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## A new visualization scheme of chemical energy density and bonds in molecules

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**Abstract** Covalent bond describes electron pairing in between a pair of atoms and molecules. The space is partitioned in mutually disjoint regions by using a new concept of the electronic drop region  $R_D$ , atmosphere region  $R_A$ , and the interface  $S$  (Tachibana in J Chem Phys 115:3497–3518, 2001). The covalent bond formation is then characterized by a new concept of the spindle structure. The spindle structure is a geometrical object of a region where principal electronic stress is positive along a line of principal axis of the electronic stress that connects a pair of the  $R_D$ s of atoms and molecules. A new energy density partitioning scheme is obtained using the Rigged quantum electrodynamics (QED). The spindle structure of the stress tensor of chemical bond has been disclosed in the course of the covalent bond formation. The chemical energy density visualization scheme is applied to demonstrate the spindle structures of chemical bonds in  $H_2$ ,  $C_2H_6$ ,  $C_2H_4$  and  $C_2H_2$  systems.

**Keywords** Visualization · Energy density · Electronic stress · Spindle structure · Rigged QED

### Introduction

Conventional quantum electrodynamics (QED) theory assumes clamped-nuclei Hamiltonian, where the atomic nuclei are clamped in space and are treated as external static source of force for electrons [1]. But in chemical reaction systems, the rearrangement of atomic configuration is of primary interest, and hence the dynamical treatments of atomic nuclei often play an important role.

In the Rigged QED theory [2, 3], we have elaborated first the incorporation of the kinetic energy density of

atomic nuclei into the general framework of QED and obtained the general theory of the field energy density in chemical reaction systems. The field of the atomic nucleus is treated as an effective Schrödinger field. This is an approximate treatment since the atomic nucleus is treated as a composite united particle, not composed at elementary particles such as quarks.

The Rigged QED theory is the theoretical background for the electronic kinetic energy density and tension density [4, 5] applied to the study of chemical reaction coordinates of various chemical reaction systems [6–16]. It is also used to study the dynamic charge concept [17] of atomic nucleus for non-adiabatic processes under electron flow [18, 19], typical of electromigration processes [20–34]. Latest interest in this series of theoretical study of energy densities is the spindle structure of the stress tensor of the chemical bond [3]. Stress tensors have also been studied in quantum mechanics [35] and QED [36].

In this article, we follow the field theoretical study of chemical interaction in terms of the Rigged QED. Combining the stress tensor and the spindle structure reveals new concept of tensorial chemical energy density that includes the electronic spin angular momentum in the underlying physics.

All the calculations are performed at the Hartree–Fock level of theory using 6-31G(d,p) basis set, using our own program package [37] and Gaussian 03 [38].

### Energy density

General framework of the energy density of the field theory is shown in Fig. 1.

The details of the theory will be presented as follows.

#### General settings

The electric field density operator  $\hat{E}(\vec{r})$  and the magnetic field density operator  $\hat{B}(\vec{r})$  are derived from the electromagnetic vector potential operator  $\hat{A}_\mu(\vec{r})$  and are

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### Field theory of energy density

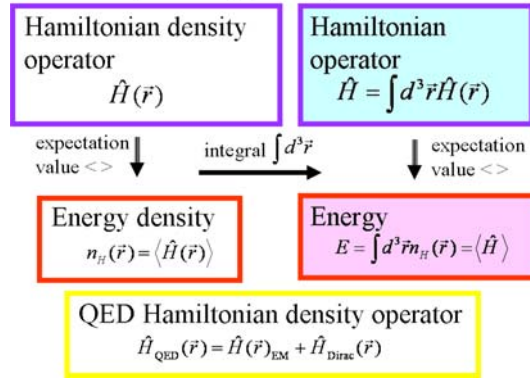


Fig. 1 Field theory of the energy density

the elements of the electromagnetic field tensor density operator  $\hat{F}_{\mu\nu}(\vec{r})$  using Coulomb gauge as follows:

$$\begin{aligned} \hat{F}_{\mu\nu}(\vec{r}) &= \partial_\mu \hat{A}_\nu(\vec{r}) - \partial_\nu \hat{A}_\mu(\vec{r}) \\ &= \begin{pmatrix} 0 & \hat{E}_x(\vec{r}) & \hat{E}_y(\vec{r}) & \hat{E}_z(\vec{r}) \\ -\hat{E}_x(\vec{r}) & 0 & -\hat{B}_z(\vec{r}) & \hat{B}_y(\vec{r}) \\ -\hat{E}_y(\vec{r}) & \hat{B}_z(\vec{r}) & 0 & -\hat{B}_x(\vec{r}) \\ -\hat{E}_z(\vec{r}) & -\hat{B}_y(\vec{r}) & \hat{B}_x(\vec{r}) & 0 \end{pmatrix}, \quad (1) \\ \partial_k \hat{A}^k(\vec{r}) &= 0. \end{aligned}$$

We use Dirac bracket for the constrained field quantization and get the canonical quantization rule:

$$\hat{A}^i(\vec{r}) \hat{A}^j(\vec{s}) - \hat{A}^j(\vec{s}) \hat{A}^i(\vec{r}) = 0, \quad (2)$$

$$\hat{E}_i(\vec{r}) \hat{E}_j(\vec{s}) - \hat{E}_j(\vec{s}) \hat{E}_i(\vec{r}) = 0, \quad (3)$$

$$\begin{aligned} \frac{1}{4\pi c} [\hat{A}^i(\vec{r}) \hat{E}_j(\vec{s}) - \hat{E}_j(\vec{s}) \hat{A}^i(\vec{r})] &= i\hbar \delta^i_j \delta^3(\vec{r} - \vec{s}) \\ &+ i\hbar \frac{\partial}{\partial s^j} \frac{\partial}{\partial r_i} \left( -\frac{1}{4\pi} \frac{1}{|\vec{r} - \vec{s}|} \right). \end{aligned} \quad (4)$$

The QED Hamiltonian density operator  $\hat{H}_{\text{QED}}(\vec{r})$  is composed of the Hamiltonian density operator of the electromagnetic field  $\hat{H}_{\text{EM}}(\vec{r})$  and the Dirac electronic Hamiltonian density operator  $\hat{H}_{\text{Dirac}}(\vec{r})$  interacting with the electromagnetic field as follows:

$$\hat{H}_{\text{QED}}(\vec{r}) = \hat{H}_{\text{EM}}(\vec{r}) + \hat{H}_{\text{Dirac}}(\vec{r}), \quad (5)$$

$$\hat{H}_{\text{EM}}(\vec{r}) = \hat{H}_\gamma(\vec{r}) - \hat{A}_0(\vec{r}) \hat{\rho}_e(\vec{r}), \quad (6)$$

$$\hat{H}_{\text{Dirac}}(\vec{r}) = \hat{M}_e(\vec{r}) + \hat{A}_0(\vec{r}) \hat{\rho}_e(\vec{r}), \quad (7)$$

where  $\hat{H}_\gamma(\vec{r})$  is the electromagnetic field energy density operator and  $\hat{M}_e(\vec{r})$  is the electronic mass density operator:

$$\hat{H}_\gamma(\vec{r}) = \frac{1}{8\pi} \left( \hat{\vec{E}}^2(\vec{r}) + \hat{\vec{B}}^2(\vec{r}) \right), \quad (8)$$

$$\hat{M}_e(\vec{r}) = c \hat{\psi}(\vec{r}) (-i\hbar \gamma^k \hat{D}_{ek}(\vec{r}) + m_e c) \hat{\psi}(\vec{r}), \quad (9)$$

with

$$\hat{D}_{e\mu}(\vec{r}) = \partial_\mu + i \frac{Z_e e}{\hbar c} \hat{A}_\mu(\vec{r}), \quad Z_e = -1, \quad (10)$$

where  $\hat{\psi}(\vec{r})$  and  $\hat{\bar{\psi}}(\vec{r}) = \hat{\psi}^\dagger(\vec{r}) \gamma^0$  is the field operator of electron and its Dirac conjugate, respectively,  $\gamma^\mu$  being the Dirac spinor matrices, and where the cls  $m_e$  and  $Z_e$  denote the mass and charge of electron, respectively.

