h.c.\right) \underbrace{- \frac{q}{c}\bar{\psi}\gamma^\mu A_\mu\psi}_{\text{Interaction between electron and photon}} - \frac{1}{16\pi}F_{\mu\nu}F^{\mu\nu}$$

# Classical field theory

- Lagrangian density
  - Lorentz invariance
  - Gauge invariance

$$I = \int L\sqrt{-g}d^4x$$

- Variation principle for $I_S$ (+ $I_G$) respect to
  - Maxwell field → Maxwell equation
  - Dirac field → equation of motion of Dirac field
  - Vierbein (tetrad) field → Einstein equation, the symmetric energy-momentum tensor and the conservation law

- Equation of motion of the photon field

$$\begin{cases} \frac{1}{c}\frac{\partial}{\partial t}\vec{\nabla}A_0(x) + \left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\vec{A}(x) = \frac{4\pi}{c}j(x) \\ -\nabla^2 A_0(x) = 4\pi\rho(x) \end{cases}$$

Euler-Lagrange equation

$$\partial_\mu \frac{\partial L}{\partial(\partial_\mu A^\nu)} - \frac{\partial L}{\partial A^\nu} = 0$$

Under the Coulomb gauge,

$$\vec{A}(ct,\vec{r}) = \vec{A}_{\text{rad}}(ct,\vec{r}) + \vec{A}_A(ct,\vec{r})$$

$$\text{div}\vec{A}_{\text{rad}}(ct,\vec{r}) = 0$$

$$\vec{A}_A(ct,\vec{r}) = \frac{1}{c}\int d^3\vec{s}\frac{\vec{j}_T(cu,\vec{s})}{|\vec{r}-\vec{s}|} \qquad u = t - \frac{|\vec{r}-\vec{s}|}{c}$$

$$A^0_{\text{rad}}(ct,\vec{r}) = 0$$

$$A_0(ct,\vec{r}) = \int d^3\vec{s}\frac{\rho(ct,\vec{s})}{|\vec{r}-\vec{s}|}$$

- Equation of motion of the electron field

$$i\hbar\gamma^\mu D_{e\mu}\psi - m_e c\psi = 0$$

Euler-Lagrange equation

$$\partial_\mu \frac{\partial L}{\partial(\partial_\mu\bar{\psi})} - \frac{\partial L}{\partial\bar{\psi}} = 0$$

The two currents $j^{\mu}(x)$ and $j_5^{\mu}(x)$ are the Noether currents $\mathcal{J}^{\mu}(x) = \dfrac{\delta L(x)}{\delta(\partial_{\mu}\psi(x))}\delta\psi(x)$ corresponding to the two transformations.

- phase transformation

$$\psi(x) \to e^{i\alpha}\psi(x) \qquad \delta\psi(x) = i\alpha\psi(x)$$

$$j^{\mu}(x) = Z_e ec\bar{\psi}(x)\gamma^{\mu}\psi(x) \qquad \text{: Electronic charge current density}$$

- chiral transformation

$$\psi(x) \to e^{i\alpha\gamma_5}\psi(x) \qquad \delta\psi(x) = i\alpha\gamma_5\psi(x)$$

$$j_5^{\mu}(x) = Z_e ec\bar{\psi}(x)\gamma^{\mu}\gamma_5\psi(x) \qquad \text{: Electronic chiral current density}$$

# Classical field theory

- Lagrangian density
  - Lorentz invariance
  - Gauge invariance

$$I = \int L\sqrt{-g}d^4x$$

- Variation principle for $I_S$ (+ $I_G$) respect to
  - Maxwell field → Maxwell equation
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## Einstein equation（General relativistic theory)

$$G_{\mu\nu} = -\frac{8\pi G}{c^4} T_{\mu\nu}$$

The symmetric energy-momentum tensor $T_{\mu\nu}$ appears in the Einstein equation.

The symmetric energy-momentum tensor is given by using the vierbein formulation.

$$T_{\mu\nu} = \frac{1}{\sqrt{-g}} \eta_{ab} e^{b}{}_{\nu} \frac{\delta\left(L\sqrt{-g}\right)}{\delta e_a{}^{\mu}}$$

This formulation is necessary to treat fermions in the relativistic theory.

$$L = L_e + L_{\mathrm{EM}} \quad \text{(QED Lagrangian)}$$

$$L_e = \frac{1}{2}\bar{\psi}\left(i\hbar\gamma^a e_a^{\mu} D_{\mu}(g) - mc\right)\psi + h.c.$$

$$L_{\mathrm{EM}} = -\frac{1}{16\pi} F_{\mu\nu} F_{\rho\sigma} g^{\mu\rho} g^{\nu\sigma}$$

Spin connection

$$D_{\mu}(g) = \partial_{\mu} + i\frac{1}{2\hbar}\gamma_{ab\mu} J^{ab} + i\frac{q}{\hbar c} A_{\mu}$$

$$J^{ab} = \frac{i\hbar}{4}\left[\gamma^a, \gamma^b\right]$$

$$T_{\mu\nu} = -\varepsilon^{\Pi}_{\mu\nu} - \tau^{\Pi}_{\mu\nu}(g) - \frac{1}{4\pi} g^{\rho\sigma} F_{\mu\rho} F_{\nu\sigma} - g_{\mu\nu}\left(L_e + L_{EM}\right) = T_{\nu\mu}; \text{symmetric}$$

Symmetry-polarized geometrical tensor

$$\varepsilon^{\Pi}_{\mu\nu} = -\frac{1}{\sqrt{-g}} \eta_{ab} e^{b}{}_{\nu} \left[ \frac{\partial\left(L_e\sqrt{-g}\right)}{\partial \gamma^{cd}{}_{\rho}} \frac{\partial \gamma^{cd}{}_{\rho}}{\partial e_a{}^{\mu}} - \partial_{\sigma}\left( \frac{\partial\left(L_e\sqrt{-g}\right)}{\partial \gamma^{cd}{}_{\rho}} \frac{\partial \gamma^{cd}{}_{\rho}}{\partial\left(\partial_{\sigma} e_a{}^{\mu}\right)} \right) \right]$$

*A. Tachibana , J. Math. Chem. 50, 669-688 (2012).*

Symmetry-polarized stress tensor

$$\tau^{\Pi}_{\mu\nu}(g) = -\frac{1}{\sqrt{-g}} \eta_{ab} e^{b}{}_{\nu} \frac{\partial\left(L_e\sqrt{-g}\right)}{\partial e_a{}^{\mu}}$$

$$\begin{pmatrix} \varepsilon^{A}_{\mu\nu} = ( \\ \tau^{A}_{\mu\nu}(g) = \end{pmatrix}$$

This equation is called "**Spin Vorticity Principle**"

The energy momentum tensor is symmetric

$$\varepsilon^{A\mu\nu} + \tau^{A\mu\nu}(g) = 0$$

$$\begin{cases} T_{e\mu\nu} = \dfrac{1}{\sqrt{-g}}\eta_{ab}e^{b}{}_{\nu}\dfrac{\delta\left(L_e\sqrt{-g}\right)}{\delta e_a{}^{\mu}} \\ T_{\mathrm{EM}\mu\nu} = \dfrac{1}{\sqrt{-g}}\eta_{ab}e^{b}{}_{\nu}\dfrac{\delta\left(L_{\mathrm{EM}}\sqrt{-g}\right)}{\delta e_a{}^{\mu}} \end{cases} \qquad \begin{aligned} L_e &= \frac{1}{2}\bar{\psi}\left(i\hbar\gamma^a e_a^{\mu}D_{\mu}(g) - mc\right)\psi + h.c. \\ L_{\mathrm{EM}} &= -\frac{1}{16\pi}F_{\mu\nu}F_{\rho\sigma}g^{\mu\rho}g^{\nu\sigma} \end{aligned}$$

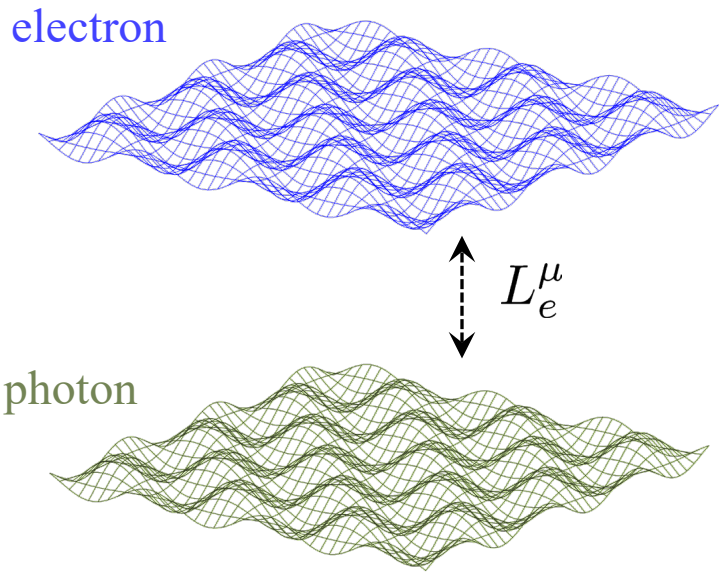
## limit to Minkowski space

$$\begin{cases} T_e^{\mu\nu} \to \begin{pmatrix} \frac{1}{2}\left(M + h.c.\right) & c\left(\vec{\Pi} + \frac{1}{2}\mathrm{rot}\vec{s}\right)_x & c\left(\vec{\Pi} + \frac{1}{2}\mathrm{rot}\vec{s}\right)_y & c\left(\vec{\Pi} + \frac{1}{2}\mathrm{rot}\vec{s}\right)_z \\ c\left(\vec{\Pi} + \frac{1}{2}\mathrm{rot}\vec{s}\right)_x & -\tau^S_{xx} + L_e & -\tau^S_{xy} & -\tau^S_{xz} \\ c\left(\vec{\Pi} + \frac{1}{2}\mathrm{rot}\vec{s}\right)_y & -\tau^S_{yx} & -\tau^S_{yy} + L_e & -\tau^S_{yz} \\ c\left(\vec{\Pi} + \frac{1}{2}\mathrm{rot}\vec{s}\right)_z & -\tau^S_{zx} & -\tau^S_{zy} & -\tau^S_{zz} + L_e \end{pmatrix} \\ T^{\mu\nu}_{\mathrm{EM}} \to \begin{pmatrix} H_\gamma & cG_x & cG_y & cG_z \\ cG_x & \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ cG_y & \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ cG_z & \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \end{cases}$$

The energy momentum tensor density is the conserved Noether current associated with spacetime translations.

$$\partial_\nu T^{\nu\mu} = 0 \qquad \begin{cases} \partial_\nu T^{\nu\mu}_{\mathrm{EM}} = -L^\mu \\ \partial_\nu T^{\nu\mu}_{e} = L^\mu_e \end{cases} \qquad \begin{aligned} L^\mu &= L^\mu_e \\ L^\mu_e &= j_{e\nu}F^{\nu\mu} \end{aligned} \qquad \left(\vec{L}_e = \vec{E}\rho_e + \frac{1}{c}\vec{j}_e \times \vec{B}\right)$$

# 【QED】

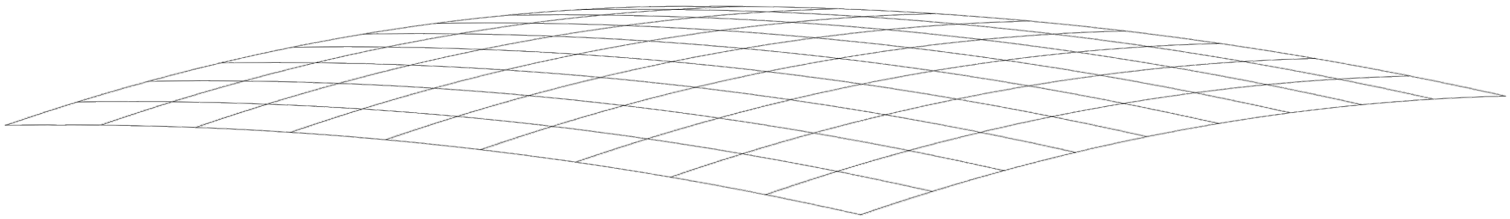



$$\partial_\nu T^{\nu\mu} = 0$$

$$T^{\nu\mu} = T^{\nu\mu}_{\rm EM} + T^{\nu\mu}_e$$

$$L^\mu = L^\mu_e$$

$$\begin{cases} \partial_\nu T^{\nu\mu}_{\rm EM} = -L^\mu \\ \partial_\nu T^{\nu\mu}_e = L^\mu_e \end{cases}$$



- Classical field theory
  - Maxwell field
  - Dirac field
  - (Schrödinger field)
  - Gravitational field
  - etc

→

- Quantum field theory
  - Maxwell field
  - Dirac field
  - (Schrödinger field)
  - etc

---

- Quantum Electrodynamics (QED)
  - Maxwell field (photon)
  - Dirac field (electron)

non-relativistic limit →

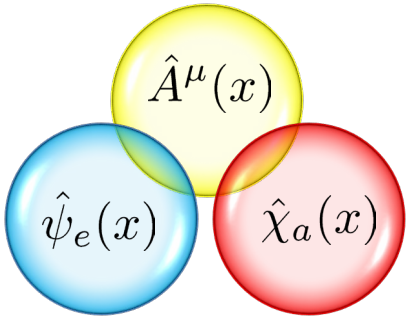
- Non-Relativistic QED (NRQED)
  - Maxwell field (photon)
  - Schrödinger field (electron)

↓ Add freedom of nuclei

- Rigged QED
  - Maxwell field (photon)
  - Dirac field (electron)
  - Schrödinger field (nuclei)

non-relativistic limit →

- Primary Rigged QED (PRQED)
  - Maxwell field (photon)
  - Schrödinger field (electron)
  - Schrödinger field (nuclei)




$$|\hat{\psi}, \hat{\chi}_a, \hat{A}\rangle$$

- Equation of motion of the photon field

$$\begin{cases} \frac{1}{c}\frac{\partial}{\partial t}\vec{\nabla}A_0(x) + \left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\vec{A}(x) = \frac{4\pi}{c}j(x) \\ -\nabla^2 A_0(x) = 4\pi\rho(x) \end{cases}$$

Euler-Lagrange equation

$$\partial_\mu \frac{\partial L}{\partial(\partial_\mu A^\nu)} - \frac{\partial L}{\partial A^\nu} = 0$$

Under the Coulomb gauge,

$$\vec{A}(ct,\vec{r}) = \vec{A}_{\text{rad}}(ct,\vec{r}) + \vec{A}_A(ct,\vec{r})$$

$$\text{div}\vec{A}_{\text{rad}}(ct,\vec{r}) = 0$$

$$\vec{A}_A(ct,\vec{r}) = \frac{1}{c}\int d^3\vec{s}\frac{\vec{j}_T(cu,\vec{s})}{|\vec{r}-\vec{s}|} \qquad u = t - \frac{|\vec{r}-\vec{s}|}{c}$$

$$A^0_{\text{rad}}(ct,\vec{r}) = 0$$

$$A_0(ct,\vec{r}) = \int d^3\vec{s}\frac{\rho(ct,\vec{s})}{|\vec{r}-\vec{s}|}$$

- Equation of motion of the electron field

$$i\hbar\gamma^\mu D_{e\mu}\psi - m_e c\psi = 0$$

Euler-Lagrange equation

$$\partial_\mu \frac{\partial L}{\partial(\partial_\mu\bar{\psi})} - \frac{\partial L}{\partial\bar{\psi}} = 0$$

# Causality

- Canonical quantization rule for photon

*Any two measurable local operators located at points separated by a spacelike interval must commute with each other.*

$$\left[\hat{A}^i(x), \hat{A}^j(y)\right]_{x^0=y^0} = 0$$

$$\left[\hat{E}^i_T(x), \hat{E}^j_T(y)\right]_{x^0=y^0} = 0$$

$$\frac{1}{4\pi c}\left[\hat{A}^i(x), \hat{E}^j_T(y)\right]_{x^0=y^0} = i\hbar\left(\eta^{ij}\delta^3(\vec{x}-\vec{y}) + \partial^i\partial^j\left(-\frac{1}{4\pi}\cdot\frac{1}{|\vec{x}-\vec{y}|}\right)\right)$$

- Canonical quantization rule for electron

$$\left\{\hat{\psi}(x), \hat{\psi}(y)\right\}_{x^0=y^0} = \left\{\hat{\psi}^\dagger(x), \hat{\psi}^\dagger(y)\right\}_{x^0=y^0} = 0$$

$$\left\{\hat{\psi}(x), \hat{\psi}^\dagger(y)\right\}_{x^0=y^0} = \delta^3(\vec{x}-\vec{y})$$

$$\left[\hat{\psi}(x), \hat{\vec{A}}(x)\right] = 0$$

- Equation of motion of the photon field

$$\begin{cases} \frac{1}{c}\frac{\partial}{\partial t}\vec{\nabla}\hat{A}_0(x) + \left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\hat{\vec{A}}(x) = \frac{4\pi}{c}\hat{\vec{j}}(x) \\ -\nabla^2\hat{A}_0(x) = 4\pi\hat{\rho}(x) \end{cases}$$

Euler-Lagrange equation

$$\partial_\mu \frac{\partial \hat{L}}{\partial(\partial_\mu \hat{A}^\nu)} - \frac{\partial \hat{L}}{\partial \hat{A}^\nu} = 0$$

Under the Coulomb gauge,

$$\hat{\vec{A}}(ct,\vec{r}) = \hat{\vec{A}}_{\text{rad}}(ct,\vec{r}) + \hat{\vec{A}}_A(ct,\vec{r}) \qquad \text{div}\,\hat{\vec{A}}_{\text{rad}}(ct,\vec{r}) = 0$$

$$\hat{A}^k_{\text{rad}}(ct,\vec{r}) = \frac{\sqrt{4\pi\hbar^2 c}}{\sqrt{(2\pi\hbar)^3}} \sum_{\sigma=\pm1} \int \frac{d^3\vec{p}}{\sqrt{2p^0}} \Big[\hat{a}(\vec{p},\sigma)e^k(\vec{p},\sigma)e^{-icp^0t/\hbar}e^{i\vec{p}\cdot\vec{r}/\hbar} + \hat{a}^\dagger(\vec{p},\sigma)e^{*k}(\vec{p},\sigma)e^{icp^0t/\hbar}e^{-i\vec{p}\cdot\vec{r}/\hbar}\Big]$$

$$\hat{\vec{A}}_A(ct,\vec{r}) = \frac{1}{c}\int d^3\vec{s}\,\frac{\hat{\vec{j}}_T(cu,\vec{s})}{|\vec{r}-\vec{s}|} \qquad u = t - \frac{|\vec{r}-\vec{s}|}{c}$$

$$\hat{A}^0_{\text{rad}}(ct,\vec{r}) = 0$$

$$\hat{A}_0(ct,\vec{r}) = \int d^3\vec{s}\,\frac{\hat{\rho}(ct,\vec{s})}{|\vec{r}-\vec{s}|}$$

- Equation of motion of the electron field

$$i\hbar\gamma^\mu \hat{D}_{e\mu}\hat{\psi} - m_e c\hat{\psi} = 0$$

Euler-Lagrange equation

$$\partial_\mu \frac{\partial \hat{L}}{\partial(\partial_\mu \hat{\bar{\psi}})} - \frac{\partial \hat{L}}{\partial \hat{\bar{\psi}}} = 0$$

Hamiltonian density operators

$$\begin{cases} \widehat{H}_{\mathrm{QED}}(x) = \widehat{H}_{\mathrm{EM}}(x) + \widehat{H}_{\mathrm{Dirac}}(x), \\ \widehat{H}_{\mathrm{EM}}(x) = \widehat{H}_{\gamma}(x) - \widehat{A}_0(x)\hat{\rho}_e(x), \\ \widehat{H}_{\mathrm{Dirac}}(x) = \widehat{M}_e(x) + \widehat{A}_0(x)\hat{\rho}_e(x), \end{cases}$$

$$\hat{H}_{\mathrm{EM}}(x) \equiv \frac{\partial \hat{L}_{\mathrm{EM}}}{\partial(\partial \hat{A}^{\mu}/\partial t)} \frac{\partial \hat{A}^{\mu}}{\partial t} - \hat{L}_{\mathrm{EM}}$$

$$\hat{H}_{\mathrm{Dirac}}(x) \equiv \frac{\partial \hat{L}_{e}}{\partial(\partial \hat{\psi}/\partial t)} \frac{\partial \hat{\psi}}{\partial t} - \hat{L}_{e}$$

Energy density and mass density operators

$$\begin{cases} \widehat{H}_{\gamma}(x) = \dfrac{1}{8\pi}\left(\widehat{\vec{E}}^2(x) + \widehat{\vec{B}}^2(x)\right), \\ \widehat{M}_e(x) = c\widehat{\bar{\psi}}(x)\left(-i\hbar\gamma^k \widehat{D}_{ek}(x) + m_e c\right)\hat{\psi}(x), \\ \hat{H}_e(x) = \hat{M}_e(x) \end{cases}$$

$$\hat{H}_{\gamma}(x) \equiv \hat{T}^{00}_{\mathrm{EM}}(x)$$

$$\hat{H}_{e}(x) \equiv \hat{T}^{00}_{e}(x)$$

$$\widehat{H}_{\mathrm{QED}}(x) = \widehat{H}_{\gamma}(x) + \widehat{H}_{e}(x).$$

$$\hat{H}_{\mathrm{QED}} = \int \hat{H}_{\mathrm{QED}}(\vec{r})d\vec{r}$$

time evolution of state vector

$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}_{\mathrm{QED}}|\Psi\rangle$$

$$E|\Psi\rangle = \hat{H}_{\mathrm{QED}}|\Psi\rangle$$

- Classical field theory
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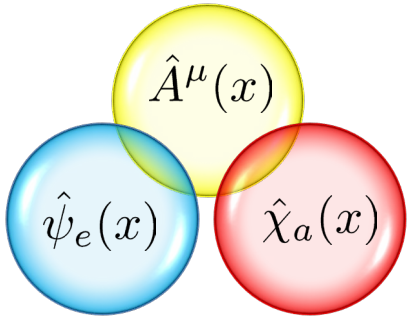
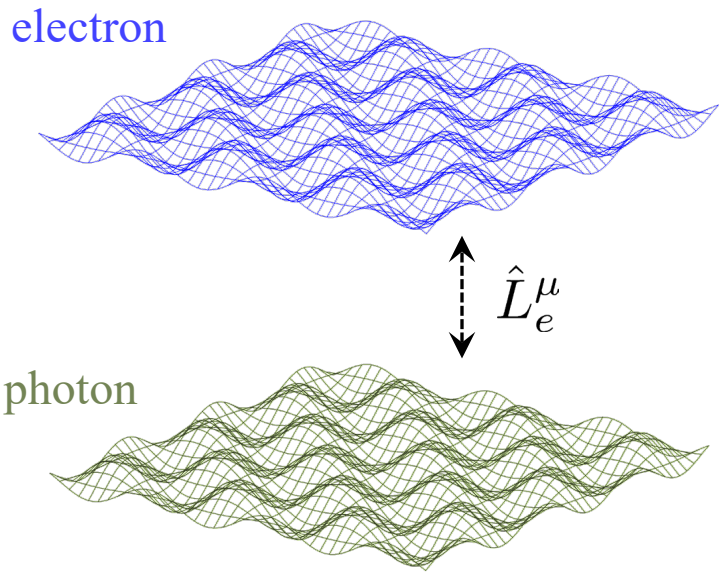



