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Finite-element gauge function optimization for accurate current density calculations

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The optimum gauge function is determined for an H_2^+ ion in an ultra strong magnetic field by using the Kennedy-Kobe theory [P. K. Kennedy and D. H. Kobe, Phys. Rev. A **30**, 51 (1984)] combined with the finite element method. The divergence-free current density obtained by this method vanishes at the positions of protons. From this observation, we put the question as to whether there exists the nuclear cusp condition of current density or not, which is analogous to Kato's cusp condition of electron density. We will show a few cases where the current density vanishes exactly at the maximum of electron density.

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I. INTRODUCTION

If one considers complex wave functions, current conservation is an essential property, which is imposed on the wave functions. Epstein pointed out that the complex functions constructed from the gauge invariant atomic orbitals (GIAO) did not satisfy this property. [1] The current conservation was also discussed by another group [2,3]. Epstein proposed the use of variable gauge atomic orbitals to resolve the problem [4–6]. Although his method did not succeed, it stimulated some further work [7–10]. For example, Parker found the exact gauge function for the ground state of an anisotropic harmonic oscillator placed in a magnetic field [7]. Kennedy and Kobe found that the same solution can be obtained from the variational principle [8]. These studies were not extended to more general wave functions. Apart from these studies, Larsen used the variable vector potential to study the hydrogen molecular ion, H_2^+, in an ultra strong magnetic field (10^5–10^8 T) [11]. In such a strong field, the gauge optimization is known to affect the energy directly.

Although the Kennedy and Kobe's (KK) variational method seemed to be very clear and promising to us, there has been no work which applies this method to general molecular systems. In this paper, we combined the KK method and the finite element method (FEM) and determined the gauge function of H_2^+ in a magnetic field of 1 a.u. (2.35×10^5 T). In previous work, we have studied the method of quantum chemical computations in such a ultra strong field [12,13]. The FEM have been commonly used for the microwave engineering [14]. The application of the FEM or the finite difference method (FDM) to quantum chemical computation was reviewed several years ago [15]. Here, we might have borrowed some idea from the recent work of Yamakawa and Hyodo presented at a conference [16,17]. The FEM and the FDM have been used for computations of real wave functions and electromagnetic fields. However, there seems to be no work which used the FEM for the optimization of a gauge function based on the KK method. As we will show later, there are some advantages of the FEM when it is used with the KK method. For comparison, we also examined the expansion of a gauge function by the Hermite polynomials and will present the results in a forthcoming paper.

The construction of this article is as follows. In the next section, the variational theory of Kennedy and Kobe will be explained. Next, the computational procedure using the FEM will be presented. Finally, we analyzed the connection of the KK theory to the other theories. The KK theory can be considered as a part of the hydrodynamic formulation of quantum mechanics [18–27]. We clarify the difference between them. In terms of the KK theory, the divergence-free current density is computed from the density and current density. Therefore, this method is closely related to Helmholtz's theorem, which divides current density into longitudinal and transverse parts. Although, Helmholtz's theorem appears in standard text books of fluid mechanics [28], electromagnetics [29], and mathematical physics [30], it has been used principally for theoretical formulations, but for only a few numerical computations of current densities [31]. The difference between these formalisms will be discussed.

In the results, we will show the current density calculated by the gauge optimization vanishes at nuclear positions. Thus it resembles to the cusp condition of electron density [32–34]. In the discussion, we will analyze this condition of current density by the KK theory in a few limiting cases.