The electronic mass density operator  $\hat{M}_e(\vec{r})$  may be written as the energy density operator of electron  $\hat{H}_e(\vec{r})$  as follows:

$$\hat{M}_e(\vec{r}) = \hat{H}_e(\vec{r}). \quad (11)$$

The canonical quantization rule of the field operators of electron is

$$\hat{\psi}(\omega) \hat{\psi}(\omega') + \hat{\psi}(\omega') \hat{\psi}(\omega) = 0, \quad (12)$$

$$\hat{\psi}^\dagger(\omega) \hat{\psi}^\dagger(\omega') + \hat{\psi}^\dagger(\omega') \hat{\psi}^\dagger(\omega) = 0, \quad (13)$$

$$\hat{\psi}(\omega) \hat{\psi}^\dagger(\omega') + \hat{\psi}^\dagger(\omega') \hat{\psi}(\omega) = \delta(\omega - \omega'), \quad (14)$$

where, for the sake of simplicity of presentation, Cartesian and spin variables altogether are represented by  $\omega$ . Moreover, the renormalization has been performed in a standard manner as summarized in Fig. 2.

Thus, the  $\hat{H}_{\text{QED}}(\vec{r})$  reduces from Eq. 5 to

$$\begin{aligned} \hat{H}_{\text{QED}}(\vec{r}) &= \hat{H}_{\text{EM}}(\vec{r}) + \hat{H}_{\text{Dirac}}(\vec{r}) \\ &= \hat{H}_\gamma(\vec{r}) + \hat{H}_e(\vec{r}). \end{aligned} \quad (15)$$

We now add the energy density operator  $\hat{H}_{\text{atom}}(\vec{r})$  of atomic nuclei interacting through the electromagnetic field and the electron field, leading to the Riggged QED Hamiltonian density operator denoted as  $\hat{H}_{\text{rigged QED}}(\vec{r})$ :

$$\hat{H}_{\text{rigged QED}}(\vec{r}) = \hat{H}_{\text{QED}}(\vec{r}) + \hat{H}_{\text{atom}}(\vec{r}). \quad (16)$$

Using canonical quantization rule for the Riggged QED theory, the  $\hat{H}_{\text{atom}}(\vec{r})$  is proved to be purely the kinetic energy density operator as follows:

### Renormalization

#### Dirac field

$$\hat{\psi}(\vec{r}) = \frac{1}{\sqrt{Z_2}} \hat{\psi}_B(\vec{r})$$

$$m_e = m_{eB} + \delta m_e$$

$$e = \sqrt{Z_3} e_B$$

#### Gauge field

$$\hat{A}^\mu(\vec{r}) = \frac{1}{\sqrt{Z_3}} \hat{A}_B^\mu(\vec{r})$$

→ infinite self-energy removed

Fig. 2 Renormalization of QED

$$\hat{H}_{\text{atom}}(\vec{r}) = \sum_a \hat{T}_a(\vec{r}), \quad (17)$$

where

$$\hat{T}_a(\vec{r}) = -\frac{\hbar^2}{2m_a} \cdot \frac{1}{2} \left( \hat{\chi}_a^\dagger(\vec{r}) \hat{D}_{ak}^2(\vec{r}) \hat{\chi}_a(\vec{r}) + \hat{D}_{ak}^{\dagger 2}(\vec{r}) \hat{\chi}_a^\dagger(\vec{r}) \cdot \hat{\chi}_a(\vec{r}) \right), \quad (18)$$

with

$$\hat{D}_{a\mu}(\vec{r}) = \partial_\mu + i \frac{Z_a e}{\hbar c} \hat{A}_\mu(\vec{r}), \quad (19)$$

where the  $m_a$  and  $Z_a$  denotes the mass and charge of atomic nucleus  $a$ , respectively. The canonical quantization rule of the Schrödinger field is anticommutation relationship for Fermions (+) and commutation relationship for Bosons (-):

$$\hat{\chi}_a(\omega) \hat{\chi}_a(\omega') \pm \hat{\chi}_a(\omega') \hat{\chi}_a(\omega) = 0, \quad (20)$$

$$\hat{\chi}_a^\dagger(\omega) \hat{\chi}_a^\dagger(\omega') \pm \hat{\chi}_a^\dagger(\omega') \hat{\chi}_a^\dagger(\omega) = 0, \quad (21)$$

$$\hat{\chi}_a(\omega) \hat{\chi}_a^\dagger(\omega') \pm \hat{\chi}_a^\dagger(\omega') \hat{\chi}_a(\omega) = \delta(\omega - \omega'). \quad (22)$$

Thus, the  $\hat{H}_{\text{rigged QED}}(\vec{r})$  reduces from Eq. 16 to

$$\begin{aligned} \hat{H}_{\text{rigged QED}}(\vec{r}) &= \hat{H}_{\text{QED}}(\vec{r}) + \hat{H}_{\text{atom}}(\vec{r}) \\ &= \hat{H}_{\text{QED}}(\vec{r}) + \sum_a \hat{T}_a(\vec{r}). \end{aligned} \quad (23)$$

It should be noted that the Rigged QED theory is gauge invariant and preserves translational and rotational symmetry but Poincare symmetry, because at the presence of the Schrödinger fields  $\hat{\chi}_a$  and  $\hat{\chi}_a^\dagger$ , violates Lorentz invariance of the Lagrangian density, as schematically summarized in Fig. 3.

If we neglect the Schrödinger fields, then we recover the conventional QED theory with the Poincare symmetry as well as the gauge invariance.

Equations of motion of fields

In this subsection, the equations of motion of fields will be presented.

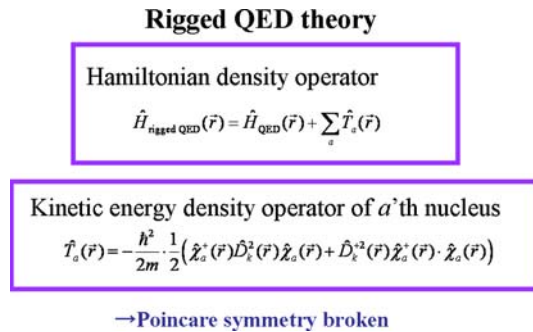


Fig. 3 Rigged QED Hamiltonian density operator

First, the Maxwell's equations of motion are found for the electromagnetic fields. Using Eq. 1 which is rewritten as

$$\hat{\vec{E}}(\vec{r}) = -\text{grad} \hat{A}_0(\vec{r}) - \frac{1}{c} \frac{\partial \hat{\vec{A}}(\vec{r})}{\partial t}, \quad \text{div} \hat{\vec{A}}(\vec{r}) = 0, \quad (24)$$

$$\hat{\vec{B}}(\vec{r}) = \text{rot} \hat{\vec{A}}(\vec{r}), \quad (25)$$

we have

$$\text{rot} \hat{\vec{E}}(\vec{r}) + \frac{1}{c} \frac{\partial \hat{\vec{B}}(\vec{r})}{\partial t} = 0, \quad (26)$$

$$\text{div} \hat{\vec{B}}(\vec{r}) = 0, \quad (27)$$

$$\text{div} \hat{\vec{E}}(\vec{r}) = 4\pi \hat{\rho}(\vec{r}), \quad (28)$$

$$\text{rot} \hat{\vec{B}}(\vec{r}) - \frac{1}{c} \frac{\partial \hat{\vec{E}}(\vec{r})}{\partial t} = \frac{4\pi}{c} \hat{\vec{j}}(\vec{r}), \quad (29)$$

where  $\hat{\rho}(\vec{r})$  is the charge density operator and  $\hat{\vec{j}}(\vec{r})$  is the charge current density operator. The  $\hat{\rho}(\vec{r})$  is decomposed into

$$\hat{\rho}(\vec{r}) = \hat{\rho}_e(\vec{r}) + \sum_a \hat{\rho}_a(\vec{r}) = \sum_\alpha \hat{\rho}_\alpha(\vec{r}), \quad (30)$$

$$\hat{\rho}_\alpha(\vec{r}) = Z_\alpha e \hat{N}_\alpha(\vec{r}), \quad (31)$$

where  $\hat{\rho}_e(\vec{r})$  is the electronic charge density operator and  $\hat{\rho}_a(\vec{r})$  is the charge density operator of atomic nucleus  $a$ , and where  $\hat{N}_e(\vec{r})$  and  $\hat{N}_a(\vec{r})$  is the position probability density operator of electron and atomic nucleus  $a$ , respectively:

$$\hat{N}_e(\vec{r}) = \hat{\psi}^\dagger(\vec{r}) \gamma^0 \hat{\psi}(\vec{r}), \quad (32)$$

$$\hat{N}_a(\vec{r}) = \hat{\chi}_a^\dagger(\vec{r}) \hat{\chi}_a(\vec{r}). \quad (33)$$