$$|\hat{\psi}, \hat{\chi}_a, \hat{A}\rangle$$

# 【QED】

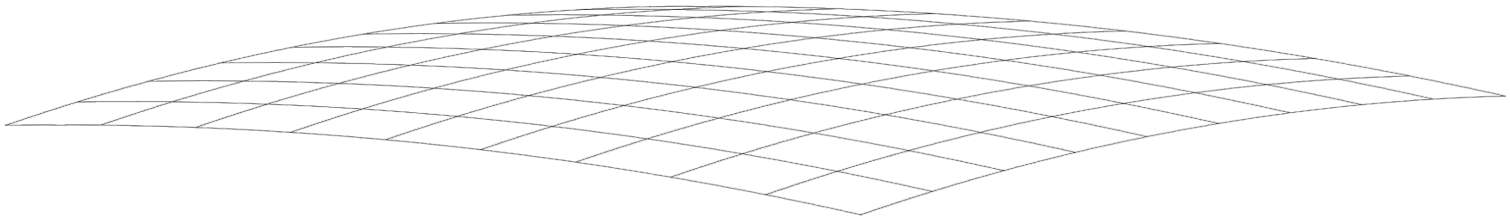



$$\partial_\nu \hat{T}^{\nu\mu} = 0$$

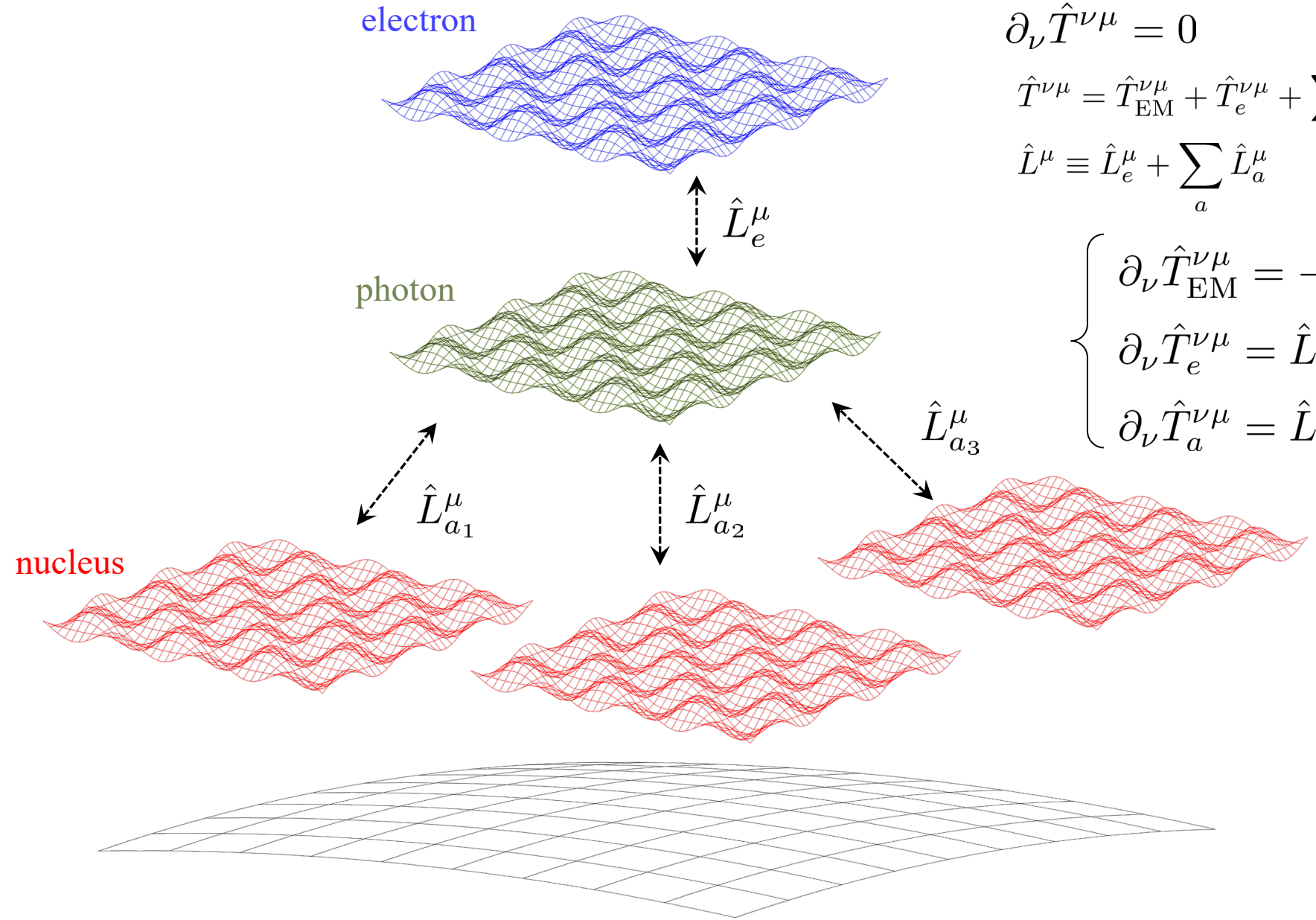
$$\hat{T}^{\nu\mu} = \hat{T}^{\nu\mu}_{\mathrm{EM}} + \hat{T}^{\nu\mu}_{e}$$

$$\hat{L}^\mu \equiv \hat{L}^\mu_e$$

$$\begin{cases} \partial_\nu \hat{T}^{\nu\mu}_{\mathrm{EM}} = -\hat{L}^\mu \\ \partial_\nu \hat{T}^{\nu\mu}_{e} = \hat{L}^\mu_e \end{cases}$$



# 【Rigged QED】




$$\partial_\nu \hat{T}^{\nu\mu} = 0$$

$$\hat{T}^{\nu\mu} = \hat{T}^{\nu\mu}_{\mathrm{EM}} + \hat{T}^{\nu\mu}_{e} + \sum_a \hat{T}^{\nu\mu}_{a}$$

$$\hat{L}^{\mu} \equiv \hat{L}^{\mu}_{e} + \sum_a \hat{L}^{\mu}_{a}$$

$$\begin{cases} \partial_\nu \hat{T}^{\nu\mu}_{\mathrm{EM}} = -\hat{L}^{\mu} \\ \partial_\nu \hat{T}^{\nu\mu}_{e} = \hat{L}^{\mu}_{e} \\ \partial_\nu \hat{T}^{\nu\mu}_{a} = \hat{L}^{\mu}_{a} \end{cases}$$

Hamiltonian density operators

$$\begin{cases} \hat{H}_{\text{QED}}(x) = \hat{H}_{\text{EM}}(x) + \hat{H}_{\text{Dirac}}(x), \\ \hat{H}_{\text{EM}}(x) = \hat{H}_{\gamma}(x) - \hat{A}_0(x)\hat{\rho}\ (x), \\ \hat{H}_{\text{Dirac}}(x) = \hat{M}_e(x) + \hat{A}_0(x)\hat{\rho}_e(x), \\ \hat{H}_{\text{Schrödinger}}(x) = \hat{T}_a(x) + \hat{A}_0(x)\hat{\rho}_a(x) \end{cases}$$

$$\hat{H}_{\text{EM}}(x) \equiv \frac{\partial \hat{L}_{\text{EM}}}{\partial(\partial \hat{A}^{\mu}/\partial t)}\frac{\partial \hat{A}^{\mu}}{\partial t} - \hat{L}_{\text{EM}}$$

$$\hat{H}_{\text{Dirac}}(x) \equiv \frac{\partial \hat{L}_{e}}{\partial(\partial \hat{\psi}/\partial t)}\frac{\partial \hat{\psi}}{\partial t} - \hat{L}_{e}$$

$$\hat{H}_{\text{Schrödinger}}(x) \equiv \frac{\partial \hat{L}_{a}}{\partial(\partial \hat{\chi}_a/\partial t)}\frac{\partial \hat{\chi}_a}{\partial t} - \hat{L}_{a}$$

Energy density and mass density operators

$$\begin{cases} \hat{H}_{\gamma}(x) = \dfrac{1}{8\pi}\left(\hat{\vec{E}}^2(x) + \hat{\vec{B}}^2(x)\right), \\ \hat{M}_e(x) = c\hat{\bar{\psi}}(x)\left(-i\hbar\gamma^k \hat{D}_{ek}(x) + m_e c\right)\hat{\psi}(x), \\ \hat{H}_e(x) = \dfrac{1}{2}\left(\hat{M}_e(x) + \hat{M}_e^{\dagger}(x)\right) \\ \hat{H}_{\text{atom}}(x) = \sum_a \hat{T}_a(x) \end{cases}$$

$$\hat{H}_{\gamma}(x) \equiv \hat{T}^{00}_{\text{EM}}(x)$$

$$\hat{H}_{e}(x) \equiv \hat{T}^{00}_{e}(x)$$

$$\hat{T}_a(x) = -\frac{\hbar^2}{2m_a}\cdot\frac{1}{2}\left(\hat{\chi}_a^{\dagger}(x)\hat{\vec{D}}_a^2(x)\hat{\chi}_a(x) + \left(\hat{\vec{D}}_a^2(x)\hat{\chi}_a(x)\right)^{\dagger}\cdot\hat{\chi}_a(x)\right)$$

$$\hat{H}_{\text{Rigged QED}}(x) = \hat{H}_{\text{QED}}(x) + \hat{H}_{\text{atom}}(x),$$

$$\hat{H}_{\text{Rigged QED}} = \int \hat{H}_{\text{Rigged QED}}(\vec{r})d\vec{r}$$

time evolution of state vector

$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}_{\text{Rigged QED}}|\Psi\rangle$$

$$E|\Psi\rangle = \hat{H}_{\text{Rigged QED}}|\Psi\rangle$$

# State vector and expectation value

- state vector

For simplicity, here we ignore photon field.

"In a relativistic theory, the wave function is a functional of these fields, not a function of particle coordinates."

$$|\Psi\rangle = \sum_{N=0}^{\infty} \int d\omega_1 \cdots d\omega_N |\omega_1, \cdots, \omega_N\rangle \Phi_N(\omega_1, \cdots, \omega_N)$$

wave function

- basis ket vector for fermion

$$|\omega_1, \cdots, \omega_N\rangle = \frac{1}{\sqrt{N!}} \hat{e}^\dagger(\omega_1) \cdots \hat{e}^\dagger(\omega_N)|0\rangle$$

- field operator (This is NOT a quantized wave function.)

$$\{\hat{\psi}(\vec{r}, t), \hat{\psi}^\dagger(\vec{r}', t)\}_+ = \delta(\vec{r} - \vec{r}')$$
$$\{\hat{e}(\omega), \hat{e}(\omega')\}_+ = \delta(\omega - \omega')$$
$$\{\hat{e}_l, \hat{e}_m\}_+ = \delta_{lm}$$

*continuous* $\hat{\psi}(ct, \vec{r}) = \int d\omega \psi(\omega, \vec{r}) \hat{e}(\omega, t)$

*discrete* $\hat{\psi}(ct, \vec{r}) = \sum_{\vec{k}\sigma} \psi_{\vec{k}\sigma}(\vec{r}) \hat{e}_{\vec{k}\sigma}(t)$

annihilation operator

expansion function

For example,

$$\psi_{\vec{k}\sigma}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$

Operators are defined at each coordinate in the real world. They do not depend on systems.

- expectation value

$$\frac{\langle\Psi|\hat{O}(x)|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

# Approximation for state vector

- conservation of the number of particles

$$|\Psi_N\rangle = \int d\omega_1 \cdots d\omega_N |\omega_1, \cdots, \omega_N\rangle \Phi_N(\omega_1, \cdots, \omega_N)$$

- Hartee-Fock

$$|\Psi_{\mathrm{HF}}\rangle = \prod_{\substack{k<k_F \\ \sigma}} \hat{c}^\dagger_{\mathbf{k}\sigma}|0\rangle \qquad |\Psi_{\mathrm{HF}}\rangle = \prod_{i}^{\mathrm{occ}} \hat{e}^\dagger_i|0\rangle$$

- Configuration Interaction (CI)

$$|\Psi_{\mathrm{CI}}\rangle = C_0|\Psi_{\mathrm{HF}}\rangle + \sum_{i}^{\mathrm{occ}}\sum_{a}^{\mathrm{unocc}} C_i^a \hat{e}_i\hat{e}^\dagger_a|\Psi_{\mathrm{HF}}\rangle + \sum_{ij}^{\mathrm{occ}}\sum_{ab}^{\mathrm{unocc}} C_{ij}^{ab}\hat{e}_i\hat{e}_j\hat{e}^\dagger_a\hat{e}^\dagger_b|\Psi_{\mathrm{HF}}\rangle + \cdots$$

- Configuration Interaction (CC)

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Psi_{\mathrm{HF}}\rangle$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots$$

$$\hat{T}_1 = \sum_{i}^{\mathrm{occ}}\sum_{a}^{\mathrm{unocc}} t_i^a \hat{e}_i\hat{e}^\dagger_a \qquad \hat{T}_2 = \sum_{ij}^{\mathrm{occ}}\sum_{ab}^{\mathrm{unocc}} \frac{1}{4} t_{ij}^{ab}\hat{e}_i\hat{e}_j\hat{e}^\dagger_a\hat{e}^\dagger_b$$

# Approximation for density matrix

- expectation value

$$\frac{\langle\Psi|\hat{O}(x)|\Psi\rangle}{\langle\Psi|\Psi\rangle} \qquad \hat{O}(x) = \hat{\psi}^{\dagger}(x)\Gamma\hat{\psi}(x)$$

- field operator expansion

$$\begin{aligned}\hat{\psi}(ct,\vec{r}) &= \int d\omega\psi(\omega,\vec{r})\hat{e}(\omega,t) \\ &= \sum_{p}\psi_{p}(\vec{r})\hat{e}_{p}(t)\end{aligned}$$

$$\langle\Psi|\hat{O}(x)|\Psi\rangle = \sum_{pq}\psi_{p}^{\dagger}(\vec{r})\Gamma\psi_{q}(\vec{r})\underline{\langle\Psi|\hat{e}_{p}^{\dagger}(t)\hat{e}_{q}(t)|\Psi\rangle}$$

≈ Density matrix of DFT

# Local picture change error

**Local picture change errors**

In order to investigate the local physical quantities in large molecular systems, the relativistic two-component formulation is suitable in comparison with the four-component formulation, which consumes much time and cost. However, local physical quantities cannot be derived rigorously by a two-component wave function. Here, we mention this problem with local physical quantities calculated from two-component relativistic wave packets. The Foldy-Wouthuysen-Tani transformation[15] is widely applied to construct a relativistic two-component formulation. The large and small components of the Hamiltonian can be decoupled by a unitary operator $U$ as

$$H_{4c}=\begin{bmatrix} h_{LL} & h_{LS} \\ h_{SL} & h_{SS} \end{bmatrix},\quad UH_{4c}U^{\dagger}=\begin{bmatrix} h_{++} & 0 \\ 0 & h_{--} \end{bmatrix}. \tag{26}$$

The wave packet is transformed as

$$\psi_{2c}=U\psi_{4c}=\begin{pmatrix} \psi_{2c+} \\ \psi_{2c-} \end{pmatrix}. \tag{27}$$

This transformation does not change integrated value of the energy density:

$$\int \psi_{4c}^{\dagger}H_{4c}\psi_{4c}d^3\vec{r}=\int \psi_{2c+}^{\dagger}h_{++}\psi_{2c+}d^3\vec{r}+\int \psi_{2c-}^{\dagger}h_{--}\psi_{2c-}d^3\vec{r}. \tag{28}$$

Integrated physical quantities are often approximated as

$$\begin{aligned}\int \psi_{4c}^{\dagger}\Omega_{4c}\psi_{4c}d^3\vec{r}&=\int \psi_{2c}^{\dagger}U\Omega_{4c}U^{\dagger}\psi_{2c}d^3\vec{r}\\ &\approx\int \psi_{2c+}^{\dagger}[\Omega_{4c}]_{LL}\psi_{2c+}d^3\vec{r},\end{aligned} \tag{29}$$

where $\Omega_{4c}$ is an arbitrary operator. This approximation causes the so-called picture change error.[16] Besides the picture change error, there is another problem when we treat local physical quantities by the two-component wave packets. Since the unitary operator $U$ includes some differential operators, local quantities are not conserved before and after the transformation:

$$\psi_{4c}^{\dagger}\Omega_{4c}\psi_{4c}\neq\psi_{2c}^{\dagger}U\Omega_{4c}U^{\dagger}\psi_{2c}. \tag{30}$$

This means that local physical quantities cannot be derived rigorously by the two-component wave function defined by this unitary transformation with the existence of the Dirac mass term. This difficulty is characteristic of evaluation of local physical quantities. For this reason, we calculate local physical quantities using the two-component relativistic wave function as an approximation of the large component of the four-component relativistic wave function.

*M. Fukuda, et al,*
*Int. J. Quant. Chem., 116, 920 (2016)*

# Local picture change error

- picture change error

$$\int \psi_{4c}^{\dagger} \Omega_{4c} \psi_{4c} d^3\vec{r} = \int \psi_{2c}^{\dagger} U \Omega_{4c} U^{\dagger} \psi_{2c} d^3\vec{r}$$

$$\approx \int \psi_{2c+}^{\dagger} [\Omega_{4c}]_{LL} \psi_{2c+} d^3\vec{r},$$

- local picture change error

$$\psi_{4c}^{\dagger} \Omega_{4c} \psi_{4c} \neq \psi_{2c}^{\dagger} U \Omega_{4c} U^{\dagger} \psi_{2c}$$

$\because$ $U$ includes differential operators

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# Table of Contents

## Einstein equation（General relativistic theory)

$$G_{\mu\nu} = -\frac{8\pi G}{c^4} T_{\mu\nu}$$

The symmetric energy-momentum tensor $T_{\mu\nu}$ appears in the Einstein equation.

The symmetric energy-momentum tensor is given by using the vierbein formulation.

$$T_{\mu\nu} = \frac{1}{\sqrt{-g}} \eta_{ab} e^{b}{}_{\nu} \frac{\delta\left(L\sqrt{-g}\right)}{\delta e_a{}^{\mu}}$$

This formulation is necessary to treat fermions in the relativistic theory.

$$L = L_e + L_{\mathrm{EM}} \quad \text{(QED Lagrangian)}$$

$$L_e = \frac{1}{2}\bar{\psi}\left(i\hbar\gamma^a e_a^{\mu} D_{\mu}(g) - mc\right)\psi + h.c.$$

$$L_{\mathrm{EM}} = -\frac{1}{16\pi} F_{\mu\nu} F_{\rho\sigma} g^{\mu\rho} g^{\nu\sigma}$$

Spin connection

$$D_{\mu}(g) = \partial_{\mu} + i\frac{1}{2\hbar}\gamma_{ab\mu} J^{ab} + i\frac{q}{\hbar c} A_{\mu}$$

$$J^{ab} = \frac{i\hbar}{4}\left[\gamma^a, \gamma^b\right]$$

$$T_{\mu\nu} = -\varepsilon^{\Pi}_{\mu\nu} - \tau^{\Pi}_{\mu\nu}(g) - \frac{1}{4\pi} g^{\rho\sigma} F_{\mu\rho} F_{\nu\sigma} - g_{\mu\nu}\left(L_e + L_{EM}\right) = T_{\nu\mu}; \text{symmetric}$$

Symmetry-polarized geometrical tensor

$$\varepsilon^{\Pi}_{\mu\nu} = -\frac{1}{\sqrt{-g}} \eta_{ab} e^{b}{}_{\nu} \left[ \frac{\partial\left(L_e\sqrt{-g}\right)}{\partial \gamma^{cd}{}_{\rho}} \frac{\partial \gamma^{cd}{}_{\rho}}{\partial e_a{}^{\mu}} - \partial_{\sigma}\left( \frac{\partial\left(L_e\sqrt{-g}\right)}{\partial \gamma^{cd}{}_{\rho}} \frac{\partial \gamma^{cd}{}_{\rho}}{\partial\left(\partial_{\sigma} e_a{}^{\mu}\right)} \right) \right]$$

*A. Tachibana , J. Math. Chem. 50, 669-688 (2012).*

Symmetry-polarized stress tensor

$$\tau^{\Pi}_{\mu\nu}(g) = -\frac{1}{\sqrt{-g}} \eta_{ab} e^{b}{}_{\nu} \frac{\partial\left(L_e\sqrt{-g}\right)}{\partial e_a{}^{\mu}}$$

$$\begin{pmatrix} \varepsilon^{A}_{\mu\nu} = ( \\ \tau^{A}_{\mu\nu}(g) = \end{pmatrix}$$

This equation is called "**Spin Vorticity Principle**"

The energy momentum tensor is symmetric

$$\varepsilon^{A\mu\nu} + \tau^{A\mu\nu}(g) = 0$$

# Spin Vorticity Theory

The "**spin vorticity theory**" is a theory which gives the time evolution equations of the electronic momentum density and spin angular momentum density as equations which relate the local physical quantities derived from the energy-momentum tensor density.

$$\hat{T}_e^{\mu\nu} = -\varepsilon^{S\mu\nu} - \tau^{S\mu\nu}(g)$$

$\hat{T}_e^{00}$ = energy density

$\hat{T}_e^{i0} \propto$ momentum density

$\hat{T}_e^{ij} \propto$ stress tensor density

$$j_5^{\mu} = Z_e e c \psi \gamma^{\mu} \gamma_5 \psi$$

☆Time evolution of electronic momentum

$$\frac{\partial}{\partial t}\left(\hat{\vec{\Pi}} + \frac{1}{2}\mathrm{rot}\hat{\vec{s}}\right) = \hat{\vec{L}} + \mathrm{div}\hat{\overleftrightarrow{\tau}}^{S}$$

Kinetic momentum density

Lorentz force density

Spin vorticity

Symmetric stress tensor

☆Time evolution of electronic spin

$$\frac{\partial}{\partial t}\hat{\vec{s}} = \hat{\vec{t}} - \mathrm{grad}\,\hat{\phi}_5 \qquad \left(\frac{\partial}{\partial t}\hat{s}^k = -\epsilon_{kln}\hat{\tau}^{Aln} - \partial_k\hat{\phi}_5\right)$$

Spin angular momentum density

Spin torque density

Zeta potential

Spin vorticity principle

$$\varepsilon^{A\mu\nu} + \tau^{A\mu\nu}(g) = 0$$

The spin vorticity principle gives the equation of motion of local spin and the vorticity of spin in the limit to the Minkowski space-time.


A. Tachibana, J. Comput. Chem. Jpn., 13, 18 (2014)
A. Tachibana, Indian J. Chem. A, **53**, 1031 (2014).
A. Tachibana, J. Math. Chem., 53:1943 (2015)

# The conservation law of momentum

Kinetic momentum

Spin vorticity

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\left(\vec{G}+\vec{G}^{\dagger}\right)+\vec{\Pi}+\frac{1}{2}\mathrm{rot}\vec{s}\right)=-\mathrm{div}\left(\overleftrightarrow{\sigma}-\overleftrightarrow{\tau}^{S}\right) \quad \Leftarrow \quad \partial_{\nu}T^{\nu j}=0$$

Poynting vector

Maxwell stress tensor

Electronic stress tensor

$$\begin{cases} \dfrac{\partial}{\partial t}\left(\vec{\Pi}+\dfrac{1}{2}\mathrm{rot}\vec{s}\right)=\vec{L}+\mathrm{div}\,\overleftrightarrow{\tau}^{S} & \text{(the electron field)} \quad \Leftarrow \quad \partial_{\nu}T_{e}^{\nu j}=L^{j} \\ \dfrac{\partial}{\partial t}\left(\dfrac{1}{2}\left(\vec{G}+\vec{G}^{\dagger}\right)\right)=-\vec{L}-\mathrm{div}\,\overleftrightarrow{\sigma} & \text{(the photon field)} \quad \Leftarrow \quad \partial_{\nu}T_{EM}^{\nu j}=-L^{j} \end{cases}$$

## ☆Electronic momentum density

$$\hat{P}_e^i = \frac{1}{c}\hat{T}_e^{i0}$$

$$\hat{\vec{P}}_e = \hat{\vec{\Pi}} + \frac{1}{2}\mathrm{rot}\hat{\vec{s}}$$

$$\hat{\Pi}^k = \frac{1}{2}\hat{\psi}^\dagger\left(-i\hbar\hat{D}_{ek}\right)\hat{\psi} + h.c.$$

$$\hat{s}^k = \frac{\hbar}{2}\hat{\psi}^\dagger\Sigma^k\hat{\psi} = \frac{\hbar}{2Z_e ec}\hat{j}_5^k$$

## ☆Time evolution of electronic momentum density

$$\hat{\vec{L}} = \hat{\vec{E}}\hat{\rho} + \frac{1}{c}\hat{\vec{j}}\times\hat{\vec{B}}$$

$$\hat{\tau}^{\Pi ln} = \frac{i\hbar c}{2}\hat{\psi}^\dagger\gamma^0\gamma^n\hat{D}_{el}\hat{\psi} + h.c.$$

$$\hat{\tau}^{Sij} = (\hat{\tau}^{\Pi ij} + \hat{\tau}^{\Pi ji})/2$$

$$\frac{\partial}{\partial t}\left(\hat{\vec{\Pi}} + \frac{1}{2}\mathrm{rot}\hat{\vec{s}}\right) = \hat{\vec{L}} + \mathrm{div}\hat{\overleftrightarrow{\tau}}^S$$

Spin vorticity

Stress tensor

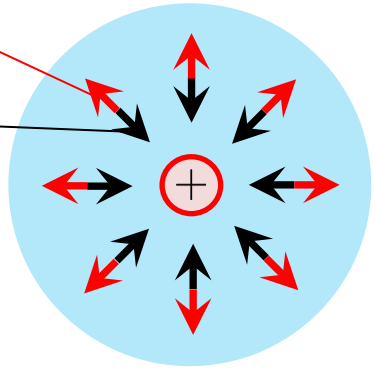
Kinetic momentum

Lorentz force

Tension

tension density

Lorentz force density



Integrating over the whole region,

$$\Rightarrow \frac{\partial}{\partial t}\left(\int\hat{\vec{\Pi}}d^3\vec{r} + \frac{1}{2}\int\mathrm{rot}\hat{\vec{s}}d^3\vec{r}\right) = \int\hat{\vec{L}}d^3\vec{r} + \int\mathrm{div}\hat{\overleftrightarrow{\tau}}^S d^3\vec{r}$$

$$= 0 \qquad = 0$$

$$\Rightarrow \frac{\partial}{\partial t}\int\hat{\vec{\Pi}}d^3\vec{r} = \int\hat{\vec{L}}d^3\vec{r}$$

This is the same as the equation of motion in quantum mechanics.