II. METHOD OF CALCULATION

A. Kennedy-Kobe theory [8]

Usually, gauge transformations in quantum mechanics consist of the two types of transformations. The first type is the transformation of the wave function,

$$\Psi'(\vec{r}) = \Psi(\vec{r})\exp\{iq\Lambda(\vec{r})\}, \tag{1}$$

$q=-1$ a.u. is the charge of an electron. Here we consider time-independent electromagnetic fields. The gauge function, $\Lambda(\vec{r})$ is also time independent. The second type is the transformation of the vector potential,

$$\vec{A}'(\vec{r}) = \vec{A}(\vec{r}) + \vec{\nabla}\Lambda(\vec{r}). \tag{2}$$

The gauge invariance of the energy expectation value means that the following relation is satisfied:

$$\langle \Psi' | \hat{H}(\vec{A} + \vec{\nabla}\Lambda) | \Psi' \rangle = \langle \Psi | \hat{H}(\vec{A}) | \Psi \rangle. \tag{3}$$

The above relation does not depend on the function Ψ. The invariance is based on the following property of the Hamiltonian operator,

$$\exp(-iq\Lambda)\hat{H}(\vec{A}+\vec{\nabla}\Lambda)\exp(iq\Lambda)=\hat{H}(\vec{A}). \tag{4}$$

Kennedy and Kobe considered a variational problem, where only one of the above transformations was applied. They considered the following Schrödinger Hamiltonian in a static magnetic field,

$$\hat{H}(\vec{A})=\frac{1}{2}\{-i\vec{\nabla}-q\vec{A}(\vec{r})\}^2+V(\vec{r}). \tag{5}$$

Furthermore, they assume that the initial wave function, $\Psi(\vec{r})$ is incomplete and does not satisfy the continuity equation; $\vec{\nabla}\cdot\vec{J}(\vec{r})\neq 0$. The current density is obtained from the wave function,

$$\vec{J}(\vec{r})=q\,\mathrm{Re}\{\Psi^*(-i\vec{\nabla}-q\vec{A})\Psi\}. \tag{6}$$

Under this condition, the following gauge energy is minimized with respect to Λ,

$$\begin{aligned} E_G(\Lambda) &\equiv \langle\Psi'|\hat{H}(\vec{A})|\Psi'\rangle-\langle\Psi|\hat{H}(\vec{A})|\Psi\rangle \\ &= \langle\Psi|\hat{H}(\vec{A}-\vec{\nabla}\Lambda)|\Psi\rangle-\langle\Psi|\hat{H}(\vec{A})|\Psi\rangle. \end{aligned} \tag{7}$$

Equation (7) can be rewritten as follows by using Eq. (5).

$$\begin{aligned} E_G(\Lambda) &= \int_{\mathbb{R}^3} d^3\vec{r}\left\{\frac{1}{2}q^2\rho(\vec{r})|\vec{\nabla}\Lambda(\vec{r})|^2+\vec{J}(\vec{r})\cdot\vec{\nabla}\Lambda(\vec{r})\right\} \\ &\quad -\frac{i}{2}\oint_{\partial\Omega(\infty)} d\vec{S}\cdot q\rho(\vec{r})\vec{\nabla}\Lambda(\vec{r}). \end{aligned} \tag{8}$$

The electron density is given by

$$\rho(\vec{r})=|\Psi(\vec{r})|^2. \tag{9}$$

The last term in Eq. (8) provides the imaginary energy and it can be omitted, since $\rho(\vec{r})\approx e^{-\alpha r^2}$ and $|\vec{\nabla}\Lambda|\approx r^n$ for the limit of $r\to\infty$.

Kennedy and Kobe showed that by optimizing $\Lambda(\vec{r})$, the continuity equation is recovered for the transformed current density,

$$\vec{\nabla}\cdot\vec{J}'(\vec{r})=0, \tag{10}$$

$$\vec{J}'(\vec{r})=q\,\mathrm{Re}\{\Psi^*[-i\vec{\nabla}-q(\vec{A}-\vec{\nabla}\Lambda)]\Psi\}=\vec{J}(\vec{r})+q^2\rho(\vec{r})\vec{\nabla}\Lambda(\vec{r}). \tag{11}$$

Equations (10) and (11) are combined to form an inhomogeneous Sturm-Louiville type partial differential equation with respect to $\Lambda(\vec{r})$,

$$-q^2\vec{\nabla}\cdot\{\rho(\vec{r})\vec{\nabla}\Lambda(\vec{r})\}=\vec{\nabla}\cdot\vec{J}(\vec{r}). \tag{12}$$

The optimum gauge function can be obtained by solving the above Kennedy-Kobe (KK) equation.