The  $\hat{\vec{j}}(\vec{r})$  is decomposed into

$$\hat{\vec{j}}(\vec{r}) = \hat{\vec{j}}_e(\vec{r}) + \sum_a \hat{\vec{j}}_a(\vec{r}) = \sum_\alpha \hat{\vec{j}}_\alpha(\vec{r}), \quad (34)$$

$$\hat{\vec{j}}_\alpha(\vec{r}) = Z_\alpha e \hat{v}_\alpha(\vec{r}), \quad (35)$$

where  $\hat{\vec{j}}_e(\vec{r})$  is the electronic charge current density operator and  $\hat{\vec{j}}_a(\vec{r})$  the charge current density operator of atomic nucleus  $a$ , and  $\hat{v}_\alpha(\vec{r})$  denotes the velocity density operator:

$$\hat{v}_e(\vec{r}) = c \hat{\psi}^\dagger(\vec{r}) \vec{\gamma} \hat{\psi}(\vec{r}), \quad (36)$$

$$\hat{v}_a(\vec{r}) = \frac{1}{2m_a} \left( -i \hbar \hat{\chi}_a^\dagger(\vec{r}) \hat{D}_{ak}(\vec{r}) \hat{\chi}_a(\vec{r}) + i \hbar \hat{D}_{ak}^\dagger(\vec{r}) \hat{\chi}_a^\dagger(\vec{r}) \cdot \hat{\chi}_a(\vec{r}) \right). \quad (37)$$

The  $\hat{v}_a(\vec{r})$  may also be written as the position probability density operator  $\hat{S}_a(\vec{r})$  as follows:

$$\hat{v}_a(\vec{r}) = \hat{S}_a(\vec{r}). \quad (38)$$

Second, the Dirac spinor field satisfies

$$i\hbar\gamma^\mu \hat{D}_{e\mu}(\vec{r})\hat{\psi}(\vec{r}) = m_e c \hat{\psi}(\vec{r}), \quad (39)$$

$$-i\hbar \hat{D}_{e\mu}^\dagger(\vec{r})\hat{\psi}(\vec{r})\gamma^\mu = m_e c \hat{\psi}(\vec{r}). \quad (40)$$

Third, the Schrödinger field satisfies

$$i\hbar \frac{\partial}{\partial t} \hat{\lambda}_a(\vec{r}) = -\frac{\hbar^2}{2m_a} \hat{D}_{ak}^2(\vec{r})\hat{\lambda}_a(\vec{r}) + Z_a e \hat{A}_0(\vec{r})\hat{\lambda}_a(\vec{r}), \quad (41)$$

$$-i\hbar \frac{\partial}{\partial t} \hat{\lambda}_a^\dagger(\vec{r}) = -\frac{\hbar^2}{2m_a} \hat{D}_{ak}^{*2}(\vec{r})\hat{\lambda}_a^\dagger(\vec{r}) + Z_a e \hat{A}_0(\vec{r})\hat{\lambda}_a^\dagger(\vec{r}). \quad (42)$$

Charge and position density equations of motion of particles

The charge density conservation laws are obtained as the continuity equations

$$\frac{\partial}{\partial t} \hat{\rho}_e(\vec{r}) + \text{div} \hat{j}_e(\vec{r}) = 0, \quad (43)$$

for electron, and

$$\frac{\partial}{\partial t} \hat{\rho}_a(\vec{r}) + \text{div} \hat{j}_a(\vec{r}) = 0, \quad (44)$$

for atomic nucleus  $a$ . Then, we obtain the continuity equation of the charged particles as a whole

$$\frac{\partial}{\partial t} \hat{\rho}(\vec{r}) + \text{div} \hat{j}(\vec{r}) = 0. \quad (45)$$

Next, the position density operator of electron and the position density operator of atomic nucleus  $a$  are defined as

$$\hat{r}_\alpha(\vec{r}) = \vec{r} \hat{N}_\alpha(\vec{r}). \quad (46)$$

The equations of motion of the position densities are then found to be

$$\frac{\partial}{\partial t} \hat{r}_\alpha(\vec{r}) = \hat{v}_\alpha(\vec{r}) - \hat{w}_\alpha(\vec{r}), \quad (47)$$

where  $\hat{v}_\alpha(\vec{r})$  is the velocity density operator, and  $\hat{w}_\alpha(\vec{r})$  denotes the field velocity vector density operator defined as

$$\hat{w}_\alpha(\vec{r}) = \partial_\ell(\vec{r} \cdot \hat{v}_\alpha^\ell(\vec{r})). \quad (48)$$

If we introduce the field velocity tensor density operator  $\hat{\hat{w}}_\alpha(\vec{r})$  as

$$\hat{\hat{w}}_\alpha^{k\ell}(\vec{r}) = x^k \cdot \hat{v}_\alpha^\ell(\vec{r}), \quad (49)$$

then Eq. 49 is rewritten as

$$\frac{\partial}{\partial t} \hat{r}_\alpha(\vec{r}) = \hat{v}_\alpha(\vec{r}) - \text{div} \hat{\hat{w}}_\alpha(\vec{r}). \quad (50)$$

Equations of motion of momentums

First, the momentum of the electromagnetic field is represented as the Poynting vector. The Poynting vector density operator  $\hat{G}(\vec{r})$  defined as

$$\hat{G}(\vec{r}) = \frac{1}{4\pi c} \hat{E}(\vec{r}) \times \hat{B}(\vec{r}) \quad (51)$$

satisfies the equation of motion

$$\frac{\partial}{\partial t} \frac{1}{2} \left( \hat{G}(\vec{r}) + \hat{G}^\dagger(\vec{r}) \right) = -\frac{1}{2} \left( \hat{L}(\vec{r}) + \hat{L}^\dagger(\vec{r}) \right) - \text{div} \hat{\sigma}(\vec{r}). \quad (52)$$

In this expression,  $\hat{\sigma}(\vec{r})$  is the Maxwell's stress tensor density operator and  $\hat{L}(\vec{r})$  is the Lorentz force density operator as follows:

$$\hat{\sigma}(\vec{r}) = \hat{\sigma}_E(\vec{r}) + \hat{\sigma}_M(\vec{r}), \quad (53)$$

$$\hat{\sigma}_E^{ij}(\vec{r}) = \frac{1}{8\pi} \left[ \hat{E}^2(\vec{r}) \delta^{ij} - (\hat{E}^i(\vec{r}) \hat{E}^j(\vec{r}) + \hat{E}^j(\vec{r}) \hat{E}^i(\vec{r})) \right], \quad (54)$$

$$\hat{\sigma}_M^{ij}(\vec{r}) = \frac{1}{8\pi} \left[ \hat{B}^2(\vec{r}) \delta^{ij} - (\hat{B}^i(\vec{r}) \hat{B}^j(\vec{r}) + \hat{B}^j(\vec{r}) \hat{B}^i(\vec{r})) \right],$$

and

$$\hat{L}(\vec{r}) = \hat{L}_e(\vec{r}) + \sum_a \hat{L}_a(\vec{r}), \quad (55)$$

$$\hat{L}_e(\vec{r}) = \hat{E}(\vec{r}) \hat{\rho}_e(\vec{r}) + \frac{1}{c} \hat{j}_e(\vec{r}) \times \hat{B}(\vec{r}), \quad (56)$$

$$\hat{L}_a(\vec{r}) = \hat{E}(\vec{r}) \hat{\rho}_a(\vec{r}) + \frac{1}{c} \hat{j}_a(\vec{r}) \times \hat{B}(\vec{r}), \quad (57)$$

where  $\hat{L}_e(\vec{r})$  is the electronic Lorentz force density operator and  $\hat{L}_a(\vec{r})$  is the Lorentz force density operator of atomic nucleus  $a$ .