In a local region, the tension of quantum field theory can compensate the Lorentz force, which is the basic mechanism leading to the quantum mechanical stationary state.

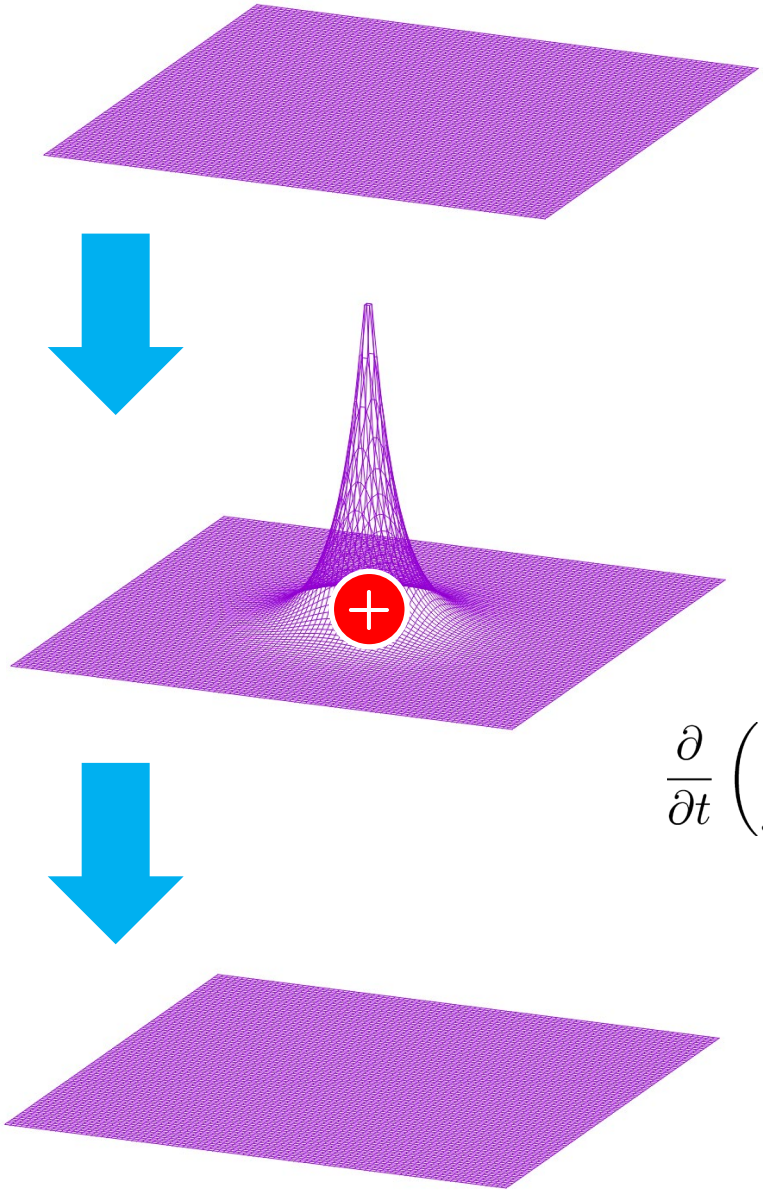
In the framework of quantum mechanics,

$$\frac{d\vec{\pi}}{dt} = Z_e e(\vec{E} + \vec{\alpha}\times\vec{B}).$$

Tension density does not appear.

*A. Tachibana , J. Math. Chem.* ***50****, 669 (2012).*
*M. Fukuda et al., AIP Advances* ***6****, 025108 (2016).*

Imagine a one electron system



☆Time evolution of electronic momentum density

$$\frac{\partial}{\partial t}\left(\hat{\vec{\Pi}}+\frac{1}{2}\mathrm{rot}\hat{\vec{s}}\right)=\hat{\vec{L}}+\mathrm{div}\,\hat{\overleftrightarrow{\tau}}^{S}$$

Spin vorticity

Stress tensor

Kinetic momentum

Lorentz force

Tension

$$\frac{\partial}{\partial t}\left(\int\hat{\vec{\Pi}}d^3\vec{r}+\underbrace{\frac{1}{2}\int\mathrm{rot}\hat{\vec{s}}d^3\vec{r}}_{=0}\right)=\int\hat{\vec{L}}d^3\vec{r}+\underbrace{\int\mathrm{div}\,\hat{\overleftrightarrow{\tau}}^{S}d^3\vec{r}}_{=0}$$

This is the same as the equation of motion in quantum mechanics.

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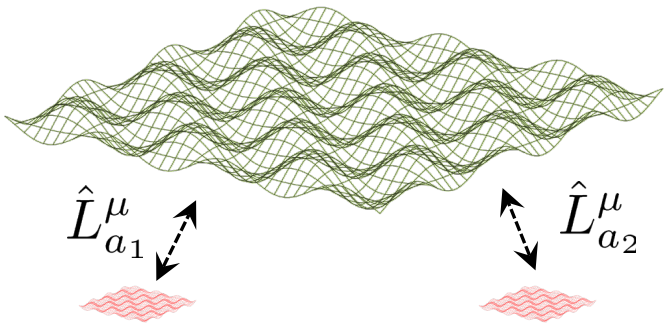
# 【Stress tensor density】

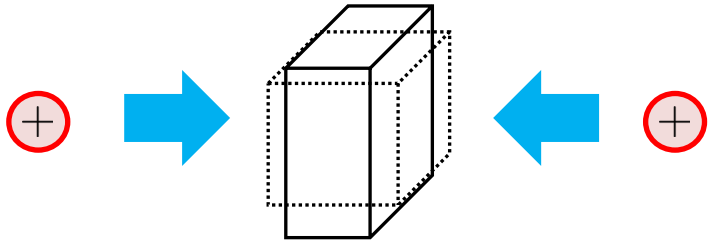
photon

nucleus




Equation of motion of the momentum density of the photon field

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\left(\vec{G}+\vec{G}^{\dagger}\right)\right)=-\vec{L}-\mathrm{div}\overleftrightarrow{\sigma}$$



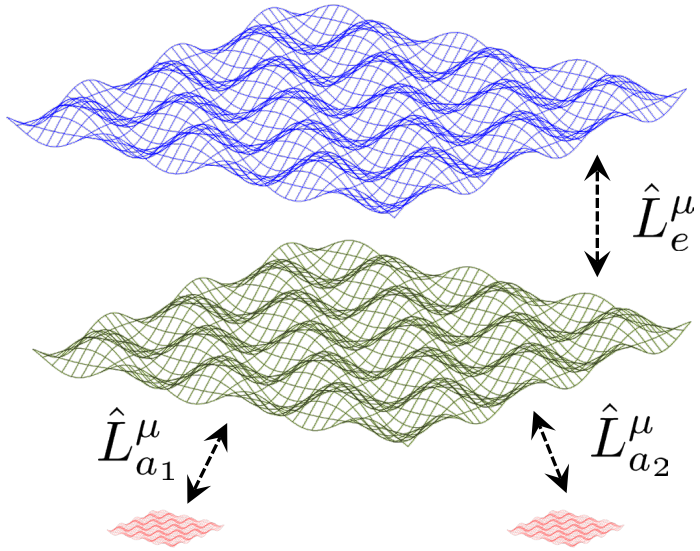
compressive stress

---

electron

photon

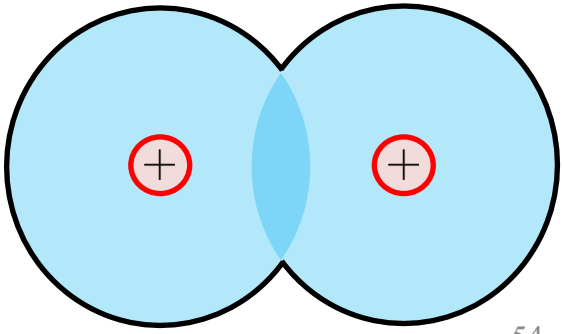
nucleus




Equation of motion of the momentum density of the electron field

$$\frac{\partial}{\partial t}\left(\vec{\Pi}_e+\frac{1}{2}\mathrm{rot}\vec{s}_e\right)=\vec{L}_e+\mathrm{div}\overleftrightarrow{\tau}^{S}_{e}$$

?



# Electronic stress tensor analysis

- Electronic stress tensor density operator

$$\hat{\tau}_e^{Sij} \equiv \frac{\hat{\tau}_e^{\Pi ij} + \hat{\tau}_e^{\Pi ij}}{2} \qquad \hat{\tau}_e^{\Pi ln} = \frac{i\hbar c}{2}\hat{\psi}^\dagger \gamma^0 \gamma^n \hat{D}_{el}\hat{\psi} + h.c.$$

$$\hat{\tau}_{e,nonrel}^{Skl}(x) = \frac{\hbar^2}{4m}\left[\hat{\psi}^\dagger(x)\hat{D}_{ek}(x)\hat{D}_{el}(x)\hat{\psi}(x) - \left(\hat{D}_{ek}(x)\hat{\psi}(x)\right)^\dagger \hat{D}_{el}(x)\hat{\psi}(x)\right] + h.c.$$

- Electronic kinetic energy density operator

$$\hat{T}_e(x) = -\frac{\hbar^2}{4m}\sum_{k=1}^{3}\left[\hat{\psi}^\dagger(x)\hat{D}_{ek}(x)\hat{D}_{ek}(x)\hat{\psi}(x)\right] + h.c.$$

- Total energy at the equilibrium state (virial theorem)

dimension of energy density

$$E = -\int d^3\vec{r}\left\langle \hat{T}_e(x)\right\rangle = \frac{1}{2}\int d^3\vec{r}\sum_{k=1}^{3}\left\langle \hat{\tau}_e^{Skk}(x)\right\rangle$$

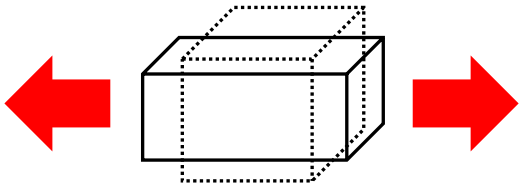
$$\left\langle \overset{\hat{\leftrightarrow}}{\tau}{}^S(x)\right\rangle = \begin{pmatrix} \tau^{Sxx}(x) & \tau^{Sxy}(x) & \tau^{Sxz}(x) \\ \tau^{Syx}(x) & \tau^{Syy}(x) & \tau^{Syz}(x) \\ \tau^{Szx}(x) & \tau^{Szy}(x) & \tau^{Szz}(x) \end{pmatrix}$$

- Energy density constructed from stress tensor

$$\varepsilon_\tau^S(x) = \frac{1}{2}\sum_{k=1}^{3}\left\langle \hat{\tau}_e^{Skk}(x)\right\rangle$$

$$\overset{\text{diag}}{\rightarrow} \begin{pmatrix} \tau^{S11}(x) & 0 & 0 \\ 0 & \tau^{S22}(x) & 0 \\ 0 & 0 & \tau^{S33}(x) \end{pmatrix}$$

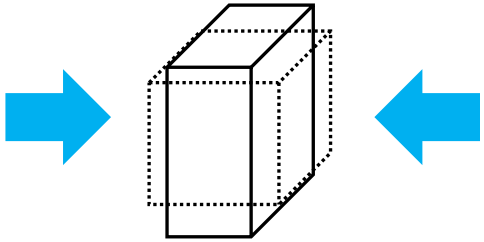
$$\tau^{S11}(x) \geq \tau^{S22}(x) \geq \tau^{S33}(x)$$



tensile stress

"Positive eigenvalue of stress tensor"

Electron in a region is pulled by the outer region.



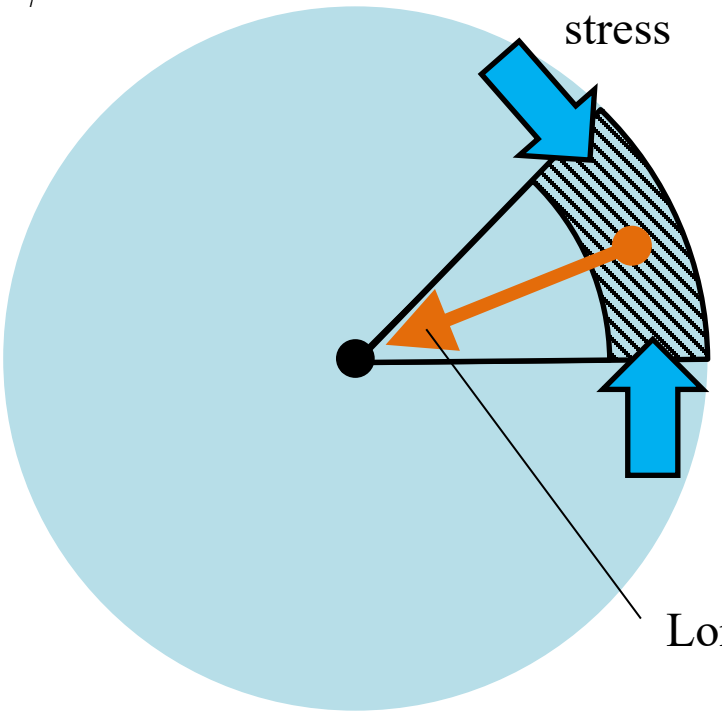
compressive stress

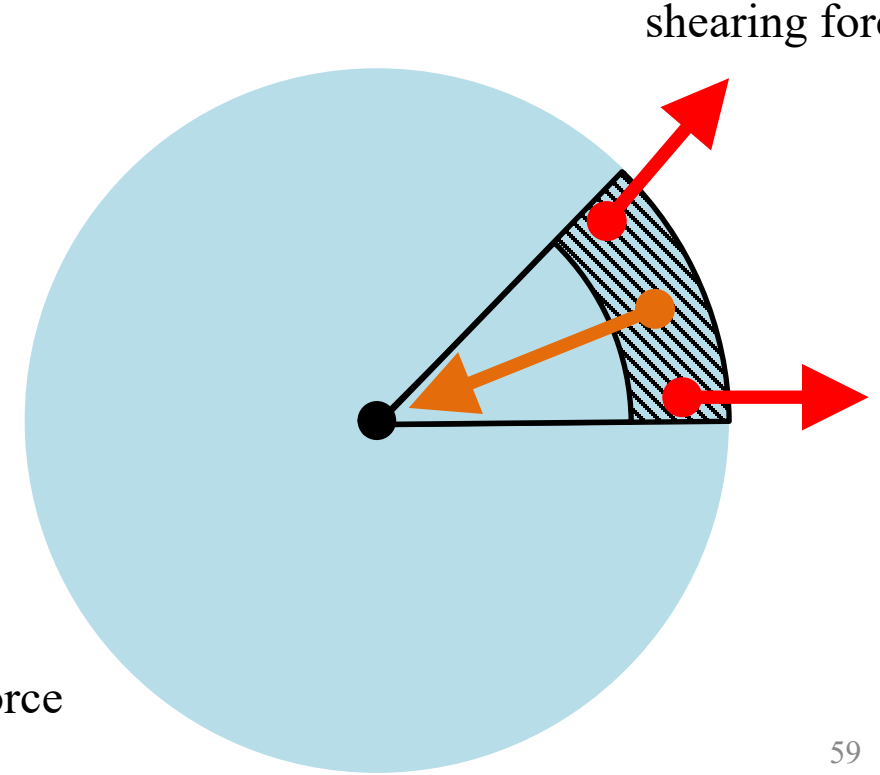
"Negative eigenvalue of stress tensor"

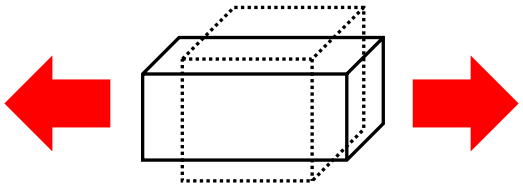
Electron in a region is compressed by the outer region.

For example, H like atom case

$\psi \propto e^{-\alpha r}$



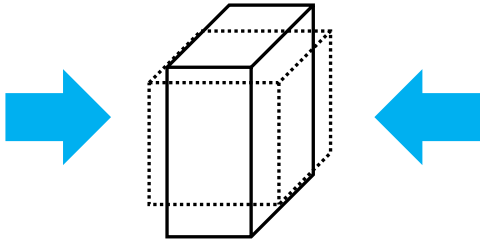





tensile stress

"Positive eigenvalue of stress tensor"

Electron in a region is pulled by the outer region.



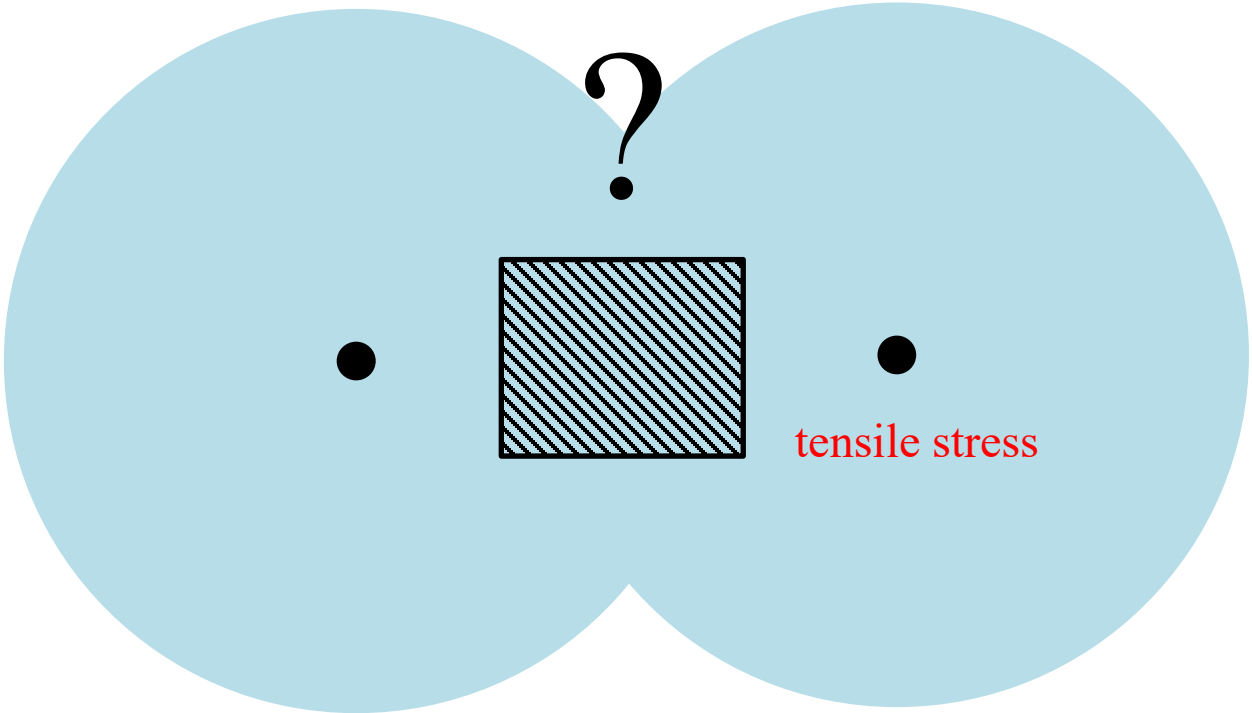
compressive stress

"Negative eigenvalue of stress tensor"

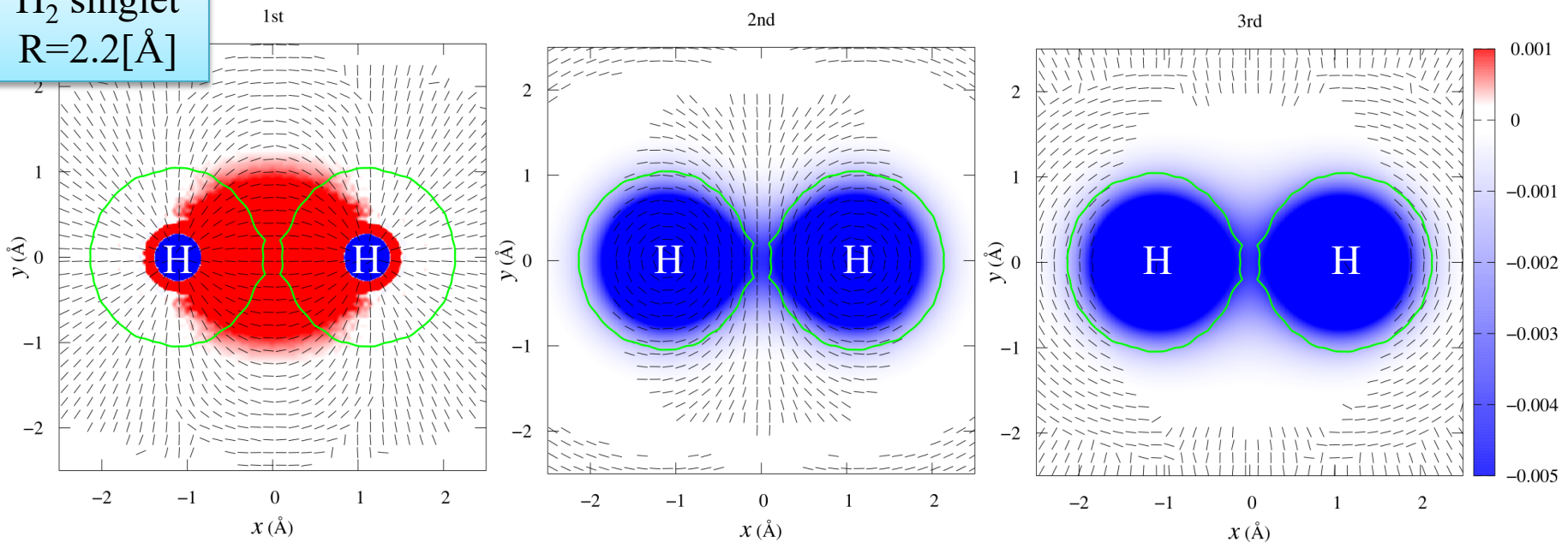
Electron in a region is compressed by the outer region.

How about $H_2$ case?