Furthermore, Kennedy and Kobe obtained the exact solution of Eq. (12) for the ground state of an anisotropic oscillator in a magnetic field. This solution was at first found by Parker for a differential equation, which differs from Eq. (12) [7]. It is also closely related to the mixed gauge function given by Larsen for a calculation of an H_2^+ ion in a ultrastrong magnetic field [11]. They assumed that the density and the current density are given by the following equations:

$$\rho(\vec{r})=C\exp(-\alpha x^2-\beta y^2-\gamma z^2), \tag{13}$$

$$\vec{J}(\vec{r})=-q^2\vec{A}(\vec{r})\rho(\vec{r}),\quad \vec{A}(\vec{r})=\tfrac{1}{2}B_z\vec{e}_z\times\vec{r}. \tag{14}$$

Here, we simplified Kennedy's treatment; the magnetic field is applied in the z direction. In addition, a symmetric vector potential is assumed. The exact solution becomes

$$\Lambda(\vec{r})=-\tfrac{1}{2}B_z xy(\alpha-\beta)/(\alpha+\beta). \tag{15}$$

Since this solution satisfies $\vec{\nabla}^2\Lambda=0$, Eq. (10) means that the transformed vector potential is perpendicular to the gradient of density,

$$\vec{\nabla}\cdot\vec{J}'(\vec{r})=-q^2\vec{A}'(\vec{r})\cdot\vec{\nabla}\rho(\vec{r})=-q^2\{\vec{A}(\vec{r})-\vec{\nabla}\Lambda\}\cdot\vec{\nabla}\rho(\vec{r})=0. \tag{16}$$

The KK approach is closely related to Helmholtz's theorem of fluid mechanics [28] and electromagnetism [29]. Helmholtz's theorem states that the vector field can be split into two parts: the longitudinal vector and the transverse vector.

$$\vec{J}(\vec{r})=\vec{J}_L(\vec{r})+\vec{J}_T(\vec{r}). \tag{17}$$

They satisfy the following equations:

$$\vec{\nabla}\times\vec{J}_L(\vec{r})=\vec{\nabla}\cdot\vec{J}_T(\vec{r})=0, \tag{18}$$

$$\vec{\nabla}\cdot\vec{J}_L(\vec{r})=\vec{\nabla}\cdot\vec{J}(\vec{r}),\quad \vec{\nabla}\times\vec{J}_T(\vec{r})=\vec{\nabla}\times\vec{J}(\vec{r}). \tag{19}$$

On the contrary, in the KK approach we divide $\vec{J}$ into the following two vectors.

$$\vec{J}_T(\vec{r})=\vec{J}'(\vec{r})=\vec{J}(\vec{r})-\vec{J}_M(\vec{r}), \tag{20}$$

$$\vec{J}_M(\vec{r})=-q^2\rho(\vec{r})\vec{\nabla}\Lambda(\vec{r}). \tag{21}$$

The two vectors satisfies the following conditions:

$$\vec{\nabla}\cdot\vec{J}_T=0,\quad \vec{\nabla}\cdot\vec{J}_M=\vec{\nabla}\cdot\vec{J},\quad \vec{\nabla}\times\vec{J}_M\neq 0. \tag{22}$$

The last condition is apparent, when we consider the anisotropic harmonic oscillator given by Eqs. (13)–(15),

$$\vec{\nabla}\times\vec{J}_M=-q^2(\vec{\nabla}\rho)\times(\vec{\nabla}\Lambda)=-q^2B_z(\alpha-\beta)^2/(\alpha+\beta)\vec{e}_z\rho. \tag{23}$$

Although $\vec{J}'$ is the pure transverse vector, $\vec{J}_M$ is a mixture of the longitudinal and the transverse vectors.