It should be noted that  $\hat{\sigma}(\vec{r})$  is symmetric:

$$\hat{\sigma}^{ij}(\vec{r}) = \hat{\sigma}^{ji}(\vec{r}). \quad (58)$$

Likewise, the angular momentum density operator  $\hat{u}(\vec{r})$  of the electromagnetic field defined as

$$\hat{u}(\vec{r}) = \vec{r} \times \hat{G}(\vec{r}), \quad (59)$$

satisfies the equation of motion

$$\frac{\partial}{\partial t} \frac{1}{2} \left( \hat{u}(\vec{r}) + \hat{u}^\dagger(\vec{r}) \right) = -\vec{r} \times \frac{1}{2} \left( \hat{L}(\vec{r}) + \hat{L}^\dagger(\vec{r}) \right) - \text{div} \left( \vec{r} \times \hat{\sigma}(\vec{r}) \right). \quad (60)$$

Second, the electronic kinetic momentum density operator  $\hat{\Pi}_e(\vec{r})$  defined as

$$\hat{\Pi}_e^k(\vec{r}) = \frac{1}{2} \left( -i\hbar \hat{\psi}^\dagger(\vec{r}) \hat{D}_{ek}(\vec{r}) \hat{\psi}(\vec{r}) + i\hbar \hat{D}_{ek}^\dagger(\vec{r}) \hat{\psi}^\dagger(\vec{r}) \cdot \hat{\psi}(\vec{r}) \right) \quad (61)$$

satisfies the equation of motion

$$\frac{\partial}{\partial t} \hat{\Pi}_e(\vec{r}) = \hat{L}_e(\vec{r}) + \hat{\tau}_e^\Pi(\vec{r}). \quad (62)$$

Aside from the electronic Lorentz force density operator  $\hat{L}_e(\vec{r})$ , the  $\hat{\tau}_e^\Pi(\vec{r})$  denotes the electronic tension density operator given as the divergence of the electronic stress tensor density operator  $\hat{\tau}_e^\Pi(\vec{r})$  as follows:

$$\hat{\tau}_e^\Pi(\vec{r}) = \text{div} \hat{\tau}_e^{\Pi}(\vec{r}), \quad (63)$$

$$\hat{\tau}_e^{\Pi k}(\vec{r}) = \partial_l \hat{\tau}_e^{\Pi kl}(\vec{r}), \quad (64)$$

where

$$\begin{aligned} \hat{\tau}_e^{\Pi k}(\vec{r}) &= \frac{i\hbar c}{2} \left[ \hat{D}_{el}^\dagger(\vec{r}) \hat{\psi}(\vec{r}) \gamma^\ell \cdot \hat{D}_{ek}(\vec{r}) \hat{\psi}(\vec{r}) + \hat{\psi}(\vec{r}) \gamma^\ell \hat{D}_{ek}(\vec{r}) \hat{D}_{el}(\vec{r}) \hat{\psi}(\vec{r}) \right. \\ &\quad \left. - \hat{D}_{ek}^\dagger(\vec{r}) \hat{D}_{el}^\dagger(\vec{r}) \hat{\psi}(\vec{r}) \gamma^\ell \cdot \hat{\psi}(\vec{r}) - \hat{D}_{ek}^\dagger(\vec{r}) \hat{\psi}(\vec{r}) \gamma^\ell \cdot \hat{D}_{el}(\vec{r}) \hat{\psi}(\vec{r}) \right] \\ &\quad - \frac{1}{c} \left( \hat{j}_e(\vec{r}) \times \vec{B}(\vec{r}) \right)^k \end{aligned} \quad (65)$$

and

$$\hat{\tau}_e^{\Pi kl}(\vec{r}) = \frac{i\hbar c}{2} \left[ \hat{\psi}(\vec{r}) \gamma^\ell \hat{D}_{ek}(\vec{r}) \hat{\psi}(\vec{r}) - \hat{D}_{ek}^\dagger(\vec{r}) \hat{\psi}(\vec{r}) \gamma^\ell \cdot \hat{\psi}(\vec{r}) \right]. \quad (66)$$

It should be noted that  $\hat{\tau}_e^\Pi(\vec{r})$  is Hermitean:

$$\hat{\tau}_e^{\Pi \dagger}(\vec{r}) = \hat{\tau}_e^\Pi(\vec{r}). \quad (67)$$

Third, the electronic spin angular momentum density operator  $\hat{\sigma}_e(\vec{r})$  is defined as

$$\hat{\sigma}_e(\vec{r}) = \hat{\psi}^\dagger(\vec{r}) \vec{\sigma} \hat{\psi}(\vec{r}), \quad (68)$$

where,  $\vec{\sigma}$  denotes the Pauli spin matrix:

$$\begin{aligned} \sigma^1 &= \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, & \sigma^2 &= \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \\ \sigma^3 &= \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \end{aligned} \quad (69)$$

The electronic spin angular momentum density satisfies the equation of motion

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \hbar \hat{\sigma}_e^k(\vec{r}) \right) = -\varepsilon_{lnk} \hat{\tau}_e^{\Pi ln}(\vec{r}) - \hat{\zeta}_e(\vec{r}), \quad (70)$$

where

$$\hat{\zeta}_e(\vec{r}) = c \partial_l \left( \hat{\psi}(\vec{r}) \gamma^l \frac{1}{2} \hbar \sigma^l \hat{\psi}(\vec{r}) \right). \quad (71)$$

Fourth, the electronic orbital angular momentum density operator  $\hat{\ell}_e(\vec{r})$  is defined as

$$\hat{\ell}_e(\vec{r}) = \vec{r} \times \hat{\Pi}_e(\vec{r}), \quad (72)$$

which satisfies the equation of motion

$$\begin{aligned} \frac{\partial}{\partial t} \left( \hat{\ell}_e(\vec{r}) + \frac{1}{2} \hbar \hat{\sigma}_e(\vec{r}) \right) &= \vec{r} \times \hat{L}_e(\vec{r}) + \text{div} \left( \vec{r} \times \hat{\tau}_e^\Pi(\vec{r}) \right) \\ &\quad - \hat{\zeta}_e(\vec{r}). \end{aligned} \quad (73)$$

Fifth, the kinetic momentum density operator  $m_a \hat{S}_a(\vec{r}) = \hat{j}_a(\vec{r})$  of atomic nucleus  $a$  satisfies the equation of motion

$$\frac{\partial}{\partial t} \left( m_a \hat{S}_a(\vec{r}) \right) = \frac{\partial}{\partial t} \hat{j}_a(\vec{r}) = \hat{L}_a(\vec{r}) + \hat{\tau}_a^S(\vec{r}) \quad (74)$$

Aside from the Lorentz force density operator  $\hat{L}_a(\vec{r})$ , the  $\hat{\tau}_a^S(\vec{r})$  denotes the tension density operator given as the divergence of the stress tensor density operator  $\hat{\tau}_a^S(\vec{r})$  as follows:

$$\hat{\tau}_a^S(\vec{r}) = \text{div} \hat{\tau}_a^S(\vec{r}), \quad (75)$$

$$\hat{\tau}_a^{Sk}(\vec{r}) = \partial_l \hat{\tau}_a^{Skl}(\vec{r}), \quad (76)$$

where

$$\begin{aligned} \hat{\tau}_a^{Sk}(\vec{r}) &= \frac{\hbar^2}{4m_a} \left[ \hat{\lambda}_a^\dagger(\vec{r}) \hat{D}_{ak}(\vec{r}) \hat{D}_{al}^2(\vec{r}) \hat{\lambda}_a(\vec{r}) \right. \\ &\quad \left. + \hat{D}_{ak}^\dagger(\vec{r}) \hat{D}_{al}^{\dagger 2}(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \cdot \hat{\lambda}_a(\vec{r}) \right. \\ &\quad \left. - \hat{D}_{ak}^\dagger(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \cdot \hat{D}_{al}^2(\vec{r}) \hat{\lambda}_a(\vec{r}) - \hat{D}_{al}^{\dagger 2}(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \right. \\ &\quad \left. \cdot \hat{D}_{ak}(\vec{r}) \hat{\lambda}_a(\vec{r}) \right] - \frac{1}{c} \left( \hat{j}_a(\vec{r}) \times \vec{B}(\vec{r}) \right)^k, \end{aligned} \quad (77)$$

$$\begin{aligned} \hat{\tau}_a^{Sk l}(\vec{r}) &= \frac{\hbar^2}{4m_a} \left[ \hat{\lambda}_a^\dagger(\vec{r}) \hat{D}_{ak}(\vec{r}) \hat{D}_{al}(\vec{r}) \hat{\lambda}_a(\vec{r}) \right. \\ &\quad \left. + \hat{D}_{ak}^\dagger(\vec{r}) \hat{D}_{al}^\dagger(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \cdot \hat{\lambda}_a(\vec{r}) \right. \\ &\quad \left. - \hat{D}_{ak}^\dagger(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \cdot \hat{D}_{al}(\vec{r}) \hat{\lambda}_a(\vec{r}) \right. \\ &\quad \left. - \hat{D}_{al}^\dagger(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \cdot \hat{D}_{ak}(\vec{r}) \hat{\lambda}_a(\vec{r}) \right]. \end{aligned} \quad (78)$$