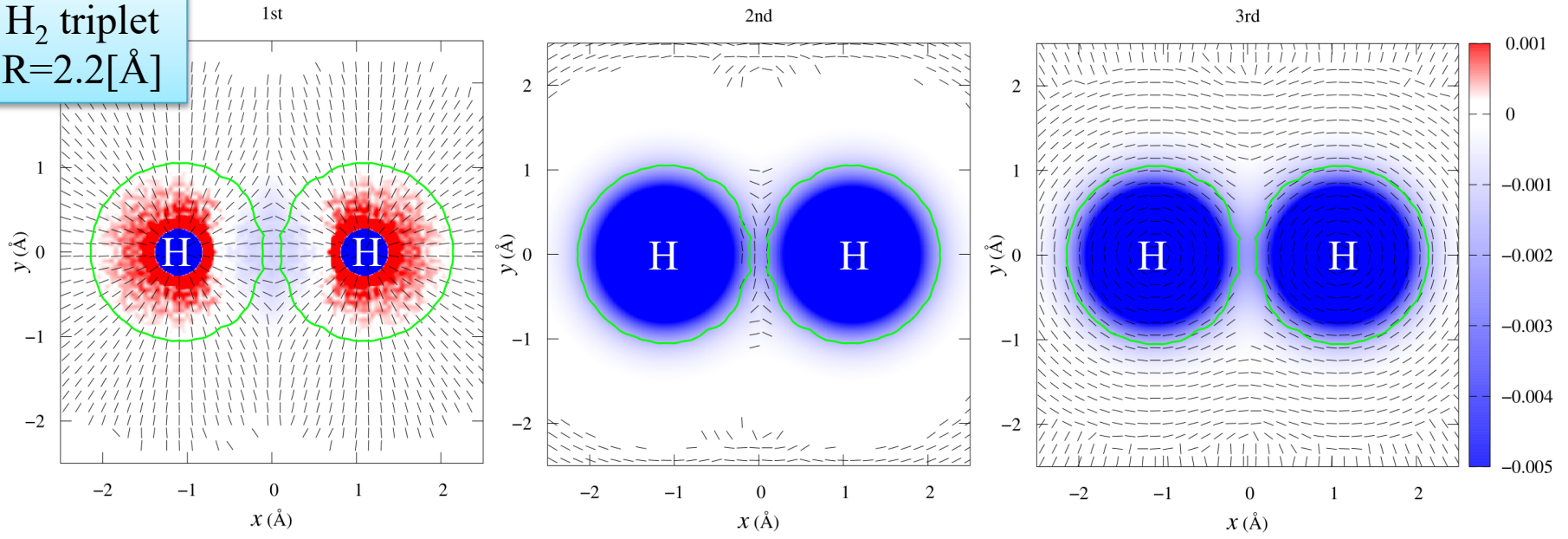
$$\psi \propto e^{-\alpha(r-R)} + e^{-\alpha(r+R)}$$



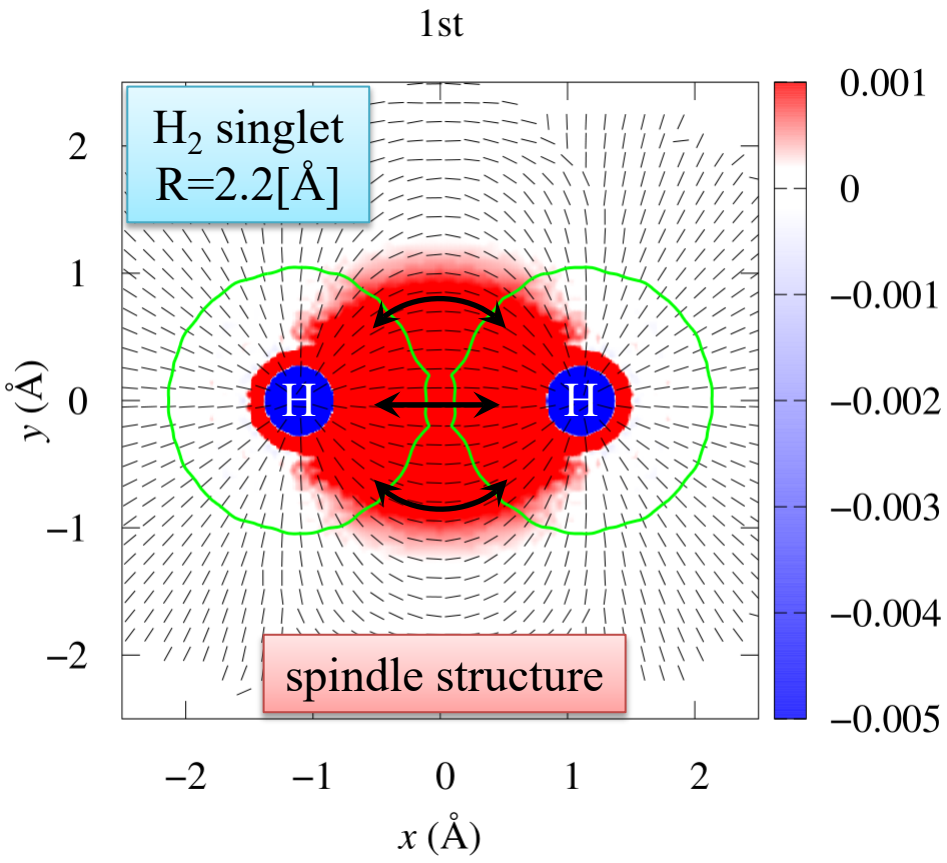
$H_2$ singlet
R=2.2[Å]

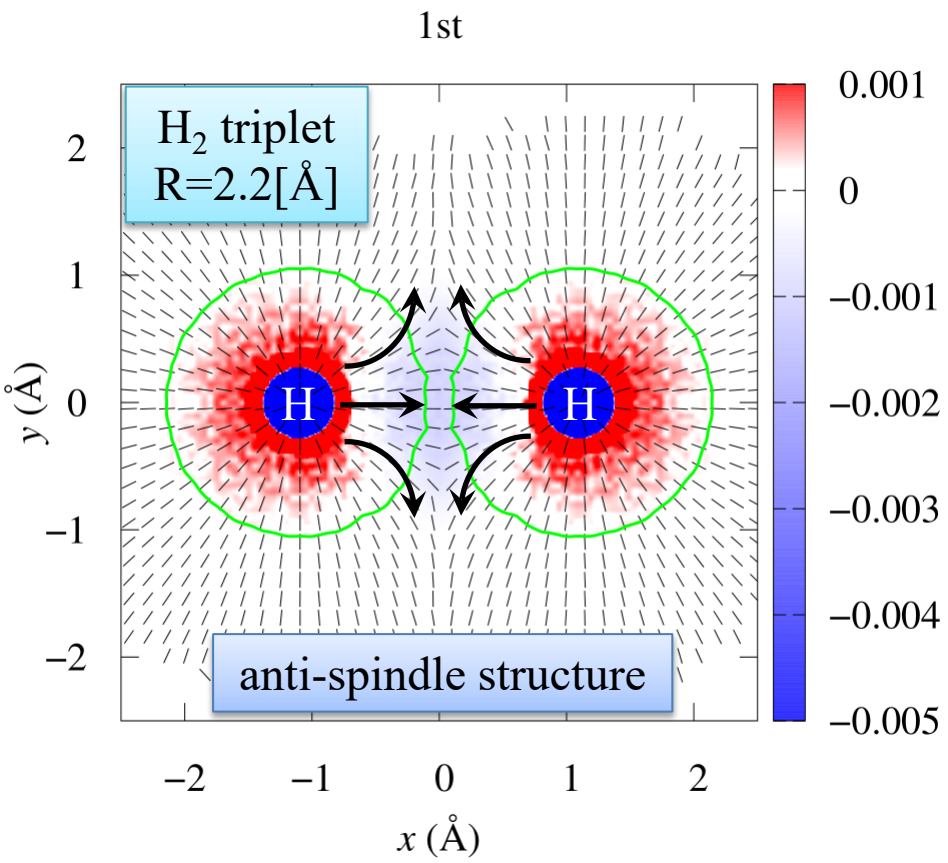


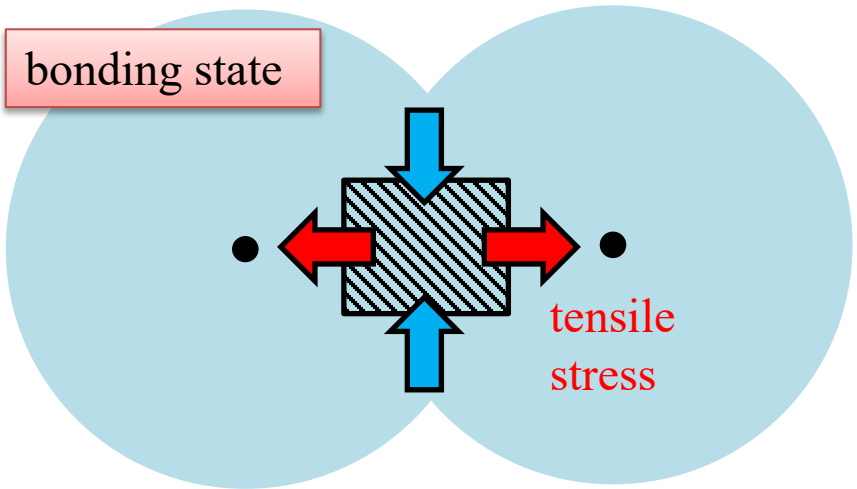

$H_2$ triplet
R=2.2[Å]

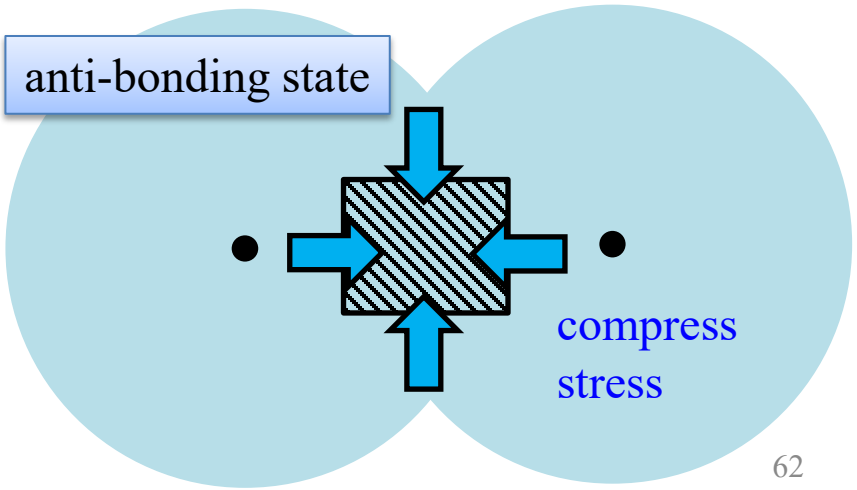



※$R_{eq} = 0.74$ [Å]


1st
H2 singlet
R=2.2[Å]
H
H
spindle structure
0.001
0
−0.001
−0.002
−0.003
−0.004
−0.005
2
1
0
−1
−2
y (Å)
−2
−1
0
1
2
x (Å)

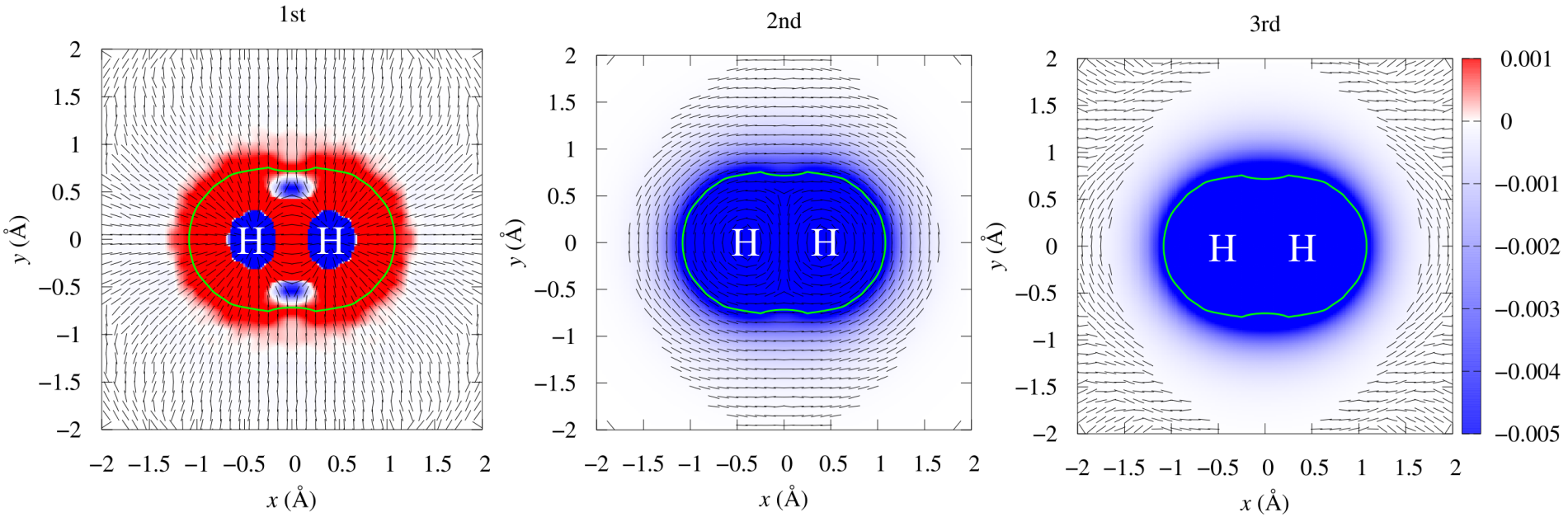

1st
H2 triplet
R=2.2[Å]
H
H
anti-spindle structure
0.001
0
−0.001
−0.002
−0.003
−0.004
−0.005
2
1
0
−1
−2
y (Å)
−2
−1
0
1
2
x (Å)


bonding state
tensile
stress


anti-bonding state
compress
stress

# $H_2$ singlet, $R=R_{eq}=0.74$[Å]

## Electronic stress tensor analysis




The $H_2$ bonding region with **covalency** can be characterized and visualized by the "spindle structure"[*], where the largest eigenvalue of the electronic stress tensor is positive and the corresponding eigenvectors form a bundle of flow lines that connects nuclei.

[*] *A. Tachibana, Int. J. Quant. Chem., 100, 981 (2004).*

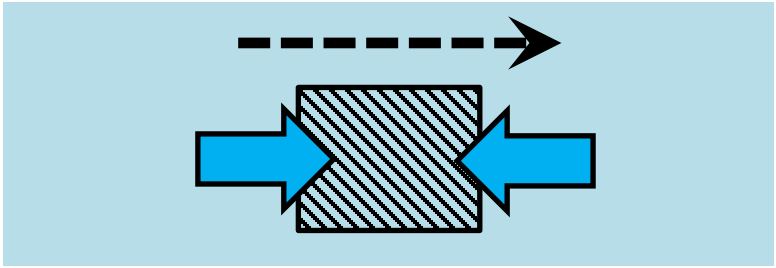
- Total energy at the equilibrium state (virial theorem)

$$E = -\int d^3\vec{r}\,\left\langle \hat{T}_e(x)\right\rangle = \frac{1}{2}\int d^3\vec{r}\sum_{k=1}^{3}\left\langle \hat{\tau}_e^{Skk}(x)\right\rangle$$

# Plane wave
# （free electron, metallic）

$$\psi = e^{-ikx}$$

$$\tau_{xx} = -\frac{\hbar^2 k^2}{m}$$



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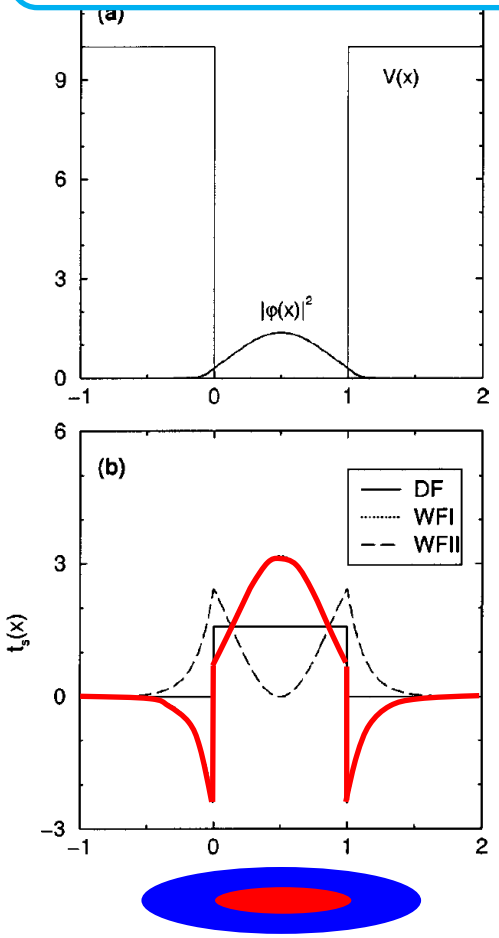
# Kinetic energy density

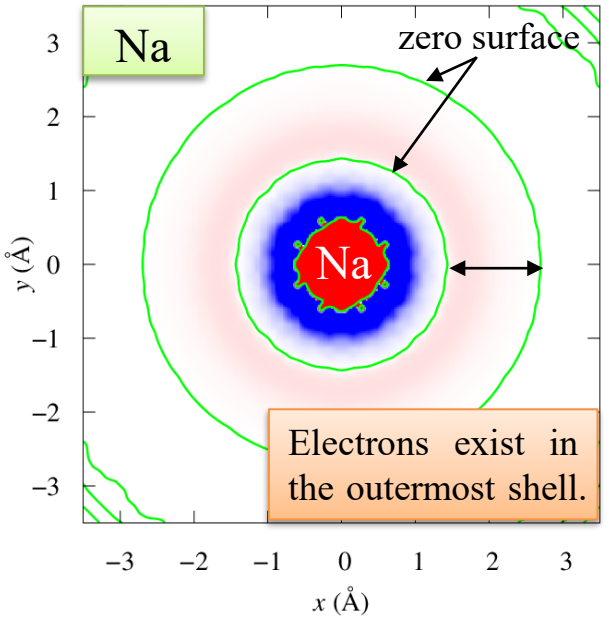
$$\hat{T}_e = -\frac{\hbar^2}{2m} \cdot \frac{1}{2}\left(\hat{\psi}^\dagger \hat{\vec{D}}_e^2 \hat{\psi} + h.c.\right)$$

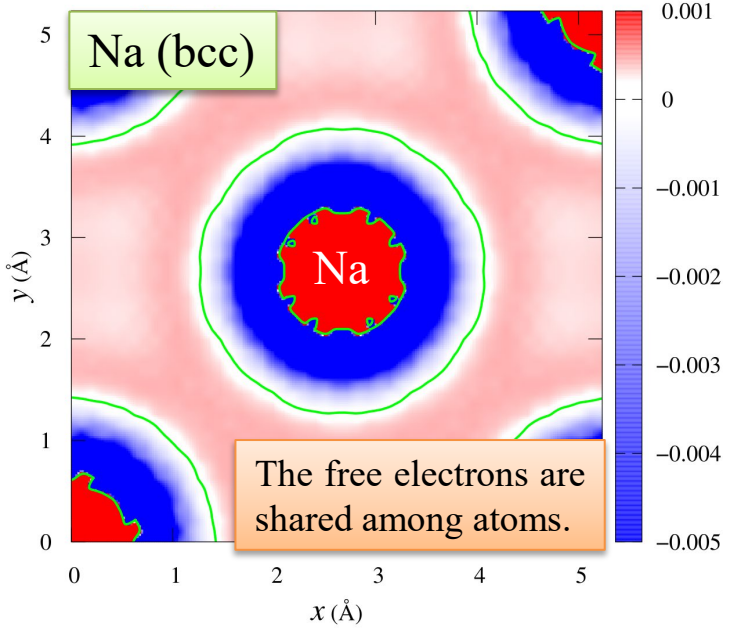
$$-\frac{\hbar}{2m}\psi^\dagger \nabla^2 \psi = \psi^\dagger (E - V)\psi$$

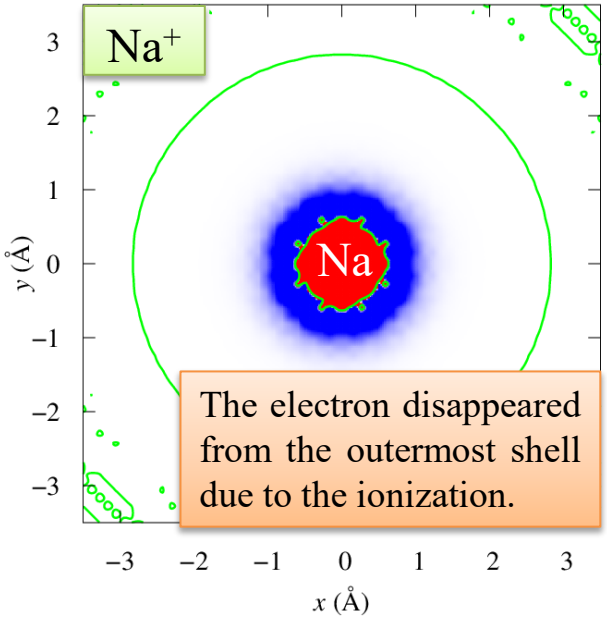


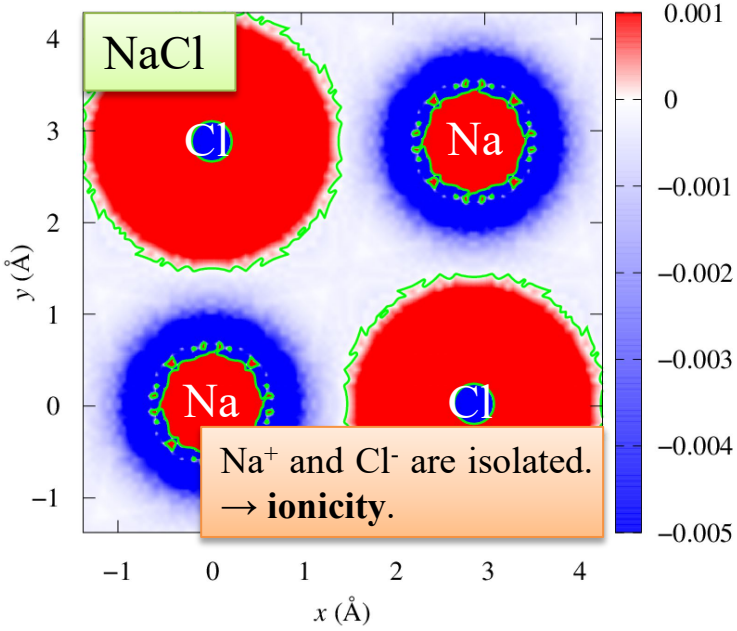

The kinetic energy density is positive inside of the well, and negative at the tunneling region.

Figures from
Sim *et al.*, J. Chem. Phys., 118, 18, (2003).