On the other hand, $\vec{J}_L$, obtained by the Helmholtz's theorem cannot be expressed by the gauge transformation as given by Eq. (21). This is because $\vec{\nabla}\times(\vec{J}_L/\rho)=0$ is not generally satisfied. The gauge transformation is the only possible transformation which does not change the electron density. The phase of a wave function $\phi(\vec{r})$ is restricted by the following condition for the loop integral,

$$\oint \vec{\nabla}\phi \cdot d\vec{l} = 2\pi n. \tag{24}$$

One can change only the scalar phase function which satisfies $\oint \vec{\nabla}\Lambda \cdot d\vec{l} = 0$. Therefore, the Helmholtz's division and the replacement of $\vec{J}$ by $\vec{J}_T$ generally changes both the phase of wave function and the electron density, simultaneously. As long as the electron density $\rho(\vec{r})$ used for the calculation is very accurate, $\vec{J}_T$ obtained by the KK method must be close to the exact current density.

B. Finite-element method

We minimized the following functional with respect to $\Lambda(\vec{r})$,

$$F(\Lambda) = \int_{\Omega} d^3\vec{r} \left\{ \frac{1}{2} q^2 \rho(\vec{r}) |\vec{\nabla}\Lambda(\vec{r})|^2 - \Lambda(\vec{r}) \vec{\nabla} \cdot \vec{J}(\vec{r}) \right\} + \oint_{\partial\Omega} d\vec{S} \cdot \Lambda(\vec{r}) \vec{J}(\vec{r}). \tag{25}$$

This functional is derived from the first volume integral of Eq. (8) by a partial integration. When we use this functional, the kinetic energy always remains finite. This is the implicit boundary condition for the solutions of Eq. (12) to have a physical reality. In general, differential equations can have nonphysical solutions. For example, second-order homogeneous ordinary differential equations have the second solutions [35].

In addition, we restricted the volume and surface integrals of Eq. (25) to a finite region, Ω, and to its surface boundary, $\partial\Omega$. Inside of Ω, the condition $\rho(\vec{r}) \geq \varepsilon > 0$ is satisfied for a small quantity ε. In the present case, $\rho(\vec{r})$ consists of Gaussian functions, which vanish rather quickly as $r \to \infty$. Therefore, this approximation can be used, as long as we consider Λ to be finite power series of r.

In the finite element method, we divide the region Ω to tetrahedral elements Ω_e, $e = 1, \ldots, N_e$. In each element, the gauge function is approximated by a linear combination of the shape functions, $N_{i,e}(\vec{r})$, multiplied by the value, $\Lambda_i = \Lambda(\vec{r}_i)$ at the ith nodal point [36,37],

$$\Lambda(\vec{r}) \approx \sum_{e=1}^{N_e} \sum_{i=1}^{N_g} \Lambda_i N_{i,e}(\vec{r}) \quad N_{i,e}(\vec{r}) = 0 \quad \vec{r} \notin \Omega_e. \tag{26}$$

In this paper, we use second-order tetrahedral elements, which have ten nodes. The explicit definitions of the shape functions for second-order tetrahedral elements are given in standard textbooks [38]. The gauge function is now expressed by a N_g dimensional vector. The discrete form of Eq. (25) is given by the following equations:

$$F(\vec{\Lambda}) = \frac{1}{2} \vec{\Lambda}^T \cdot \hat{K} \cdot \vec{\Lambda} - \vec{g}^T \cdot \vec{\Lambda}, \quad \vec{\Lambda}^T = [\Lambda_1, \Lambda_2, \ldots, \Lambda_{N_g}], \tag{27}$$

$$\hat{K} = \sum_{e=1}^{N_e} \hat{K}^e, \quad K^e_{i,j} = \int_{\Omega_e} d^3\vec{r} q^2 \rho(\vec{r}) \vec{\nabla} N_{i,e}(\vec{r}) \cdot \vec{\nabla} N_{j,e}(\vec{r}), \tag{28}$$

$$\vec{g} = \vec{g}_1 - \vec{g}_2, \tag{29}$$

$$g_{1,i} = \sum_{e=1}^{N_g} \int_{\Omega_e} d^3\vec{r} N_{i,e}(\vec{r}) \vec{\nabla} \cdot \vec{J}(\vec{r}), \tag{30}$$

$$g_{2,i} = \sum_{e} \oint_{\partial\Omega_e} d\vec{S} \cdot N_{i,e}(\vec{r}) \vec{J}(\vec{r}). \tag{31}$$