It should be noted that the stress tensor density operator  $\hat{\tau}_a^S(\vec{r})$  is Hermitean and symmetric:

$$\hat{\tau}_a^{S \dagger}(\vec{r}) = \hat{\tau}_a^S(\vec{r}), \quad (79)$$

$$\hat{\tau}_a^{Sk l}(\vec{r}) = \hat{\tau}_a^{Sl k}(\vec{r}). \quad (80)$$

The electronic orbital angular momentum density operator  $\hat{\ell}_a(\vec{r})$  is defined as

$$\hat{\ell}_a(\vec{r}) = \vec{r} \times \hat{j}_a(\vec{r}), \quad (81)$$

and satisfies the equation of motion:

$$\frac{\partial}{\partial t} \hat{\ell}_a(\vec{r}) = \vec{r} \times \hat{L}_a(\vec{r}) + \text{div} \left( \vec{r} \times \hat{\tau}_a^S(\vec{r}) \right). \quad (82)$$

Combining these, we obtain

$$\frac{\partial}{\partial t} \hat{\Pi}(\vec{r}) = \hat{L}(\vec{r}) + \hat{\tau}(\vec{r}) = \hat{L}(\vec{r}) + \text{div} \hat{\tau}(\vec{r}), \quad (83)$$

where

$$\hat{\Pi}(\vec{r}) = \hat{\Pi}_e(\vec{r}) + \sum_a \hat{J}_a(\vec{r}), \quad (84)$$

$$\hat{\tau}(\vec{r}) = \hat{\tau}_e^\Pi(\vec{r}) + \sum_a \hat{\tau}_a^S(\vec{r}), \quad (85)$$

$$\hat{\tau}(\vec{r}) = \hat{\tau}_e^\Pi(\vec{r}) + \sum_a \hat{\tau}_a^S(\vec{r}). \quad (86)$$

Likewise, we obtain

$$\frac{\partial}{\partial t} \left[ \frac{1}{2} \left( \hat{G}(\vec{r}) + \hat{G}^\dagger(\vec{r}) \right) + \hat{\Pi}(\vec{r}) \right] = -\text{div} \left( \hat{\sigma}(\vec{r}) - \hat{\tau}(\vec{r}) \right), \quad (87)$$

which is the momentum conservation law of the Rigged QED system.

For the angular momentum, we have

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \hat{\ell}_e(\vec{r}) + \frac{1}{2} \hbar \hat{\sigma}_e(\vec{r}) + \sum_a \hat{\ell}_a(\vec{r}) \right) \\ &= \vec{r} \times \hat{L}(\vec{r}) + \text{div} \left( \vec{r} \times \hat{\tau}(\vec{r}) \right) - \hat{\zeta}_e(\vec{r}), \end{aligned} \quad (88)$$

and if the  $\hat{u}(\vec{r})$  is added to, we obtain

$$\begin{aligned} & \frac{\partial}{\partial t} \left( \hat{u}(\vec{r}) + \hat{\ell}_e(\vec{r}) + \frac{1}{2} \hbar \hat{\sigma}_e(\vec{r}) + \sum_a \hat{\ell}_a(\vec{r}) \right) \\ &= -\text{div} \left[ \vec{r} \times \left( \hat{\sigma}(\vec{r}) - \hat{\tau}(\vec{r}) \right) \right] - \hat{\zeta}_e(\vec{r}), \end{aligned} \quad (89)$$

which is the angular momentum conservation law of the Rigged QED system.

Energy densities

The energy flow is found as follows:

$$\begin{aligned} \frac{\partial}{\partial t} \hat{H}_\nu(\vec{r}) &= -c^2 \text{div} \frac{1}{2} \left( \hat{G}(\vec{r}) + \hat{G}^\dagger(\vec{r}) \right) \\ &\quad - \frac{1}{2} \left( \hat{E}(\vec{r}) \cdot \hat{j}(\vec{r}) + \hat{j}(\vec{r}) \cdot \hat{E}(\vec{r}) \right), \end{aligned} \quad (90)$$

$$\frac{\partial}{\partial t} \hat{H}_e(\vec{r}) = -c^2 \text{div} \hat{\Pi}_e(\vec{r}) + \frac{1}{2} \left( \hat{E}(\vec{r}) \cdot \hat{j}_e(\vec{r}) + \hat{j}_e(\vec{r}) \cdot \hat{E}(\vec{r}) \right), \quad (91)$$

$$\begin{aligned} \frac{\partial}{\partial t} \hat{H}_{\text{atom}}(\vec{r}) &= -\text{div} \sum_a \hat{s}_a(\vec{r}) \\ &\quad + \frac{1}{2} \left( \hat{E}(\vec{r}) \cdot \sum_a \hat{j}_a(\vec{r}) + \sum_a \hat{j}_a(\vec{r}) \cdot \hat{E}(\vec{r}) \right), \end{aligned} \quad (92)$$

with

$$\begin{aligned} \hat{s}_a^k(\vec{r}) &= \frac{1}{2i\hbar} \left( \frac{\hbar^2}{2m_a} \right) \left[ \hat{D}_{ak}^\dagger(\vec{r}) \hat{D}_{al}^{\dagger 2}(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \cdot \hat{\lambda}_a(\vec{r}) \right. \\ &\quad \left. - \hat{D}_{al}^{\dagger 2}(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \cdot \hat{D}_{ak}(\vec{r}) \hat{\lambda}_a(\vec{r}) \right. \\ &\quad \left. + \hat{D}_{ak}^\dagger(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \cdot \hat{D}_{al}^2(\vec{r}) \hat{\lambda}_a(\vec{r}) \right. \\ &\quad \left. - \hat{\lambda}_a^\dagger(\vec{r}) \hat{D}_{ak}(\vec{r}) \hat{D}_{al}^2(\vec{r}) \hat{\lambda}_a(\vec{r}) \right], \end{aligned} \quad (93)$$

leading to

$$\begin{aligned} & \frac{\partial}{\partial t} \hat{H}_{\text{rigged QED}}(\vec{r}) \\ &= -\text{div} \left( c^2 \hat{G}(\vec{r}) + c^2 \hat{\Pi}_e(\vec{r}) + \sum_a \hat{s}_a(\vec{r}) \right), \end{aligned} \quad (94)$$

which is the energy conservation law of the Rigged QED system.

The virial theorem has been found to be:

$$\begin{aligned} E_{\text{rigged QED}} &= \int d^3\vec{r} \langle \hat{H}_{\text{rigged QED}}(\vec{r}) \rangle \\ &= \int d^3\vec{r} \left\langle m_e c^2 \hat{\psi}(\vec{r}) \hat{\psi}(\vec{r}) - \sum_a \hat{T}_a(\vec{r}) \right\rangle, \end{aligned} \quad (95)$$

which in the non-relativistic limit becomes

$$E_{\text{non-relativistic rigged QED}} = - \int d^3\vec{r} \left\langle \sum_a \hat{T}_a(\vec{r}) \right\rangle. \quad (96)$$

It should be noted that the stress tensor density has the dimension of the energy density. Indeed, the trace of the stress tensor density becomes

$$\begin{aligned} \hat{\tau}_{e\ k}^\Pi(\vec{r}) &= \frac{c}{2} \left( -i \hbar \hat{\psi}(\vec{r}) \gamma^k \hat{D}_{ek}(\vec{r}) \hat{\psi}(\vec{r}) + i \hbar \hat{D}_{ek}^\dagger(\vec{r}) \hat{\psi}(\vec{r}) \gamma^k \cdot \hat{\psi}(\vec{r}) \right) \\ &= \frac{1}{2} \left( \hat{M}_e(\vec{r}) + \hat{M}_e^\dagger(\vec{r}) \right) - m_e c^2 \hat{\psi}(\vec{r}) \hat{\psi}(\vec{r}), \end{aligned} \quad (97)$$

$$\begin{aligned} \hat{\tau}_a^S{}^k(\vec{r}) &= \frac{\hbar^2}{4m_a} \left[ -\hat{\lambda}_a^\dagger(\vec{r}) \hat{D}_{al}^2(\vec{r}) \hat{\lambda}_a(\vec{r}) - \hat{D}_{al}^{\dagger 2}(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \cdot \hat{\lambda}_a(\vec{r}) \right. \\ &\quad \left. + \hat{D}_{al}^\dagger(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \cdot \hat{D}_{al}(\vec{r}) \hat{\lambda}_a(\vec{r}) \right. \\ &\quad \left. + \hat{D}_{al}^\dagger(\vec{r}) \hat{\lambda}_a^\dagger(\vec{r}) \cdot \hat{D}_{al}(\vec{r}) \hat{\lambda}_a(\vec{r}) \right]. \end{aligned} \quad (98)$$

This is equivalent to two times the kinetic energy density; in the non-relativistic limit, the integral of the trace of the stress tensor density gives two times that of the kinetic energy density as follows

$$\int d^3\vec{r} \left\langle \hat{\tau}_e^{\Pi k}(\vec{r}) + \sum_a \hat{\tau}_a^S k(\vec{r}) \right\rangle \xrightarrow{\text{nonrelativistic limit}} \int d^3\vec{r} \left\langle \sum_x \hat{\tau}_x^S k(\vec{r}) \right\rangle = 2 \int d^3\vec{r} \left\langle \sum_x \hat{T}_x(\vec{r}) \right\rangle. \quad (99)$$

Hence, the stress tensor density gives a local picture of two times the kinetic energy density.