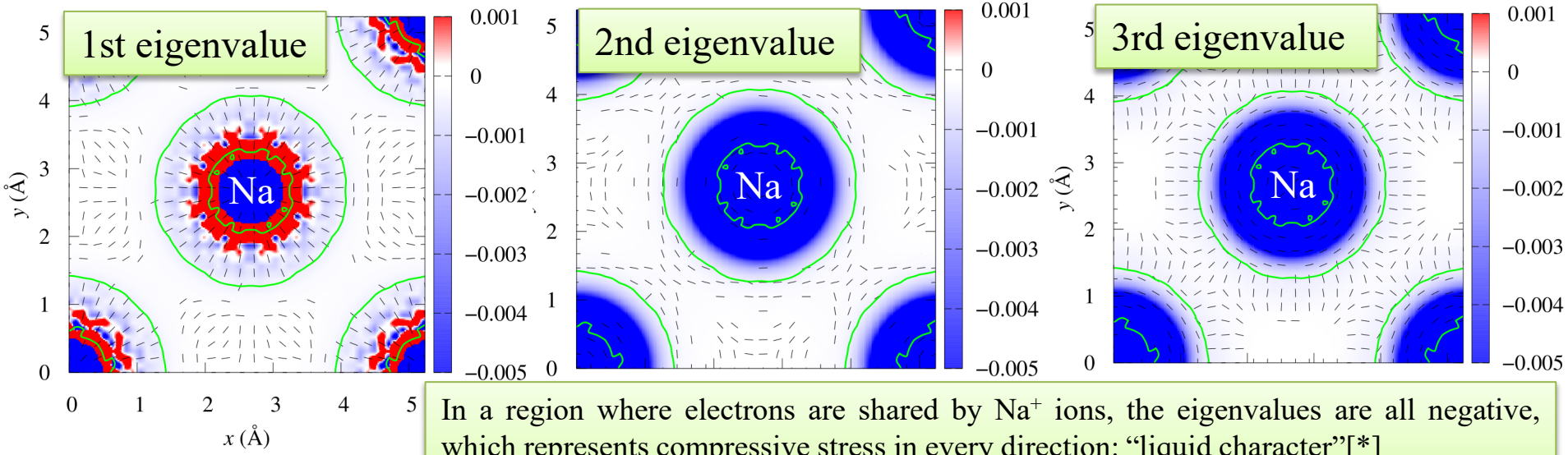


# Na (bcc), eigenvalue of electronic stress tensor density

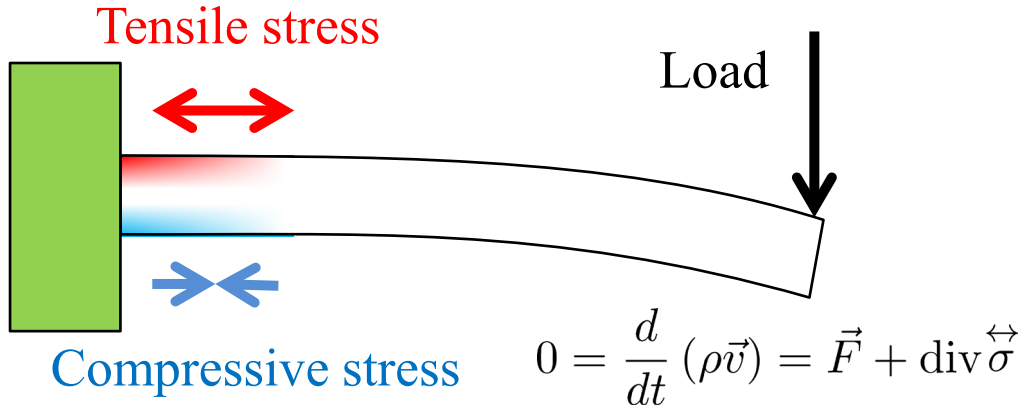



In a region where electrons are shared by $Na^+$ ions, the eigenvalues are all negative, which represents compressive stress in every direction: "liquid character"[*]
→ **metallicity**

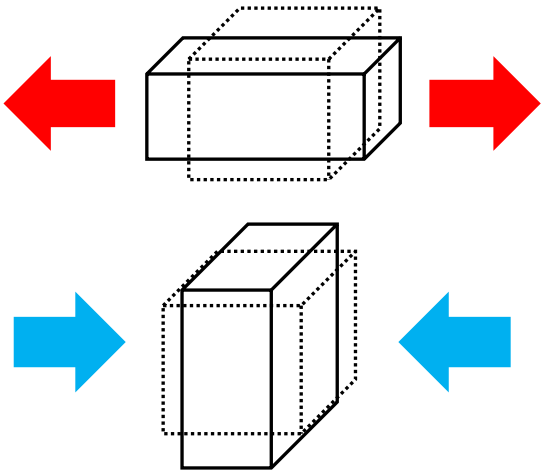
[*] *A. Tachibana, J. Comput. Chem., 40, 316 (2018).*

Time-independent steady state : $0 = \frac{\partial}{\partial t}\left\langle \hat{\vec{\Pi}} + \frac{1}{2}\mathrm{rot}\hat{\vec{s}} \right\rangle = \langle \hat{\vec{L}} \rangle + \mathrm{div}\langle \hat{\overleftrightarrow{\tau}}^S \rangle$

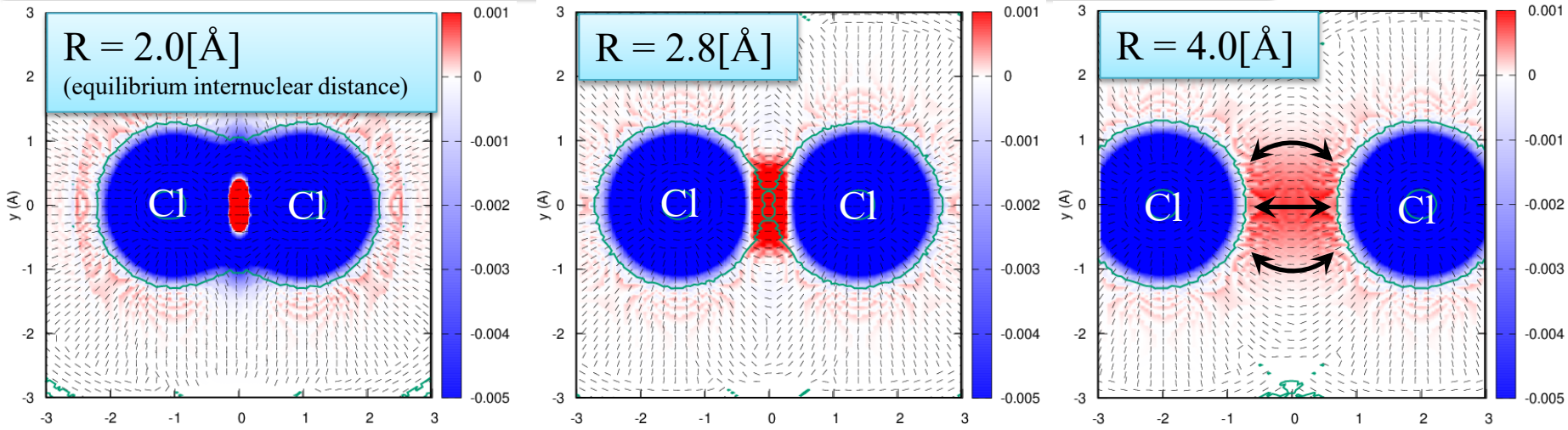
★Image of stress tensor in continuum mechanics




$0 = \frac{d}{dt}(\rho\vec{v}) = \vec{F} + \mathrm{div}\overleftrightarrow{\sigma}$



## ☆$Cl_2$ ground state, maximum eigenvalue of electronic stress tensor density

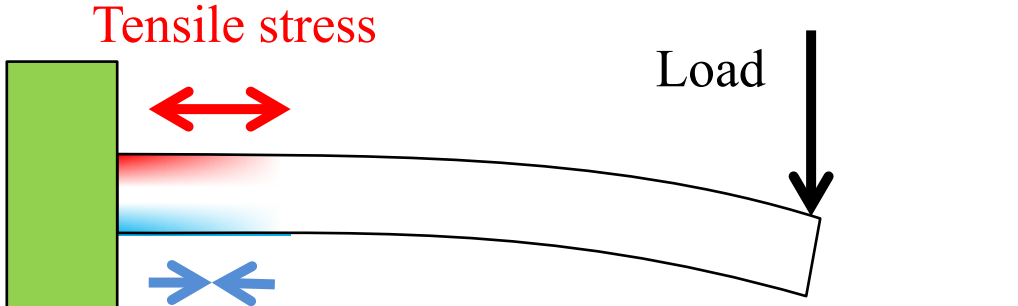



The Cl bonding region with **covalency** can be characterized and visualized by the "spindle structure"[*], where the largest eigenvalue of the electronic stress tensor is positive and the corresponding eigenvectors form a bundle of flow lines that connects nuclei.

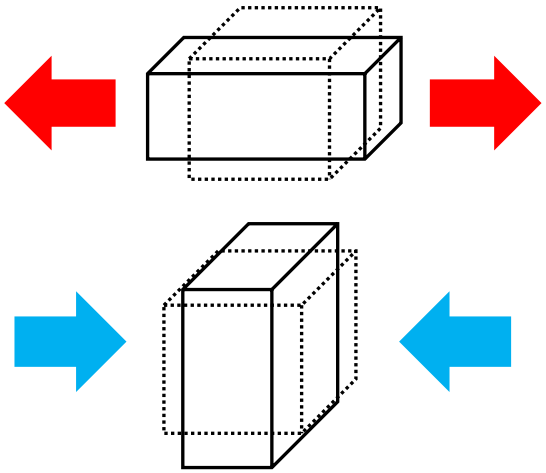
[*] *A. Tachibana, Int. J. Quant. Chem., 100, 981 (2004).*

Time-independent steady state : $0 = \frac{\partial}{\partial t}\left\langle \hat{\vec{\Pi}} + \frac{1}{2}\mathrm{rot}\hat{\vec{s}} \right\rangle = \langle \hat{\vec{L}} \rangle + \mathrm{div}\langle \hat{\overleftrightarrow{\tau}}^{S} \rangle$

## ★Image of stress tensor in continuum mechanics




$0 = \frac{d}{dt}(\rho\vec{v}) = \vec{F} + \mathrm{div}\overleftrightarrow{\sigma}$

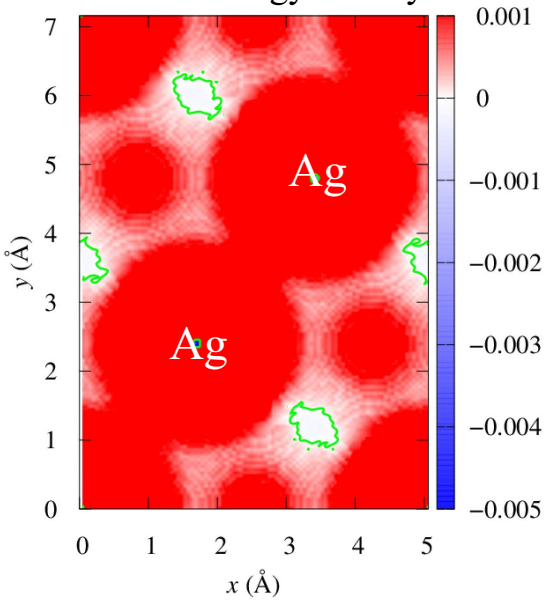


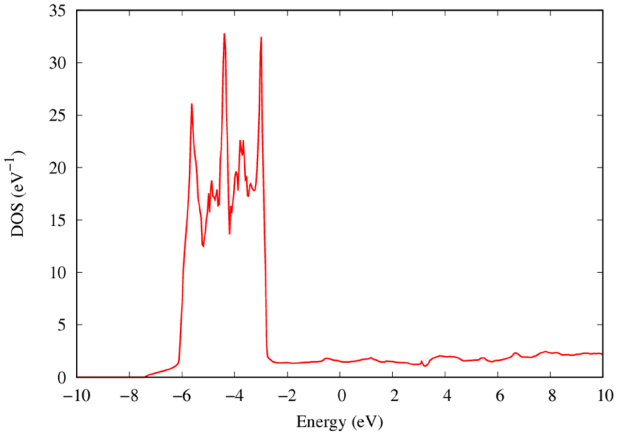
# Ag

- Electronic stress tensor density
- Zero surface of kinetic energy density

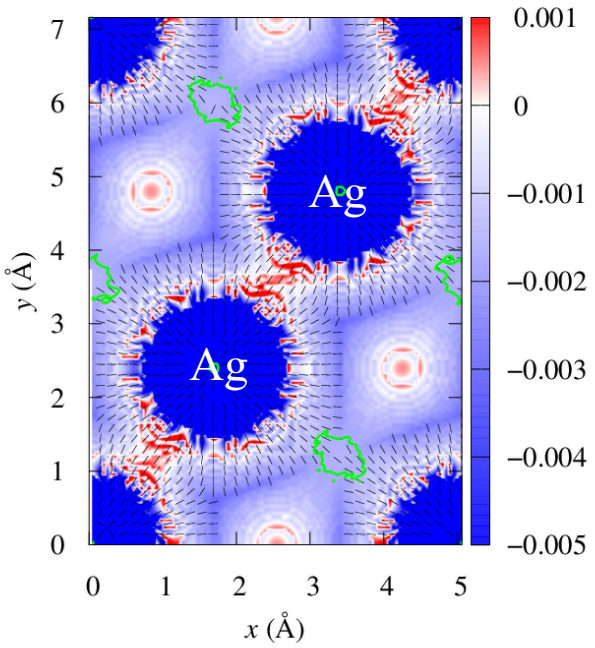
- The 2nd and 3rd eigenvalues are degenerated.
  → Compressive stress
- The largest eigenvalue
  → Spindle structure?

Kinetic energy density

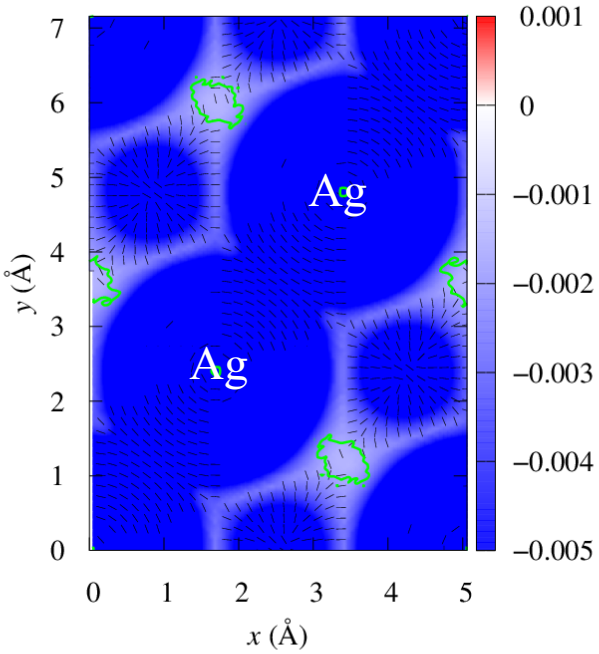


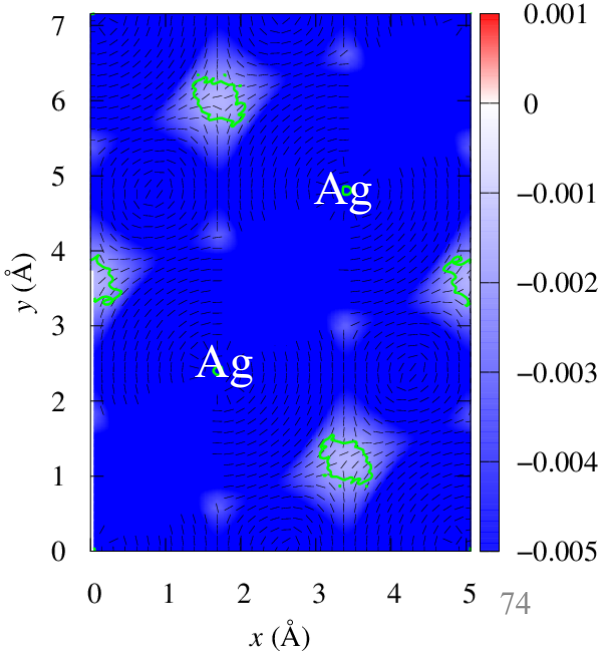

1st




2nd



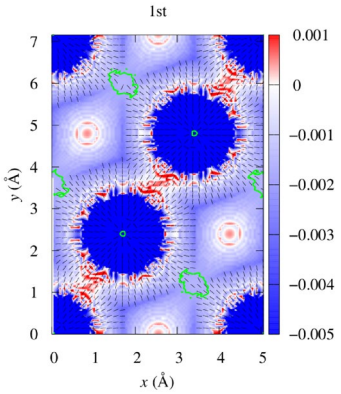

3rd

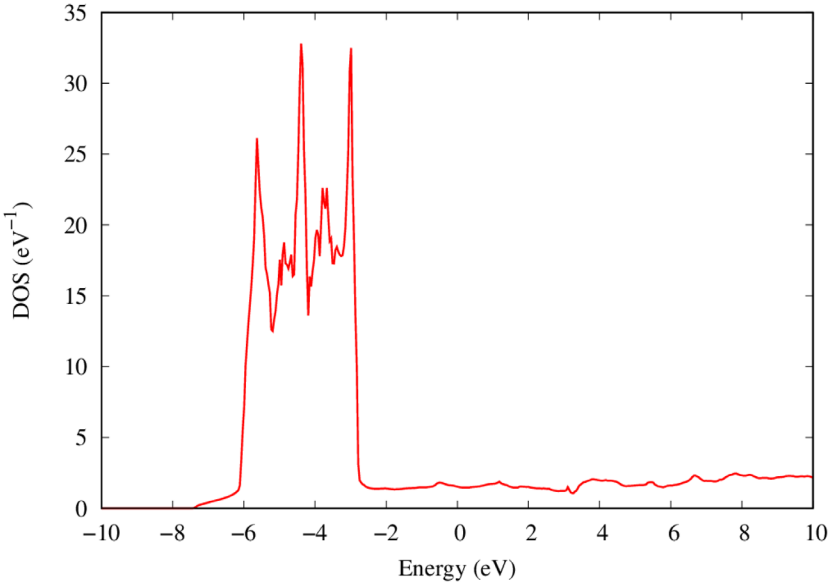


# Ag

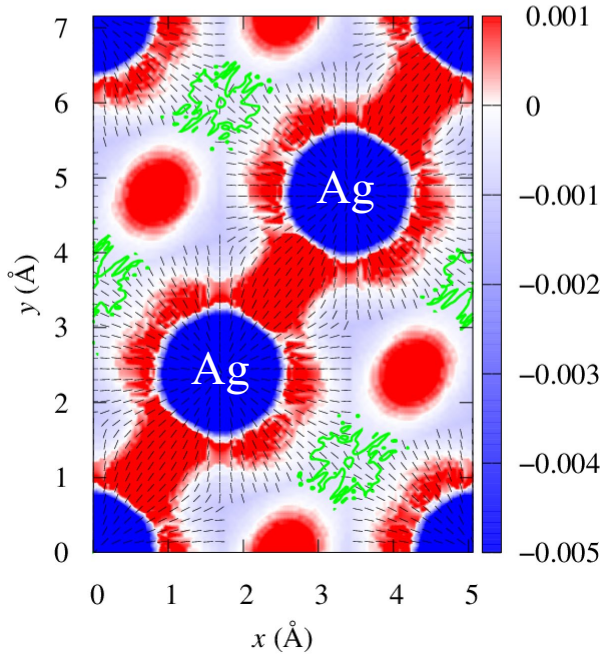
- Electronic stress tensor density
- Zero surface of kinetic energy density

The figures show the largest eigenvalue of stress tensor in several energy ranges. Around the Fermi level, the compress stress (metallic) state can be seen. At the lower energy level region, the spindle and anti-spindle structure are dominant.

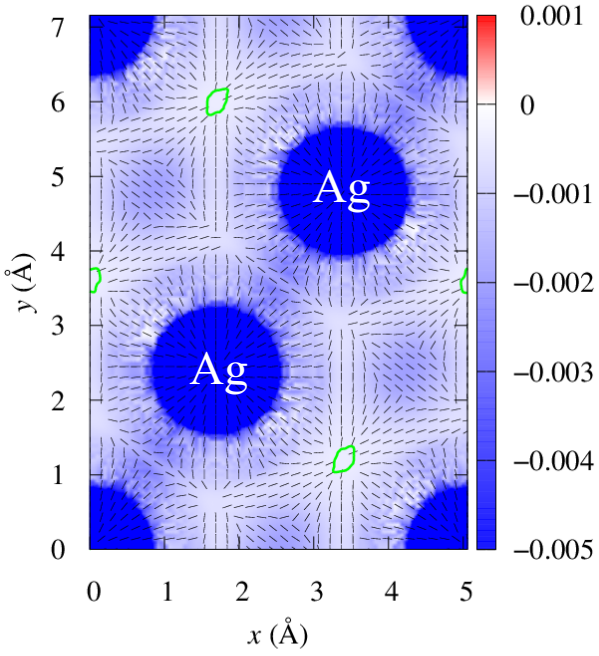


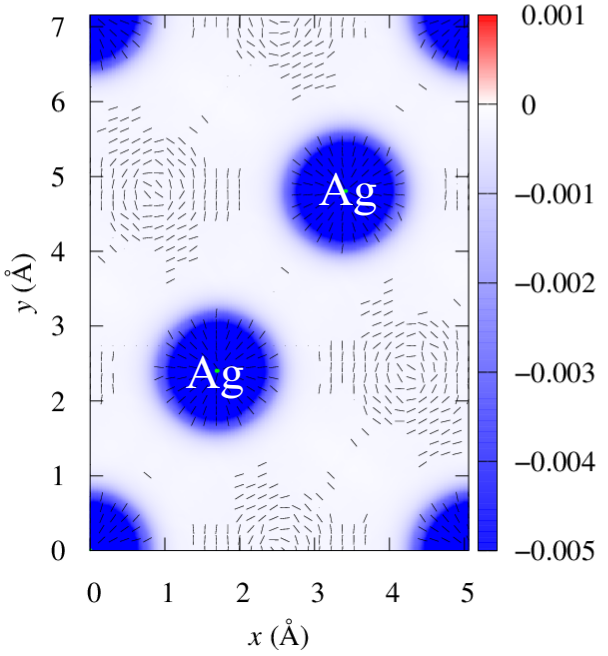

-5eV ~ -4eV




-4eV ~ -3eV



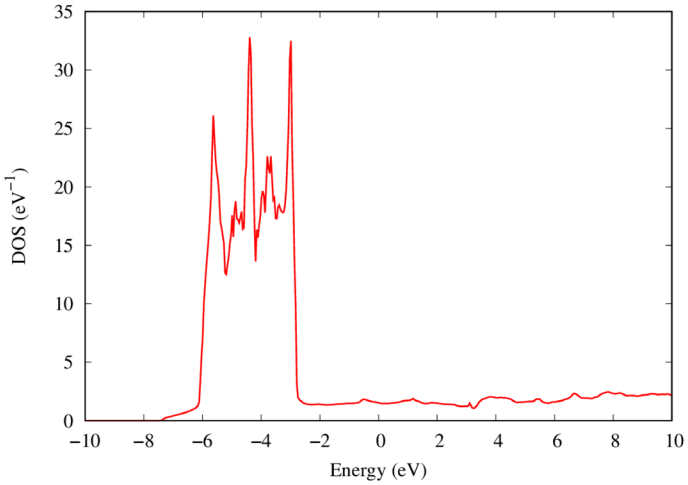

-1eV ~ 1eV



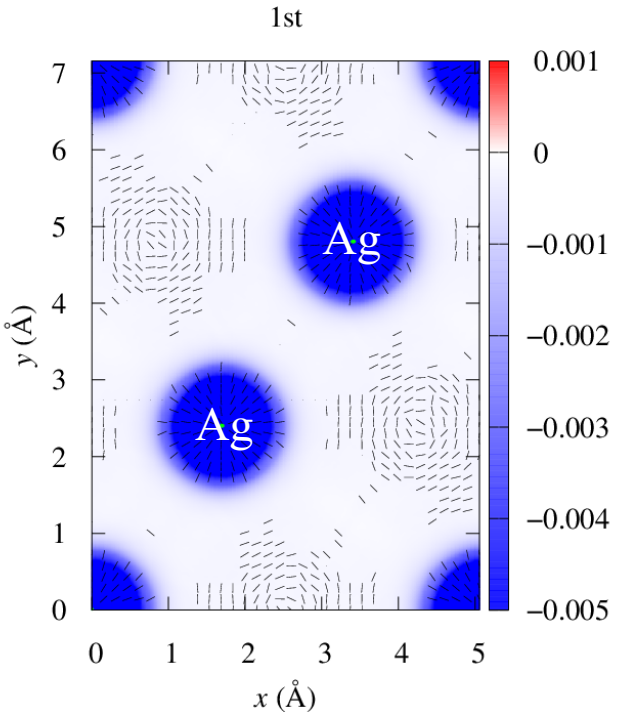
# Ag

- Electronic stress tensor density
- Zero surface of kinetic energy density

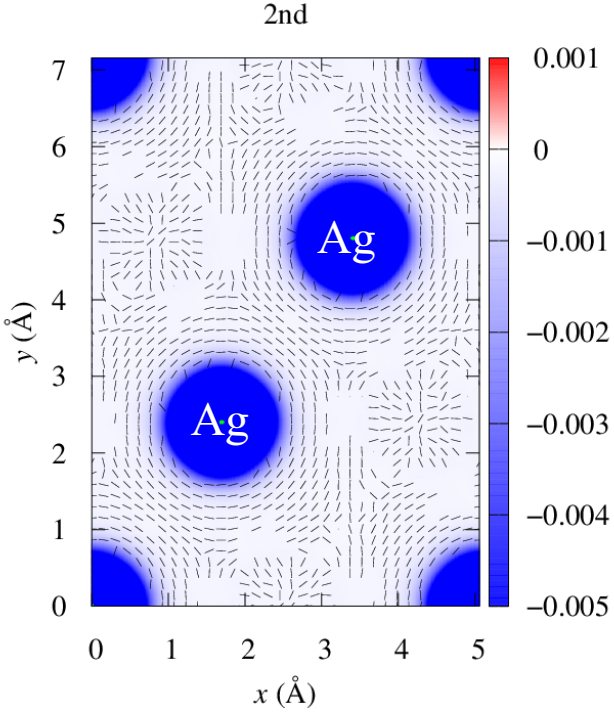
Around the Fermi level, eigenvalues of electronic stress tensor are minus and degenerate.
→ “liquid character”



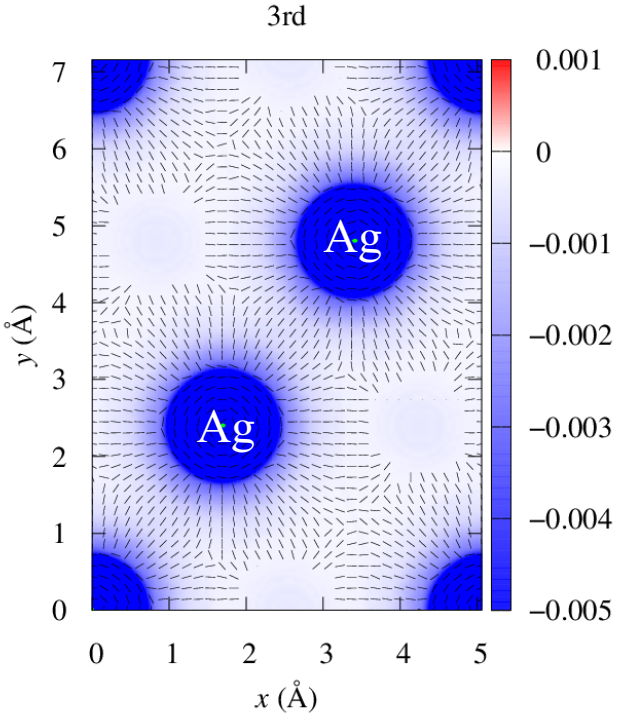

-1eV ~ 1eV




-1eV ~ 1eV




-1eV ~ 1eV



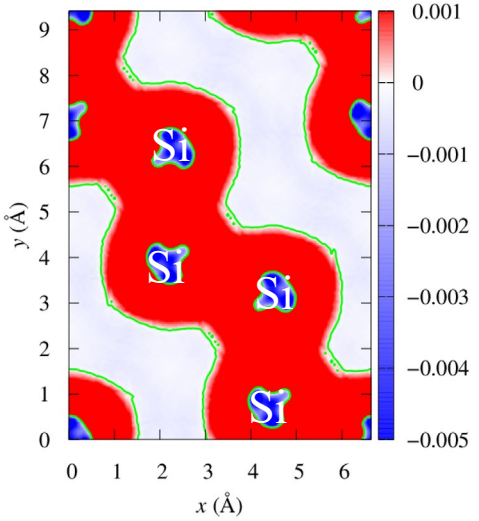
# Si

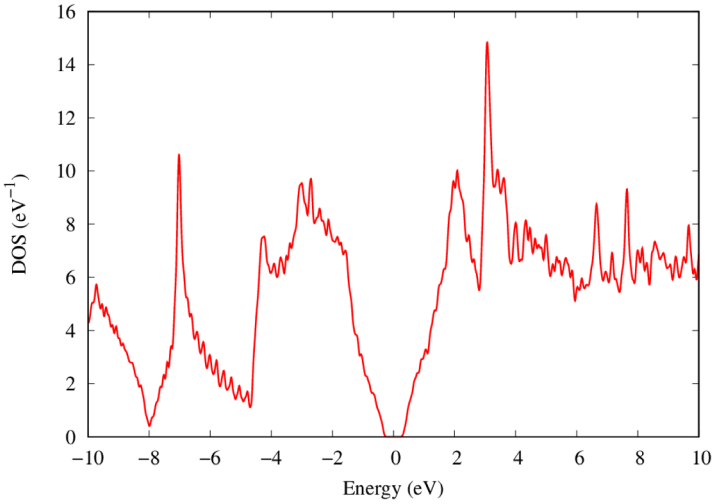
- Electronic stress tensor density
- Zero surface of kinetic energy density

The distribution of the kinetic energy density is sparse comparing to the bulk of Ag and Na.

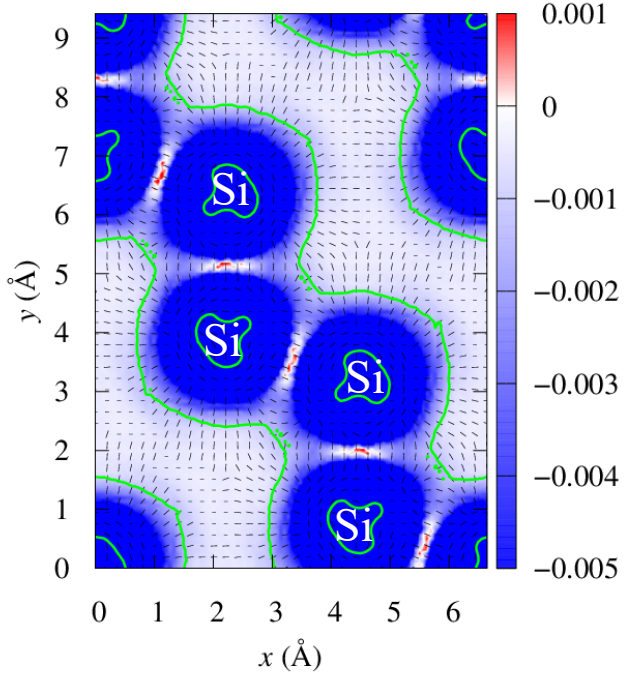
Similar to the Ag case, the 2nd and 3rd eigenvalues are degenerate (compress stress state). The largest eigenvalue and eigenvector form slightly a spindle structure.

Kinetic energy density

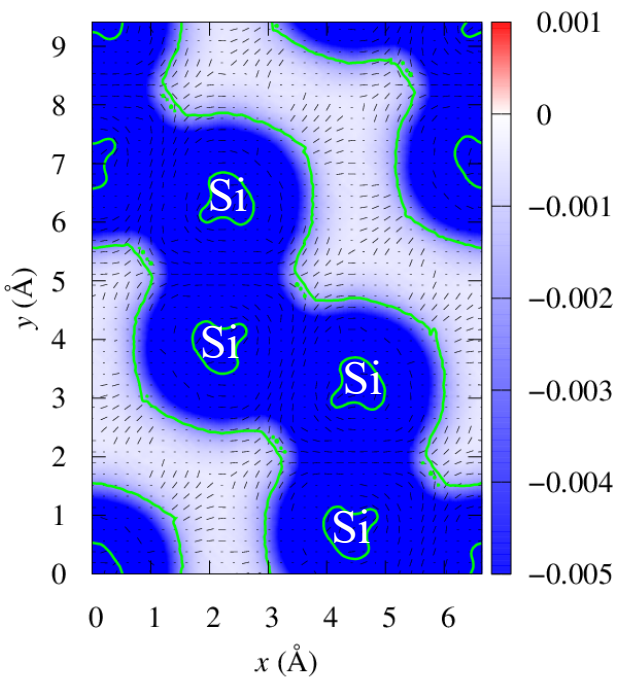


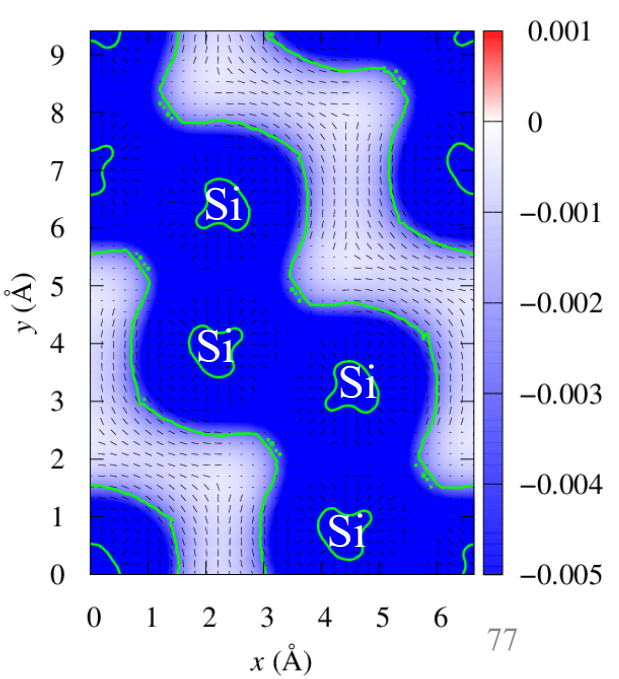

1st




2nd



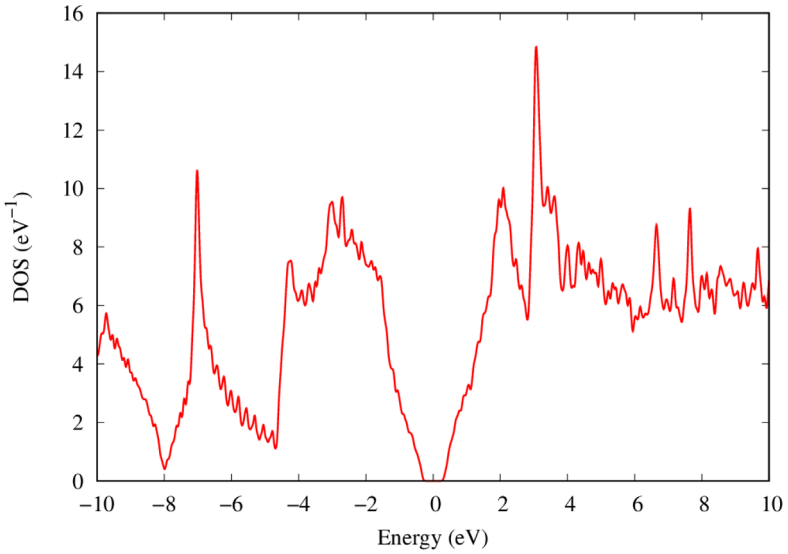

3rd



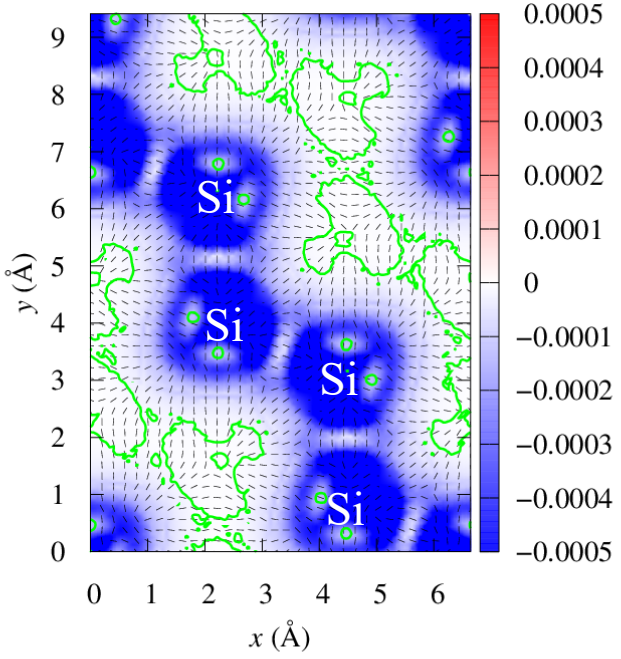
# Si

- Electronic stress tensor density
- Zero surface of kinetic energy density

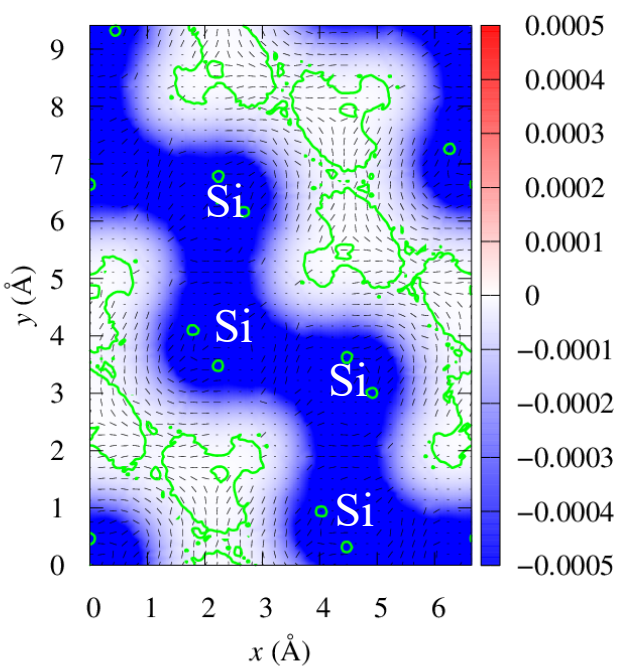
Around the Fermi level, the stress tensor forms slightly a spindle structure in the bonding region.
→ Covalent bonding



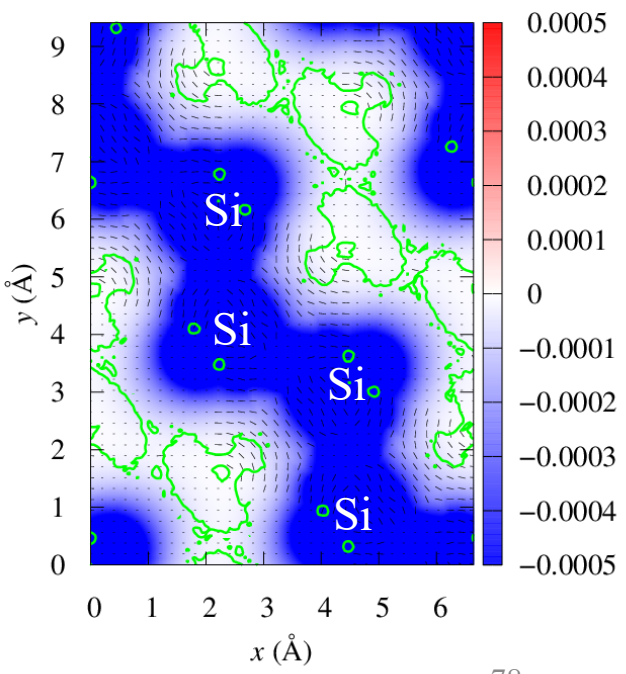

-1eV∼1eV




-1eV∼1eV

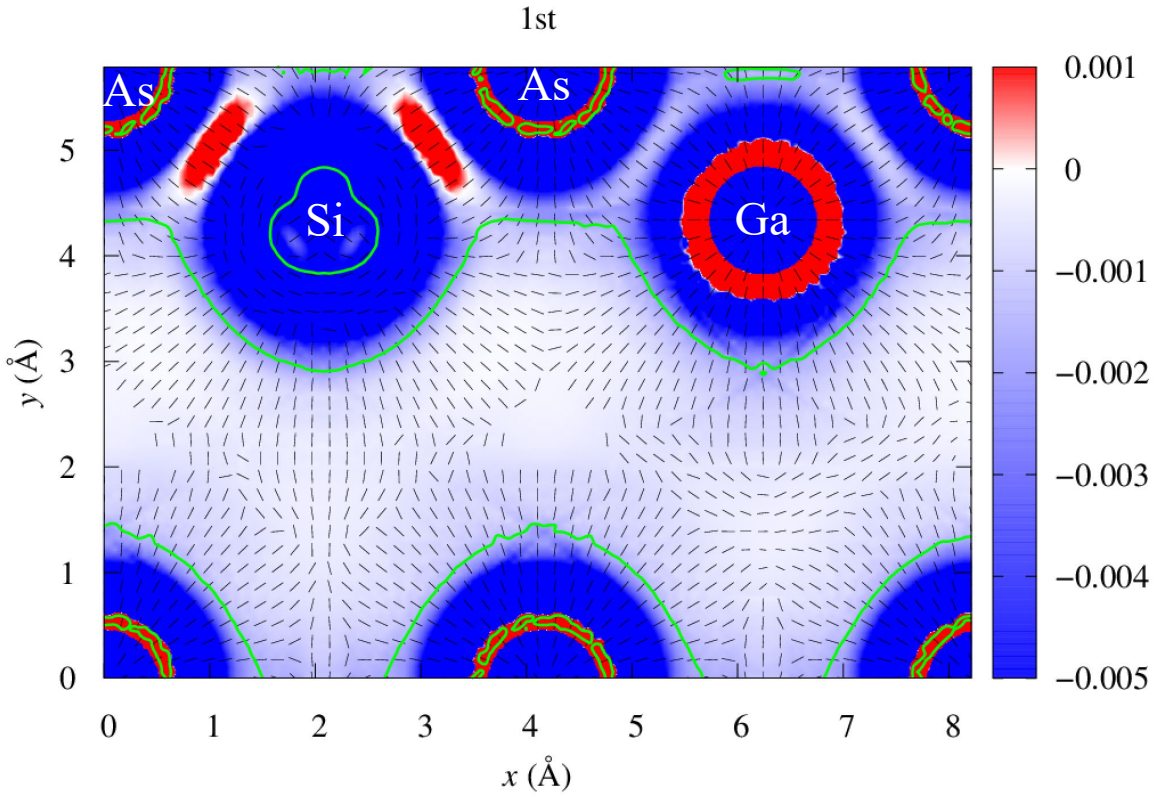


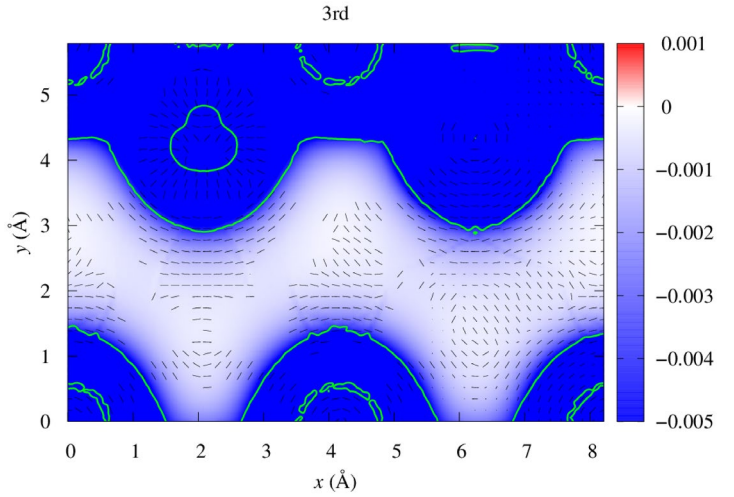

-1eV∼1eV

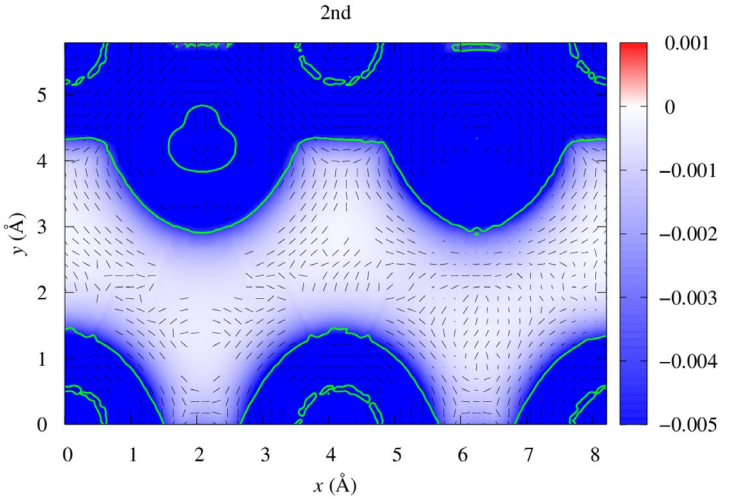


# GaAs Si doped (d0)

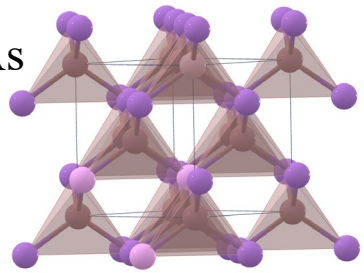
- Electronic stress tensor density
- Zero (0.001 a.u.) surface of kinetic energy density



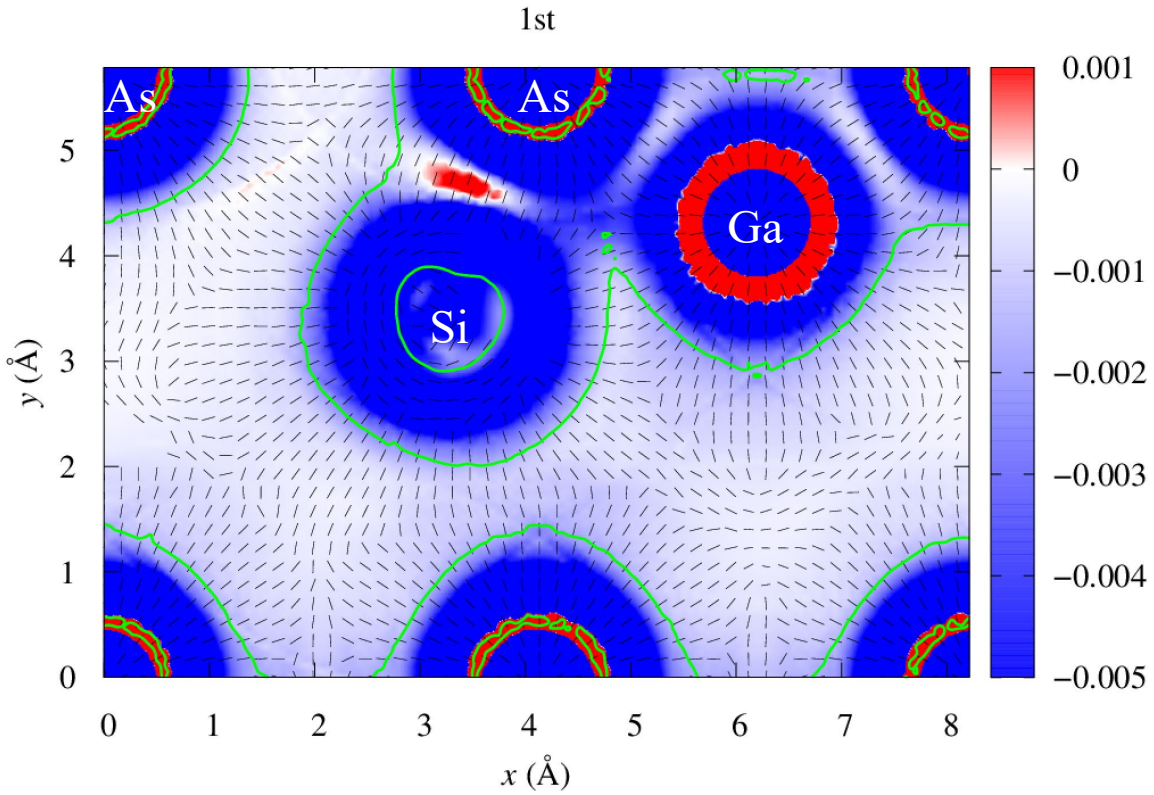



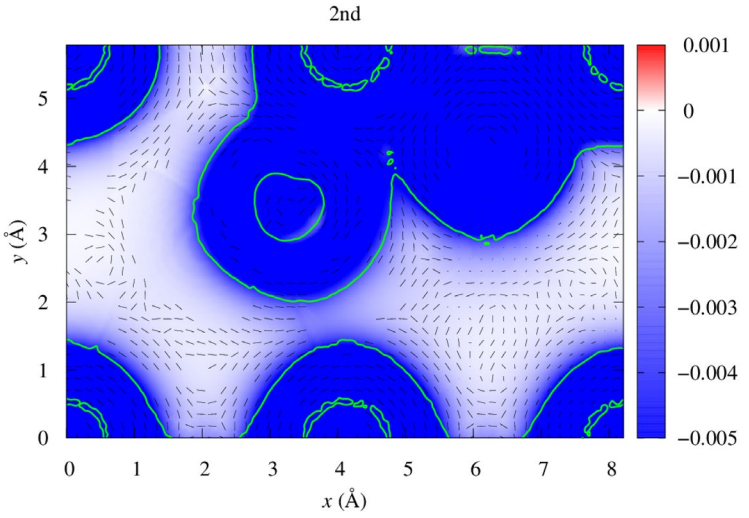

GaAs

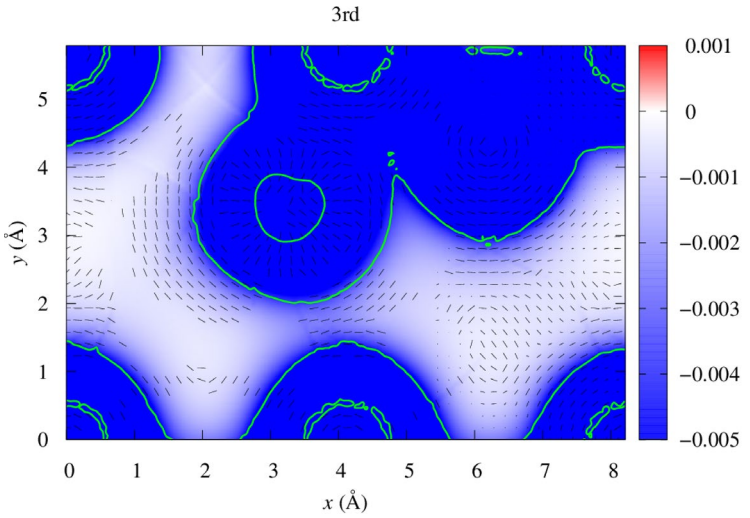


# GaAs Si doped ($DX^-$)

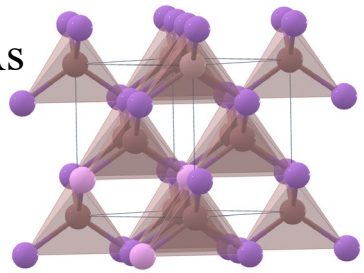
- Electronic stress tensor density
- Zero (0.001 a.u.) surface of kinetic energy density