The eigenvalue is the principal stress and the eigenvector is the principal axis as summarized in Fig. 4.

The eigenvalue of the stress tensor density gives a measure of the kinetic energy. If the local principal stress is positive, it is called the tensile stress, while if it is negative, compressive. The discrimination is schematically shown in Fig. 5.

Since the metric tensor  $g^{ij}$  has negative eigenvalues  $(-1, -1, -1)$ , we should note that the compressive stress gives a positive contribution to the kinetic energy density, while the tensile stress provides a negative contribution. This relationship provides the new picture of the local chemical interaction energy density. The atomic electron density exhibits positive kinetic energy density, leading to the formation of the electronic drop region  $R_D$  [4], leading to the compressive stress [3]. This tendency should of course be intact in between ionic species interactions. The situation would change dramatically for covalent bond formation, where a pair of electrons should be bound tightly and thereby creating tensile stress. Many systems exhibit such generic features, which are called spindle structure [3].

### Stationary condition

Stationary state is of primary importance since the local force can vanish, when the equation of motions for the stationary state is equivalent to the local equilibrium condition and where the tension density exactly cancels the Lorentz force density at every point of space [2–5]. The tension is given by the divergence of the stress tensor. Since the stress tensor has the dimensions of the energy

### Stress tensor, principal stress and principal axis

$$\langle \hat{\tau}_\alpha^S(\vec{r}) \rangle = \begin{pmatrix} \tau_{\alpha\alpha}^S(\vec{r}) & \tau_{\alpha\beta}^S(\vec{r}) & \tau_{\alpha\gamma}^S(\vec{r}) \\ \tau_{\beta\alpha}^S(\vec{r}) & \tau_{\beta\beta}^S(\vec{r}) & \tau_{\beta\gamma}^S(\vec{r}) \\ \tau_{\gamma\alpha}^S(\vec{r}) & \tau_{\gamma\beta}^S(\vec{r}) & \tau_{\gamma\gamma}^S(\vec{r}) \end{pmatrix}$$

$$\xrightarrow{\text{diag}} \begin{pmatrix} \tau_\alpha^{\sigma 11}(\vec{r}) & 0 & 0 \\ 0 & \tau_\alpha^{\sigma 22}(\vec{r}) & 0 \\ 0 & 0 & \tau_\alpha^{\sigma 33}(\vec{r}) \end{pmatrix}$$

$$\tau_\alpha^{\sigma 11}(\vec{r}) \leq \tau_\alpha^{\sigma 22}(\vec{r}) \leq \tau_\alpha^{\sigma 33}(\vec{r})$$

Fig. 4 Diagonalized form of the stress tensor

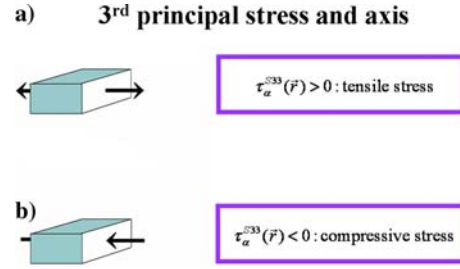


Fig. 5 Tensile (a) and compressive (b) stresses

density, a completely new realization of the tensorial chemical interaction energy density is then realized.

### Application

Let us demonstrate the usefulness of our theory by demonstrating the spindle structures. The spindle structure is a geometrical object of a region where principal electronic stress is positive along a line of principal axis of the electronic stress that connects a pair of the  $R_D$ s of atoms and molecules [3].

### H<sub>2</sub> molecule

A schematic of the spindle structure of the H–H  $\sigma$  bond is shown in Fig. 6.

The numerical data are shown on the cross section of the molecule in the plane containing the H–H  $\sigma$  bond axis in Fig. 7.

As shown in Fig. 7, the spindle structure of the  $\sigma$  bond has the sheath structure surrounding the spindle. The sheath of the spindle has marginally parallel principal axes as the adjacent spindle but the eigenvalue has negative sign instead.

Single, double and triple bonds in  $C_2H_6$ ,  $C_2H_4$  and  $C_2H_2$

The spindle structure in  $C_2H_6$  is shown on the cross section of the molecule in the plane containing the C–C  $\sigma$  bond axis and two C–H  $\sigma$  bonds in Fig. 8.

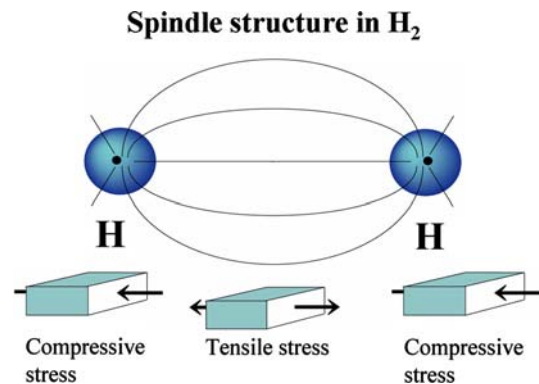


Fig. 6 Spindle structure

As shown in Fig. 8, the spindle structures for C–H and C–C  $\sigma$  bonds are demonstrated. Note also that the spindle structures in between inter-shell structures within the C atom. Marginal stability around atoms is represented by compressive principal stresses. Only the bonds of a pair of electrons are singled out as the spindle structure.

The spindle structure in  $C_2H_4$  is shown on the cross section of the molecular plane containing four C–H  $\sigma$  bonds in Fig. 9.

As shown in Fig. 9, the spindle structures for the C–C and C–H  $\sigma$  bonds are clearly demonstrated. Marginal stability around atoms is represented by compressive principal stresses. The spindle structure for the C–H  $\sigma$  bond remains the same as in the  $C_2H_6$  case. However, the spindle structure for the C–C  $\sigma$  bond shrinks both in region and magnitude as compared with that in the  $C_2H_6$  case. This is because the second C–C  $\pi$  bond that spreads perpendicular to the molecular plane makes the

$H_2$ ,  $R = 0.7324\text{\AA}$  (optimized geometry at this level)  
RHF/6-31G(d,p)level

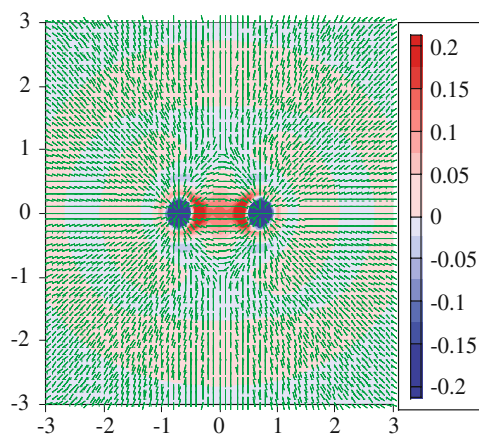


Fig. 7 Spindle structure in  $H_2$

$C_2H_6$ , optimized geometry at this level, horizontal plane  
RHF/6-31G(d,p)level

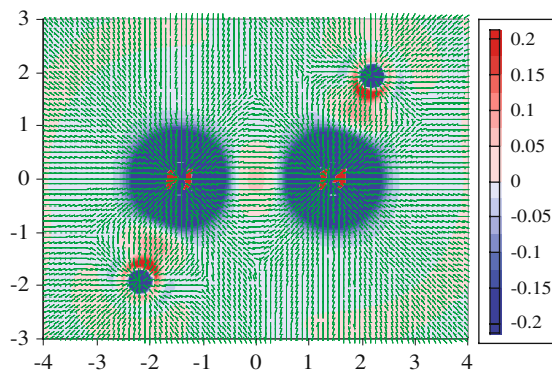


Fig. 8 Spindle structure in  $C_2H_6$

C–C distance shorter, and therefore the C–C  $\sigma$  bond approaches the united atom limit where the tensile stress region is immersed under the atomic compressive one.