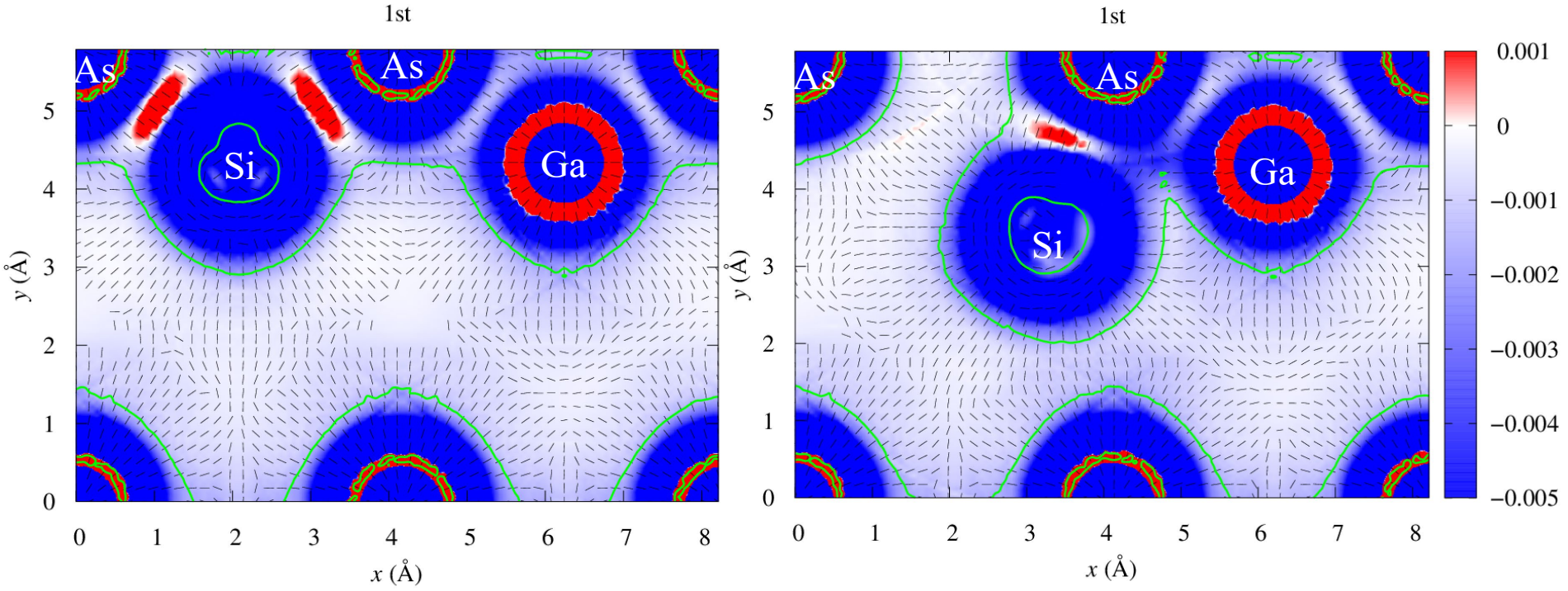




GaAs

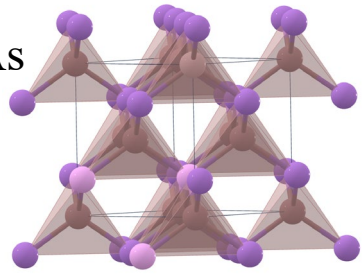


# GaAs Si doped (d0, $DX^-$)

- Electronic stress tensor density
- Zero (0.001 a.u.) surface of kinetic energy density




GaAs



# Table of Contents

# Spin Vorticity Theory

The "**spin vorticity theory**" is a theory which gives the time evolution equations of the electronic momentum density and spin angular momentum density as equations which relate the local physical quantities derived from the energy-momentum tensor density.

$$\hat{T}_e^{\mu\nu} = -\varepsilon^{S\mu\nu} - \tau^{S\mu\nu}(g)$$

$\hat{T}_e^{00}$ = energy density

$\hat{T}_e^{i0} \propto$ momentum density

$\hat{T}_e^{ij} \propto$ stress tensor density

$$j_5^{\mu} = Z_e e c \psi \gamma^{\mu} \gamma_5 \psi$$

☆Time evolution of electronic momentum

$$\frac{\partial}{\partial t}\left(\hat{\vec{\Pi}} + \frac{1}{2}\mathrm{rot}\hat{\vec{s}}\right) = \hat{\vec{L}} + \mathrm{div}\hat{\overleftrightarrow{\tau}}^{S}$$

Kinetic momentum density

Lorentz force density

Spin vorticity

Symmetric stress tensor

☆Time evolution of electronic spin

$$\frac{\partial}{\partial t}\hat{\vec{s}} = \hat{\vec{t}} - \mathrm{grad}\,\hat{\phi}_5 \qquad \left(\frac{\partial}{\partial t}\hat{s}^k = -\epsilon_{kln}\hat{\tau}^{Aln} - \partial_k\hat{\phi}_5\right)$$

Spin angular momentum density

Spin torque density

Zeta potential

Spin vorticity principle

$$\varepsilon^{A\mu\nu} + \tau^{A\mu\nu}(g) = 0$$

The spin vorticity principle gives the equation of motion of local spin and the vorticity of spin in the limit to the Minkowski space-time.


A. Tachibana, J. Comput. Chem. Jpn., 13, 18 (2014)
A. Tachibana, Indian J. Chem. A, **53**, 1031 (2014).
A. Tachibana, J. Math. Chem., 53:1943 (2015)

# Spin vorticity

Electron momentum density

$$\vec{P}_e = \vec{\Pi} + \frac{1}{2}\mathrm{rot}\vec{s}$$

half of the spin vorticity

kinetic momentum

Angular momentum density

$$\vec{J} = \vec{r} \times \vec{P}_e$$

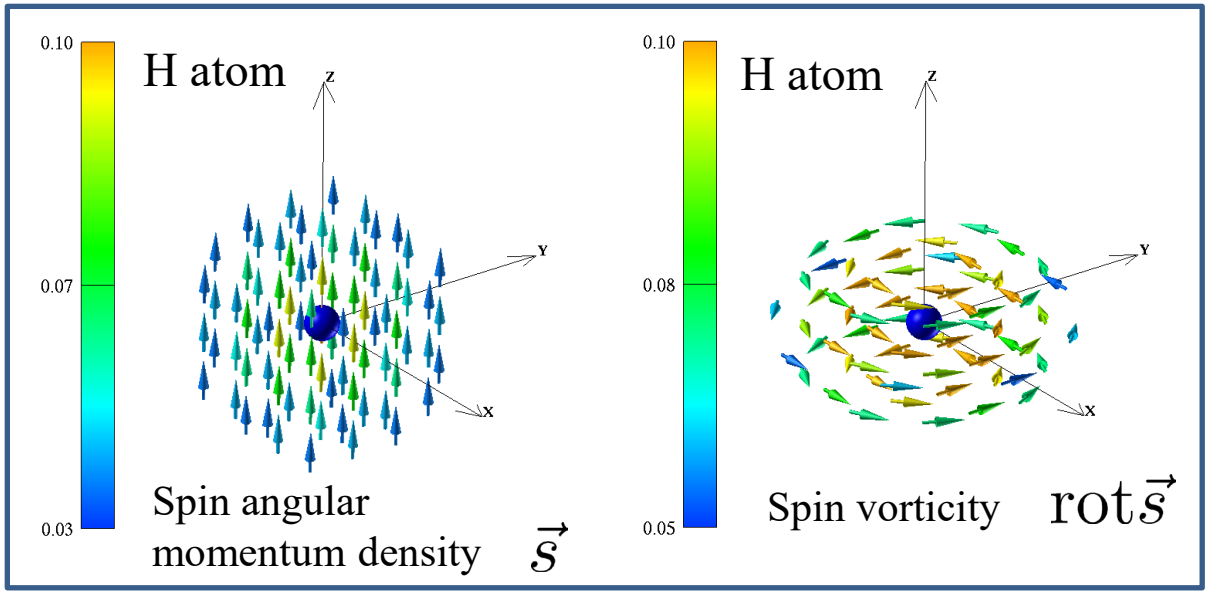
The spin vorticity appears in the electron momentum density.

The spin vorticity is zero after integrating over the whole region.

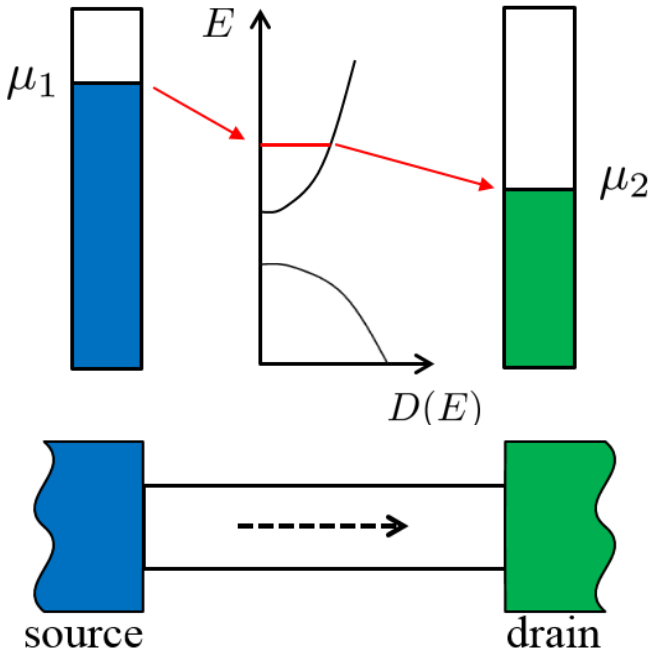
$$\int \frac{1}{2}\mathrm{rot}\vec{s}\, d^3\vec{r} = 0$$

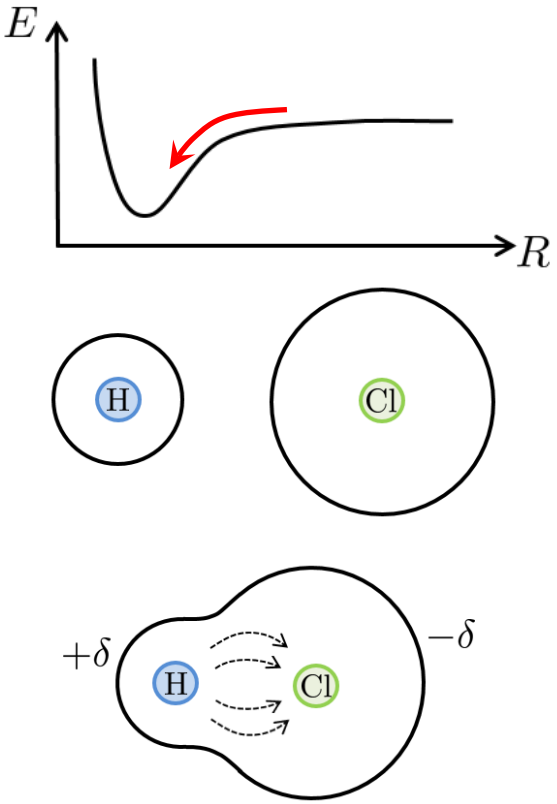
However, the spin vorticity can exist in a local region.

$$\int_D \frac{1}{2}\mathrm{rot}\vec{s}\, d^3\vec{r} \neq 0$$



# Local images of an electronic state by the quantum spin vorticity theory




☆Time evolution of electronic momentum

Kinetic momentum density

Lorentz force density

$$\frac{\partial}{\partial t}\left(\hat{\vec{\Pi}}+\frac{1}{2}\mathrm{rot}\hat{\vec{s}}\right)=\hat{\vec{L}}+\mathrm{div}\hat{\overleftrightarrow{\tau}}^{S}$$

Spin vorticity

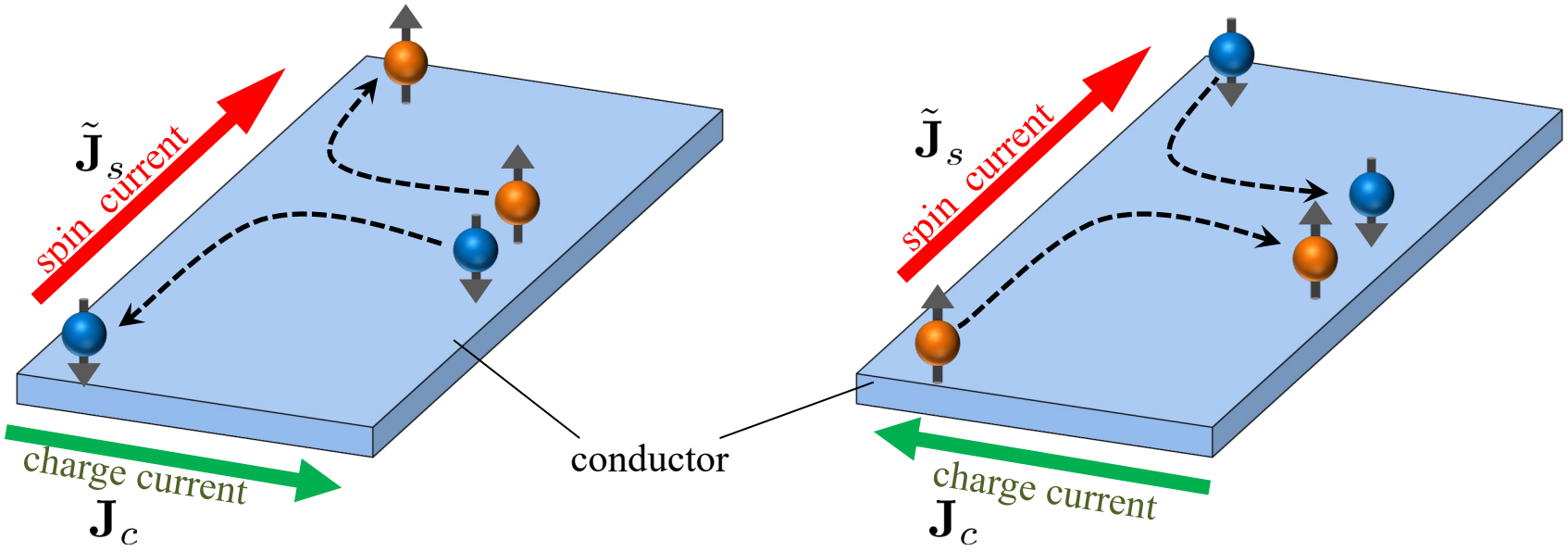
Symmetric stress tensor

The local images of an electronic state by the quantum spin vorticity theory can help us to understand spin phenomena in condensed matter and molecular systems from a unified viewpoint.

# Spin Hall effect

Spin Hall effect

Inverse spin Hall effect




The SHE is understood a conversion of a charge current into a transverse spin current.

The ISHE is understood a conversion of an injected spin current into a transverse charge current.

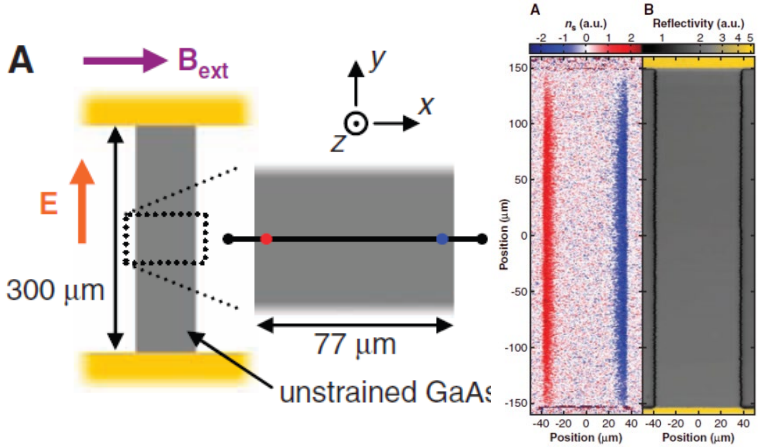
$$\tilde{\mathbf{J}}_s = \theta_{\mathrm{H}} \hat{\sigma} \times \mathbf{J}_c$$

spin current — spin — charge current

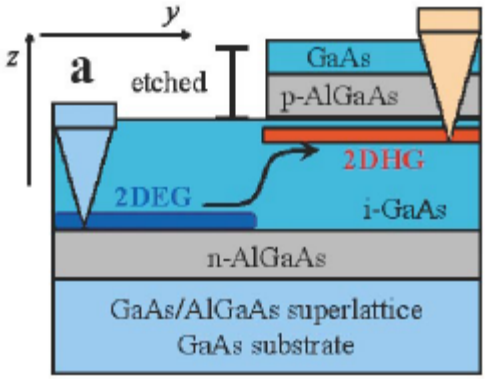
$$\mathbf{J}_c = \theta_{\mathrm{H}} \hat{\sigma} \times \tilde{\mathbf{J}}_s$$

M. I. Dyakonov and V. I. Perel,
JETP Lett. **13**, 467 (1971);
Phys. Lett. **A35**, 459 (1971).

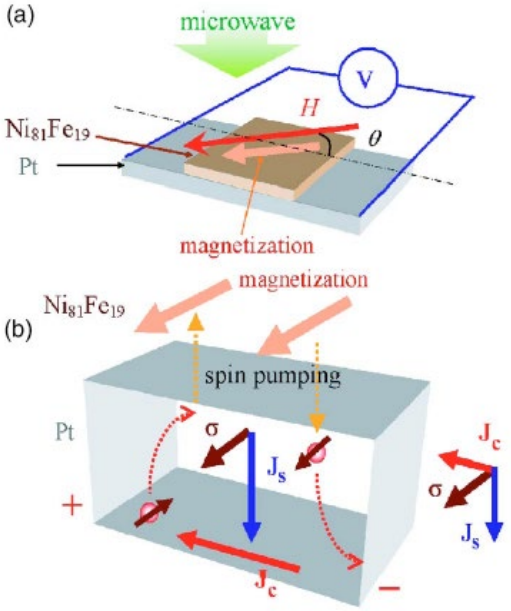
# Experiments of SHE and ISHE



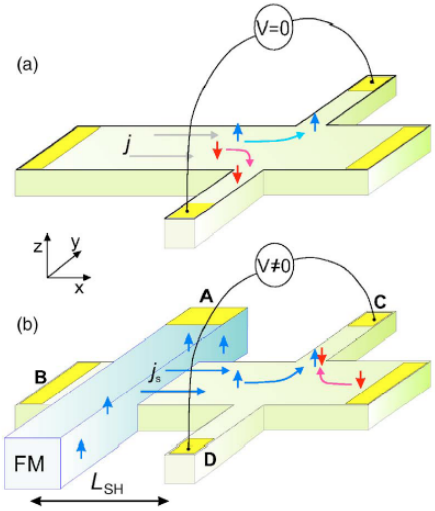

Kato *et. al.,* Science **306**, 1910 (2004)



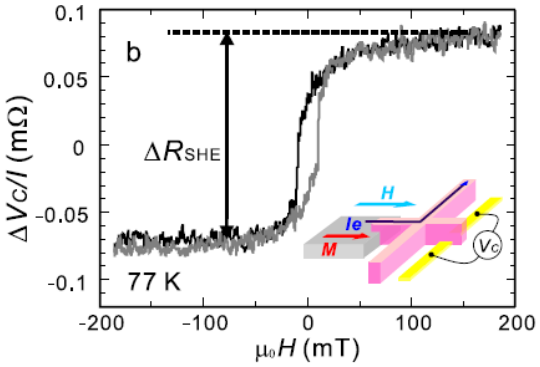

Wunderlich *et. al.,*
Phys. Rev. Lett. **94**, 047204 (2005)



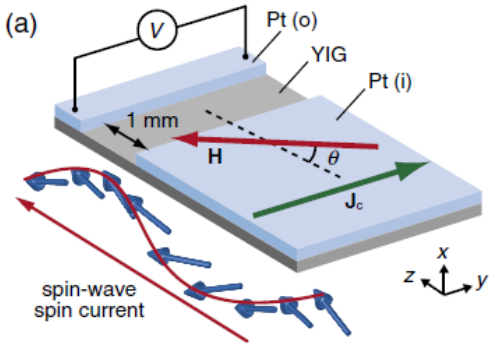

Saitoh *et. al.,*
Appl. Phys. Lett. **88**, 182509 (2006)




Valenzuela *et. al.,* Nature **442**, 176-179 (2007)



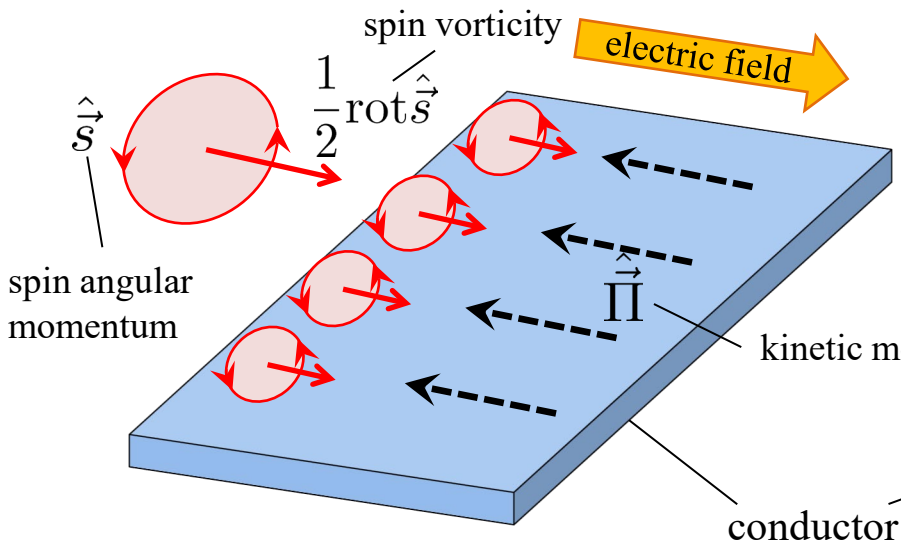

Kimura *et. al.,*
Phys. Rev. Lett. **98**, 156601 (2007)




Maekawa *et. al.,*
J. Phys. Soc. Jpn. **82**, 102002 (2013)

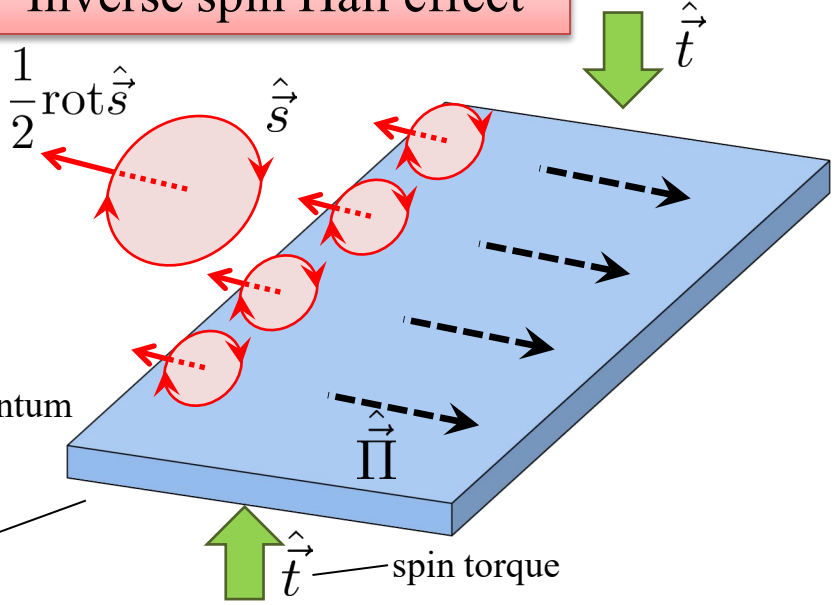
# 【 New concept based on the spin vorticity theory】

## Spin Hall effect




The spin vorticity is generated by the applied electric field in the conductor, and then, the spin angular momentum is generated at the both edges of the conductor.

## Inverse spin Hall effect




The electron is accelerated by the rotation of the spin torque density as driving force accompanying the generation of half of the spin vorticity in the conductor.

## Time evolution of the momentum density

$$\frac{\partial}{\partial t}\left(\hat{\vec{\Pi}}+\frac{1}{2}\mathrm{rot}\hat{\vec{s}}\right)=\hat{\vec{L}}+\mathrm{div}\,\hat{\overleftrightarrow{\tau}}^{S}$$

## Time evolution of the spin vorticity

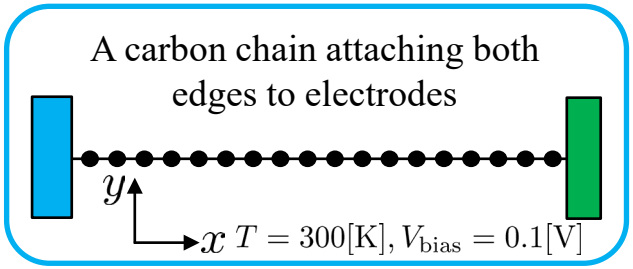
$$\frac{\partial}{\partial t}\left(\frac{1}{2}\mathrm{rot}\,\hat{\vec{s}}\right)=\frac{1}{2}\mathrm{rot}\,\hat{\vec{t}}=-\,\mathrm{div}\,\hat{\overleftrightarrow{\tau}}^{A}$$

$$\frac{\partial}{\partial t}\hat{\vec{\Pi}}=\hat{\vec{L}}+\mathrm{div}\left(\hat{\overleftrightarrow{\tau}}^{S}+\hat{\overleftrightarrow{\tau}}^{A}\right)$$

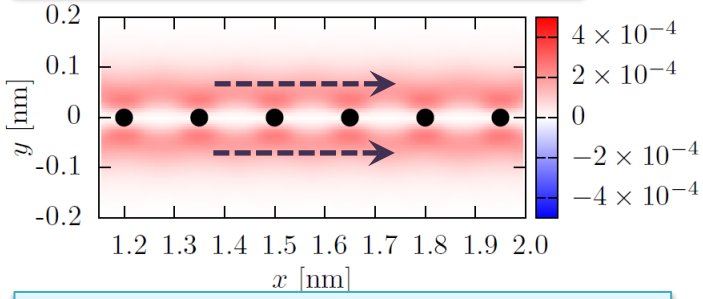
*M. Fukuda et al.,*
*AIP Advances 6, 025108 (2016)*

# Generation of the spin vorticity in a local region

In these calculations, a relativistic quantum mechanical wave packet by the non-equilibrium Green's function method is used as an approximation to the quantum field theoretical state vector.




Kinetic momentum density $(\vec{\Pi})_x$




The kinetic momentum density is distributed along the π-bondings.

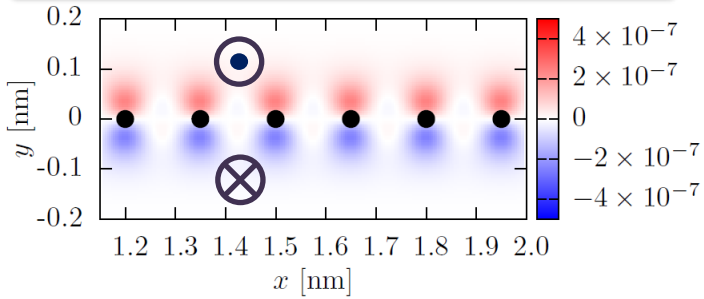
☆Time evolution of electronic momentum

$$\frac{\partial}{\partial t}\left(\hat{\vec{\Pi}} + \frac{1}{2}\mathrm{rot}\hat{\vec{s}}\right) = \hat{\vec{L}} + \mathrm{div}\hat{\overleftrightarrow{\tau}}^{S}$$

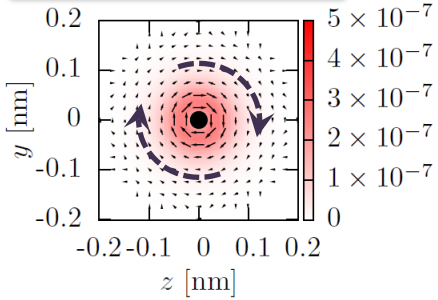
Kinetic momentum density; Lorentz force density; Spin vorticity; Symmetric stress tensor

*M. Fukuda et al., AIP Advances 6, 025108 (2016)*

Spin angular momentum density $(\vec{s})_z$



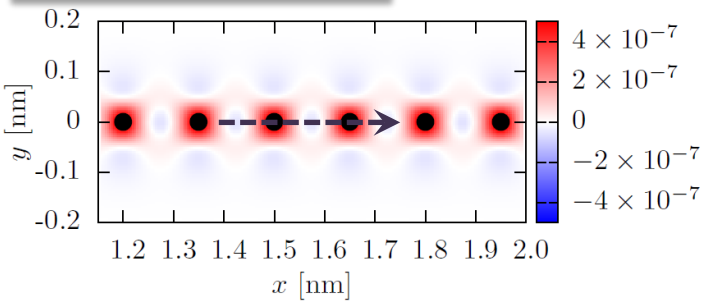

$(\vec{s})_y$, $(\vec{s})_z$




$\vec{s}$ on a cross section

On the other hand, the spin angular momentum density is distributed circularly around the nuclei. Therefore, the spin vorticity is concentrated around a nucleus.

Spin vorticity $(\mathrm{rot}\vec{s})_x$




Half of the spin vorticity, which is introduced naturally as a component of the electron momentum density, plays an important role for spin transport phenomena.

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# Spin Vorticity Theory

The "**spin vorticity theory**" is a theory which gives the time evolution equations of the electronic momentum density and spin angular momentum density as equations which relate the local physical quantities derived from the energy-momentum tensor density.

$$\hat{T}_e^{\mu\nu} = -\varepsilon^{S\mu\nu} - \tau^{S\mu\nu}(g)$$

$\hat{T}_e^{00}$ = energy density

$\hat{T}_e^{i0} \propto$ momentum density

$\hat{T}_e^{ij} \propto$ stress tensor density

$$j_5^{\mu} = Z_e e c \psi \gamma^{\mu} \gamma_5 \psi$$

☆Time evolution of electronic momentum

$$\frac{\partial}{\partial t}\left(\hat{\vec{\Pi}} + \frac{1}{2}\mathrm{rot}\hat{\vec{s}}\right) = \hat{\vec{L}} + \mathrm{div}\hat{\overleftrightarrow{\tau}}^{S}$$

Kinetic momentum density

Lorentz force density

Spin vorticity

Symmetric stress tensor

☆Time evolution of electronic spin

$$\frac{\partial}{\partial t}\hat{\vec{s}} = \hat{\vec{t}} - \mathrm{grad}\,\hat{\phi}_5 \qquad \left(\frac{\partial}{\partial t}\hat{s}^k = -\epsilon_{kln}\hat{\tau}^{Aln} - \partial_k\hat{\phi}_5\right)$$

Spin angular momentum density

Spin torque density

Zeta potential

Spin vorticity principle

$$\varepsilon^{A\mu\nu} + \tau^{A\mu\nu}(g) = 0$$

The spin vorticity principle gives the equation of motion of local spin and the vorticity of spin in the limit to the Minkowski space-time.


A. Tachibana, J. Comput. Chem. Jpn., 13, 18 (2014)
A. Tachibana, Indian J. Chem. A, **53**, 1031 (2014).
A. Tachibana, J. Math. Chem., 53:1943 (2015)

# Quantum electron spin vorticity principle

$$\hat{\varepsilon}^{A\mu\nu} + \hat{\tau}^{A\mu\nu}(g) = 0$$

Anti-symmetric component of geometrical tensor

$$\hat{\varepsilon}^{A\mu\nu} = \left(\hat{\varepsilon}^{\Pi\mu\nu} - \hat{\varepsilon}^{\Pi\mu\nu}\right)/2$$

Anti-symmetric component of stress tensor

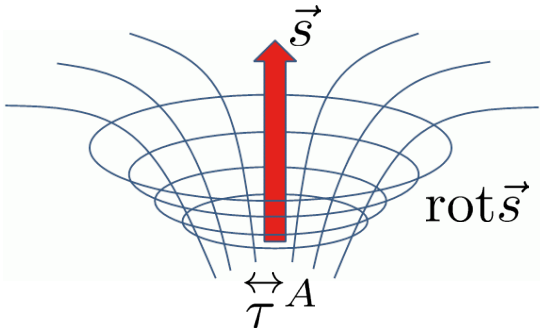
$$\hat{\tau}^{A\mu\nu} = \left(\hat{\tau}^{\Pi\mu\nu} - \hat{\tau}^{\Pi\mu\nu}\right)/2$$

limit to the Minkowski space

## Spin vorticity of electron

$$\mathrm{rot}\hat{\vec{s}} = \frac{1}{2}\left(\hat{\bar{\psi}}\vec{\gamma}\left(i\hbar\hat{D}_0\right)\hat{\psi} + h.c.\right) - \hat{\vec{\Pi}}$$

Spin vorticity — Kinetic momentum



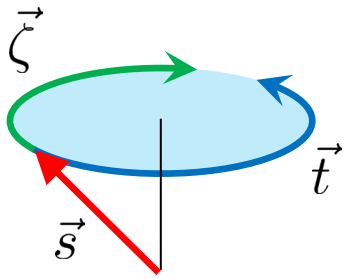

## Time evolution of electronic spin

$$\frac{\partial}{\partial t}\hat{\vec{s}} = \hat{\vec{t}} + \hat{\vec{\zeta}}$$

Spin torque — Zeta force

$$\hat{t}^k = -\varepsilon_{kln}\hat{\tau}^{Aln}$$

$$\hat{\zeta}^k = -\partial_k\hat{\phi}_5$$




Electronic spin can be accelerated by the torque derived by the anti-symmetric component of the stress tensor, which is also compensated by the zeta force, which is a basic mechanism leading to the stationary state of electronic spin.


A. Tachibana, J. Comput. Chem. Jpn., 13, 18 (2014)

A. Tachibana , J. Math. Chem. 50, 669-688 (2012); A. Tachibana, Electronic Stress with Spin Vorticity. In *Concepts and Methods in Modern Theoretical Chemistry,* S. K. Ghosh and P. K. Chattaraj Eds., CRC Press, Florida (2013), pp 235-251.

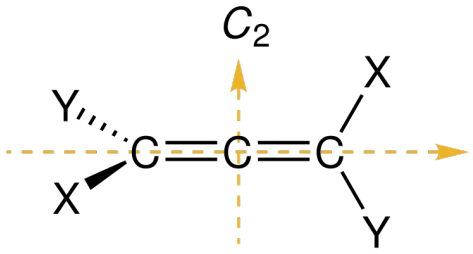
Local distributions of the spin torque and zeta force in the steady state of allene

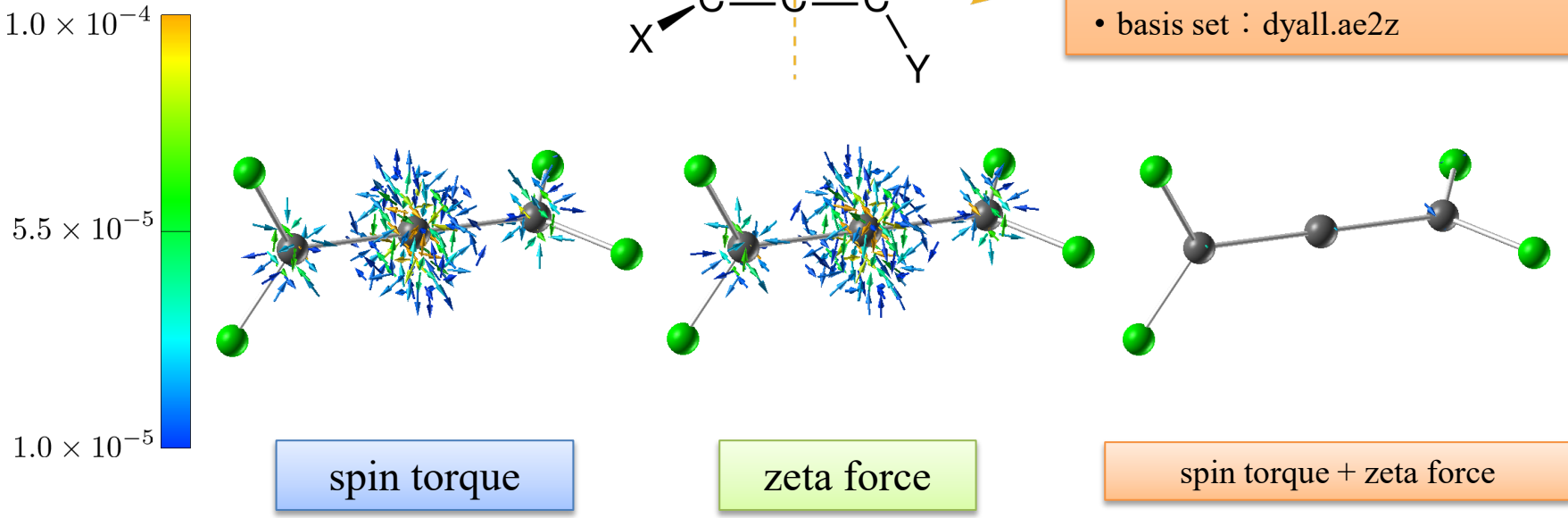
$$0 = \frac{\partial \langle \hat{s}_e^k(x) \rangle}{\partial t} = \langle \hat{t}_e^k(x) \rangle + \langle \hat{\zeta}_e^k(x) \rangle$$

The relativistic wave packet is used as an approximation to the quantum field theoretical state vector.

Relativistic electronic state calculation
- program code：DIRAC13
- calculation method：CISD
- basis set：dyall.ae2z

$C_3H_4$




spin torque

zeta force

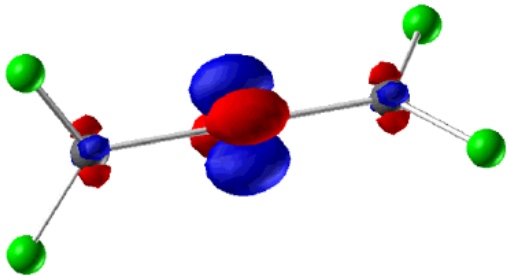
spin torque + zeta force

The allene has nonzero local spin torque density and its counter torque density, zeta force density, even in the steady state. These results are consistent with the fact that the nonzero spin torque density is in balance with the zeta force density for the spin steady state.

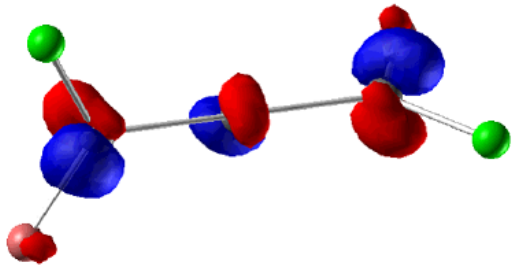
# Zeta potential in allene type structures

Iso-surface value of the zeta potential： $\pm 1 \times 10^{-6}$ [a.u.]

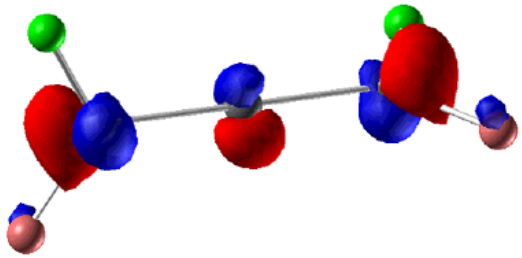
Chiral models A and B are enantiomers.



(a) $C_3H_4$



(b) $C_3H_2Li_2$ (chiral A)



(c) $C_3H_2Li_2$ (chiral B)

$$\hat{\phi}_5 = \frac{\hbar c}{2}\left(\hat{\psi}_R^{\dagger}\hat{\psi}_R - \hat{\psi}_L^{\dagger}\hat{\psi}_L\right)$$

The zeta potential is proportional to the difference of right-handed and left-handed electron densities.

**Integrated value of the zeta potential**

| $C_3H_2Li_2$ (chiral A) | $C_3H_2Li_2$ (chiral B) |
|---|---|
| $1.33 \times 10^{-7}$ [a.u.] | $-1.33 \times 10^{-7}$ [a.u.] |

☆Time evolution of electronic spin

$$\frac{\partial}{\partial t}\hat{\vec{s}} = \hat{\vec{t}} - \mathrm{grad}\,\hat{\phi}_5$$

Spin torque density　　Zeta potential

A molecular chirality can bring about a difference of right-handed and left-handed electron densities.

# Local physical quantities for spin in the ground steady state of $C_6H_6$

☆Time evolution of spin

Spin angular momentum

Zeta potential

$$\frac{\partial}{\partial t}\hat{\vec{s}} = \hat{\vec{t}} - \mathrm{grad}\,\phi_5$$

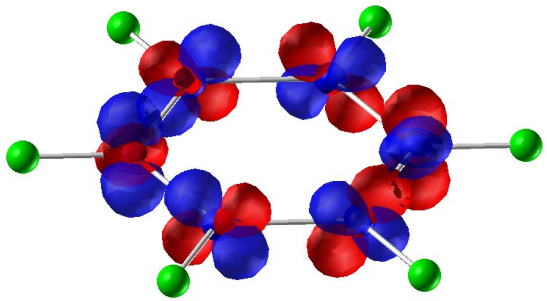
spin torque

zeta force

Relativistic electronic state calculation
- program code：DIRAC13
- calculation method：CISD
- basis set：dyall.ae2z

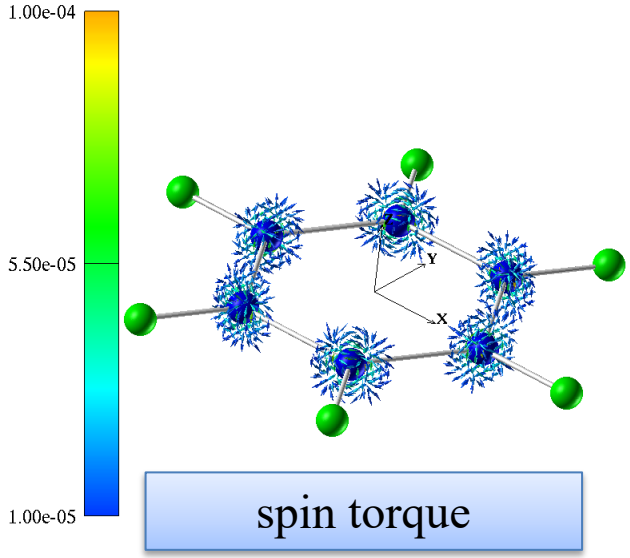
The cancellation between the nonzero zeta force and spin torque densities has been seen clearly even in the singlet ground state of $C_6H_6$, even though the spin angular momentum density is zero over the whole region.

*M. Fukuda, K. Soga, M. Senami, and A. Tachibana, Int. J. Quant. Chem., 116, 920 (2016)*

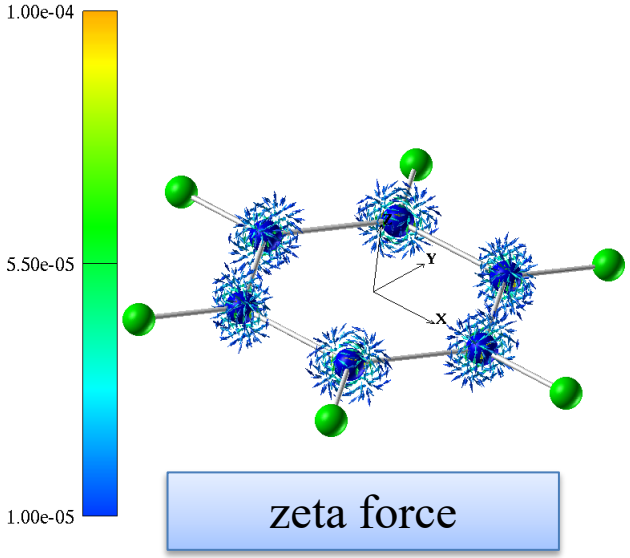


zeta potential

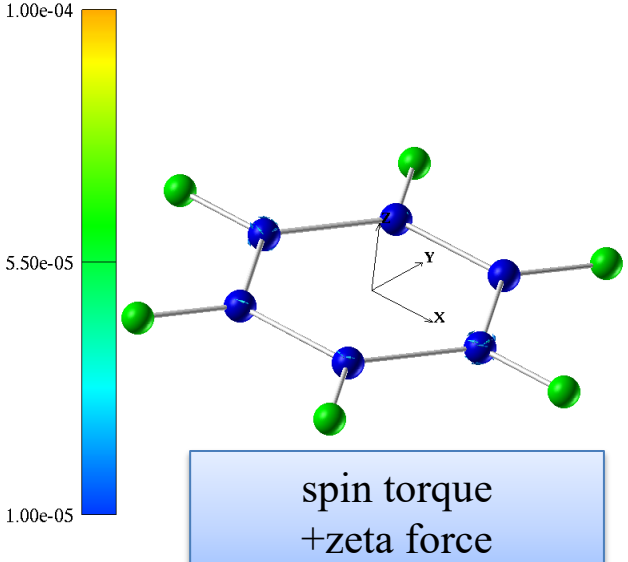
等値面：±1×10$^{-6}$ [a.u.]




spin torque




zeta force




spin torque
+zeta force

# Summary

1. Introduction
   - What is the “local” physical quantity in QED?

2. Theoretical framework of quantum electrodynamics (quantum fields of electron, nuclei and photon)
   - Classical field theory
     - Lagrangian
     - Symmetry → Equations and local physical quantities
   - Classical field theory → Quantum field theory

3. Spin vorticity theory (physics explained by energy momentum density)
   1. Momentum of electron (Lorentz force and the counter force)
   2. Electronic stress tensor density (simple examples)

4. Application
   1. Electronic stress tensor analysis for atoms, molecules and bulks
   2. Spin vorticity → spin Hall effect
   3. Spin torque and the counter torque