The spindle structure for the C–C  $\pi$  bond in  $C_2H_4$  is shown on the cross section of the plane that is both perpendicular to the molecular plane and containing the C–C axis in Fig. 10.

As shown in Fig. 10, the spindle structure for C–C  $\pi$  bond is clearly demonstrated. The dumbbell-type spindle structure for the C–C  $\pi$  bond spreads in a wider region than that of the C–C  $\sigma$  bond and shows the magnitude of the tensile eigenvalue has two maxima in the symmetric position out of the C–C axis. The sheath structure surrounding the C–C  $\pi$  bond spindle inevitably spreads extensively and represents the region of rather loosely bound electrons. Again, the spindle structure for the C–C  $\sigma$  bond shrinks both in space and magnitude compared to that in the  $C_2H_6$  case, where the tensile stress region for the C–C  $\sigma$  bond is immersed under the atomic compressive one.

The spindle structure in  $C_2H_2$  is shown in the plane containing the C–C  $\sigma$  bond axis in Fig. 11.

As shown in Fig. 11, the spindle structures for the two C–H  $\sigma$  bonds remain intact as in the  $C_2H_6$  case. However, it should be noted that the spindle structure for the C–C  $\sigma$  and  $\pi$  bonds disappear but the dumbbell-type sheath structure corresponding to the C–C  $\pi$  bond remains as in the  $C_2H_4$  case instead. Apparently, the tensile stress region for the C–C  $\sigma$  and  $\pi$  bonds is immersed completely under the atomic compressive one.

## Conclusion

The field theory of the energy density has been presented in terms of the Rigged QED theory. Maxwell's equations are fundamental to our approach in addition to those of Schrödinger and Dirac.

The vibronic interaction that goes beyond the adiabatic approximation has been incorporated in addition to the electronic spin-dependent interaction.

$C_2H_4$ , optimized geometry at this level, horizontal plane  
RHF/6-31G(d,p)level

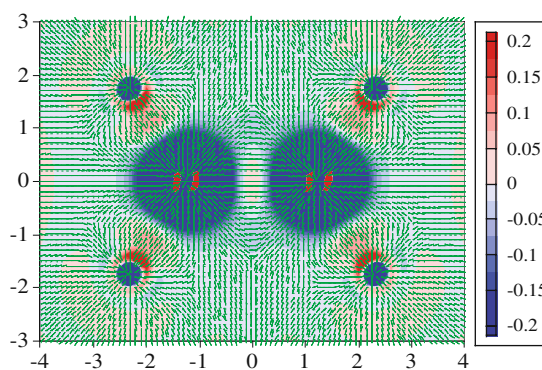
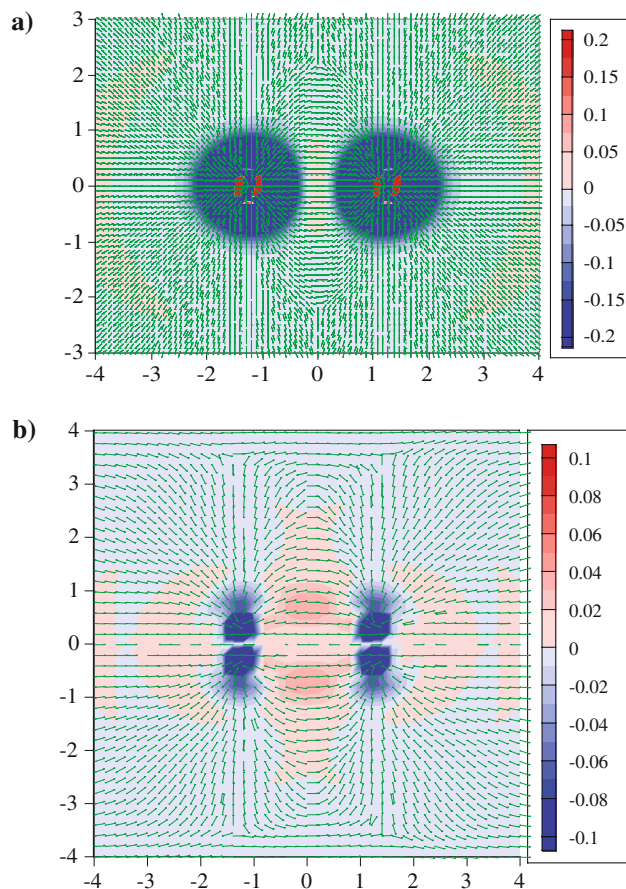


Fig. 9 Spindle structure in  $C_2H_4$  on the molecular plane



$C_2H_4$ , optimized geometry at this level, vertical plane  
RHF/6-31G(d,p)level

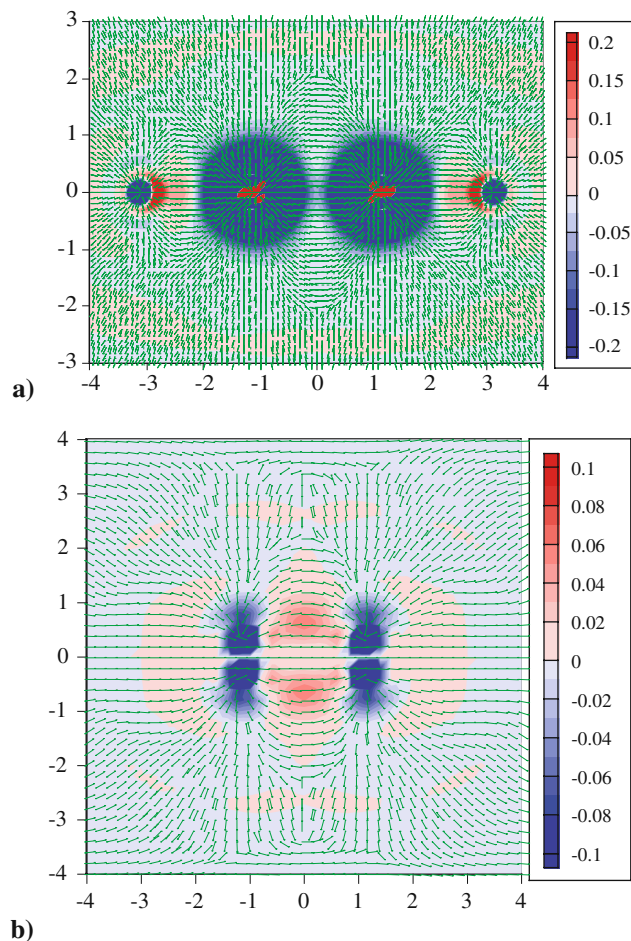


**Fig. 10** Spindle structure for the C-C  $\pi$  bond in  $C_2H_4$ . **a** All occupied MOs. **b** HOMO

Covalent bond describe electron pairing in between a pair of atoms and molecules. In this paper, the space is partitioned in mutually disjoint regions by using a new concept of the electronic drop region  $R_D$ , atmosphere region  $R_A$ , and the interface  $S$  [2–5]. The covalent bond formation is then characterized by a new concept of the spindle structure. The spindle structure is a geometrical object of a region where principal electronic stress is positive along a line of principal axis of the electronic stress that connects a pair of the  $R_D$ 's of atoms and molecules. A new energy density partitioning scheme is obtained using the Rigged QED.

Local equilibrium condition equivalent to the Schrödinger equation of the stationary state is found as the balance of (1) the Lorentz force exerted on the particle and (2) the tension of the field at every point in space. Tensorial chemical interaction energy density is revealed as the integral of the tension, and the Lorentz force in the case of the stationary state. Spindle structure connects a pair of the electronic  $R_D$ 's of atoms and molecules, and proves the intrinsic tensorial chemical interaction energy density. Rigged QED theory lacks the Poincare symmetry but encompasses the nuclear

$C_2H_2$ , optimized geometry at this level  
RHF/6-31G(d,p)level



**Fig. 11** Spindle structure in  $C_2H_2$ . **a** All occupied MOs. **b** HOMO

dynamics, for example, the nuclear currents constitute the elements of the Maxwell's equations, as well as the nuclear charges does, and the virial theorem allows the kinetic energy density partitioning. Applications have shown the usefulness of our theory for classifying various modes of chemical interaction energies.

The nuclear spin should have been treated using full Poincare symmetry, which should be found by using the gauge fields of QCD(Quantum chromodynamics)reduced from GUT(Grand unified theory)as follows:

$$SU(3)_c \times SU(2)_w \times U(1)_y \rightarrow SU(3)_c \times U(1)_{QED},$$

where the Higgs field breaks the electroweak gauge group  $SU(2)_w \times U(1)_y$  down to  $U(1)_{QED}$ , but the color and charge symmetries remain intact. This topic will be treated elsewhere.

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## Appendix

In the Rigged QED theory, the interaction of a system and its environment is tractable using regional charge and current densities.

Let a system A be embedded in the environment medium M. The corresponding gauge potentials [2] are the regional integrals of the charge and transversal current densities, defined as follows

$$\hat{A}_{0A}(\vec{r}) = \int_A d^3\vec{s} \frac{\hat{\rho}(\vec{s})}{|\vec{r} - \vec{s}|}, \quad (100)$$

$$\hat{A}_{0M}(\vec{r}) = \int_M d^3\vec{s} \frac{\hat{\rho}(\vec{s})}{|\vec{r} - \vec{s}|}, \quad (101)$$

and

$$\hat{A}_A(\vec{r}) = \frac{1}{c} \int_A d^3\vec{s} \frac{\hat{j}_T(\vec{s}, u)}{|\vec{r} - \vec{s}|}, \quad (102)$$

$$\hat{A}_M(\vec{r}) = \frac{1}{c} \int_M d^3\vec{s} \frac{\hat{j}_T(\vec{s}, u)}{|\vec{r} - \vec{s}|}, \quad (103)$$

where the subscript A or M of the integral sign denotes the regional integrals confined to the region A or M, respectively.

Since the regions A and M altogether span the whole space, we have

$$\hat{A}_0(\vec{r}) = \hat{A}_{0A}(\vec{r}) + \hat{A}_{0M}(\vec{r}), \quad (104)$$

$$\hat{A}(\vec{r}) = \hat{A}_A(\vec{r}) + \hat{A}_M(\vec{r}) + \hat{A}_{\text{radiation}}(\vec{r}), \quad (105)$$

where  $\hat{A}_{\text{radiation}}(\vec{r})$  denotes that portion of the radiation field.

The electric field  $\hat{E}(\vec{r})$  is decomposed into the electric displacement  $\hat{D}(\vec{r})$  of the medium M and the polarization  $\hat{P}(\vec{r})$  of the system A, defined, respectively, as

$$\hat{D}(\vec{r}) = -\text{grad}\hat{A}_{0M}(\vec{r}) - \frac{1}{c} \frac{\partial}{\partial t} \hat{A}_M(\vec{r}), \quad (106)$$

$$\hat{P}(\vec{r}) = \frac{1}{4\pi} \text{grad}\hat{A}_{0A}(\vec{r}) + \frac{1}{4\pi c} \frac{\partial}{\partial t} \hat{A}_A(\vec{r}), \quad (107)$$

so that we have

$$\begin{aligned} \hat{E}(\vec{r}) &= -\text{grad}\hat{A}_0(\vec{r}) - \frac{1}{c} \frac{\partial}{\partial t} \hat{A}(\vec{r}) \\ &= \hat{D}(\vec{r}) - 4\pi\hat{P}(\vec{r}) - \frac{1}{c} \frac{\partial}{\partial t} \hat{A}_{\text{radiation}}(\vec{r}). \end{aligned} \quad (108)$$

Likewise, let the magnetic field  $\hat{H}(\vec{r})$  of the medium M and the magnetization  $\hat{M}(\vec{r})$  of the system A be defined, respectively, as

$$\hat{H}(\vec{r}) = \text{rot}\hat{A}_M(\vec{r}), \quad (109)$$

$$\hat{M}(\vec{r}) = \frac{1}{4\pi} \text{rot}\hat{A}_A(\vec{r}), \quad (110)$$

then we have

$$\hat{B}(\vec{r}) = \text{rot}\hat{A}(\vec{r}) = \hat{H}(\vec{r}) + 4\pi\hat{M}(\vec{r}) + \text{rot}\hat{A}_{\text{radiation}}(\vec{r}). \quad (111)$$

The regional charge densities are then represented, respectively, as

$$\hat{\rho}_A(\vec{r}) = -\frac{1}{4\pi} \Delta\hat{A}_{0A}(\vec{r}), \quad (112)$$

$$\hat{\rho}_M(\vec{r}) = -\frac{1}{4\pi} \Delta\hat{A}_{0M}(\vec{r}), \quad (113)$$

and hence

$$\hat{\rho}(\vec{r}) = \hat{\rho}_A(\vec{r}) + \hat{\rho}_M(\vec{r}). \quad (114)$$

Likewise, the regional current densities are represented as

$$\begin{aligned} \hat{j}_A(\vec{r}) &= \frac{c}{4\pi} \left( \frac{1}{c} \text{grad} \frac{\partial}{\partial t} \hat{A}_{0A}(\vec{r}) + \square\hat{A}_A(\vec{r}) \right) \\ &= \frac{\partial}{\partial t} \hat{P}(\vec{r}) + \text{crot}\hat{M}(\vec{r}), \end{aligned} \quad (115)$$

$$\hat{j}_M(\vec{r}) = \frac{c}{4\pi} \left( \frac{1}{c} \text{grad} \frac{\partial}{\partial t} \hat{A}_{0M}(\vec{r}) + \square\hat{A}_M(\vec{r}) \right), \quad (116)$$

and hence

$$\hat{j}(\vec{r}) = \hat{j}_A(\vec{r}) + \hat{j}_M(\vec{r}) = \frac{\partial}{\partial t} \hat{P}(\vec{r}) + \text{crot}\hat{M}(\vec{r}) + \hat{j}_M(\vec{r}). \quad (117)$$

The regional decomposition of the longitudinal and transversal components of the current densities are represented as follows

$$\hat{j}(\vec{r}) = \hat{j}_L(\vec{r}) + \hat{j}_T(\vec{r}), \quad (118)$$

with

$$\hat{j}_L(\vec{r}) = \hat{j}_{L_A}(\vec{r}) + \hat{j}_{L_M}(\vec{r}), \quad (119)$$

$$\hat{j}_T(\vec{r}) = \hat{j}_{T_A}(\vec{r}) + \hat{j}_{T_M}(\vec{r}), \quad (120)$$

where

$$\hat{j}_{L_A}(\vec{r}) = \frac{c}{4\pi} \cdot \frac{1}{c} \text{grad} \frac{\partial}{\partial t} \hat{A}_{0A}(\vec{r}), \quad (121)$$

$$\hat{j}_{L_M}(\vec{r}) = \frac{c}{4\pi} \cdot \frac{1}{c} \text{grad} \frac{\partial}{\partial t} \hat{A}_{0M}(\vec{r}), \quad (122)$$

$$\hat{j}_{T_A}(\vec{r}) = \frac{c}{4\pi} \cdot \square\hat{A}_A(\vec{r}), \quad (123)$$

$$\hat{j}_{T_M}(\vec{r}) = \frac{c}{4\pi} \cdot \square\hat{A}_M(\vec{r}). \quad (124)$$

Using Eqs. 121, 122, 123 and 124, we have the alternative forms of Eqs. 16 and 17, respectively, as

$$\hat{j}_A(\vec{r}) = \hat{j}_{L_A}(\vec{r}) + \hat{j}_{T_A}(\vec{r}), \quad (125)$$

$$\hat{j}_M(\vec{r}) = \hat{j}_{L_M}(\vec{r}) + \hat{j}_{T_M}(\vec{r}). \quad (126)$$

The linear response properties of the system A under the interaction with the environment medium M may formally be represented with obvious notation as follows

$$\hat{D}(\vec{r}) = \left(1 + 4\pi\hat{\chi}_e(\vec{r})\right)\hat{E}(\vec{r}) = \hat{\varepsilon}(\vec{r})\hat{E}(\vec{r}), \quad (127)$$

$$\hat{B}(\vec{r}) = \left(1 + 4\pi\hat{\chi}_m(\vec{r})\right)\hat{H}(\vec{r}) = \hat{\mu}(\vec{r})\hat{H}(\vec{r}), \quad (128)$$

$$\hat{j}(\vec{r}) = \hat{G}(\vec{r})\hat{E}(\vec{r}). \quad (129)$$

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