The matrix elements $K_{i,j}$ and the vector components $g_{1,i}$, $g_{2,i}$ are evaluated by numerical integrations [39,40]. The minimum condition of Eq. (27) leads to the following linear equation:

$$\hat{K} \cdot \vec{\Lambda} = \vec{g}. \tag{32}$$

Since the gauge energy of Eq. (7) does not depend the constant in $\Lambda(\vec{r})$, the matrix $\hat{K}$ has at least one zero eigenvalue.

The FEM has the following two advantages when it is used with the KK method. First, the computational space can be reduced to the finite region where electron density does not vanish. We also investigate the analytical method based on the Hermite polynomials in the next paper. Such a method is limited to the case where electrons are distributed near the origin. Polynomial functions diverge rapidly apart from the origin, and easily lead to a floating point error. Another possibility may be the Fourier expansion. Second, the functional of the KK method is local, therefore, the FEM enables parallel computations.

C. Relevant methods

Rebane [19], MacLachlan-Baker [20], and Riess [21] have published similar methods to the KK theory. In their approaches, the wave function is written as follows:

$$\Psi(\vec{r}) = \rho(\vec{r})^{1/2} e^{i\phi(\vec{r})}. \tag{33}$$

The transverse current density is obtained by inserting Eq. (33) into Eq. (11),

$$\vec{J}_T(\vec{r}) = q\{\vec{\nabla}\phi - q(\vec{A} - \vec{\nabla}\Lambda)\}\rho(\vec{r}). \tag{34}$$

Riess included the gauge function in the phase,

$$\phi'(\vec{r}) = \phi(\vec{r}) + q\Lambda(\vec{r}). \tag{35}$$

As a result, he obtained a partial differential equation with respect to $\phi'(\vec{r})$,

$$\vec{\nabla} \cdot \vec{J}_T(\vec{r}) = q\vec{\nabla} \cdot \{\rho(\vec{r})[\vec{\nabla}\phi'(\vec{r}) - q\vec{A}(\vec{r})]\} = 0. \tag{36}$$

The above equation is a part of the quantum hydrodynamic equations proposed by Madelung [18,22,27]. This equation is not easy to solve, since $\phi'(\vec{r})$ is a multivalued function. For example, $\phi = n \tan^{-1}(y/x)$ is a multivalued function in a two-dimensional space. It is not clear which functions should be used for the general expansion of $\phi'(\vec{r})$ in a three-dimensional space. In this paper, we will use $\phi(\vec{r})$ calculated by other methods, and will solve the differential equation with respect to the scalar function, $\Lambda(\vec{r})$.

Furthermore, many earlier studies were based on the linear response theory. If the transformation of Eq. (1) is expanded to first order in a magnetic field, we obtain the following expression:

$$\Psi'(\vec{r}) \approx \Psi_0(\vec{r})\{1 + i\gamma_z(\vec{r})B_z\} = \Psi_0(\vec{r}) + i\Psi_1(\vec{r}). \qquad (37)$$

Strictly, Eq. (37) is no longer a unitary transformation. The original transformation of Eq. (1) does not change the electron density $\rho(\vec{r})$. By ignoring the second-order terms of B_z, one can write $\rho'(\vec{r}) = \Psi_0(\vec{r})^2 + \Psi_1(\vec{r})^2 \approx \Psi_0(\vec{r})^2 = \rho_0(\vec{r})$. However, it also creates a strange situation. Consider the case when $\Psi_0(\vec{r})$ has a nodal plane parallel to a magnetic field. The paramagnetic current density $\vec{J}_p(\vec{r}) = \frac{1}{2}(\Psi_0\vec{\nabla}\Psi_1 - \Psi_1\vec{\nabla}\Psi_0)$ can be finite on the nodal plane if $\vec{\nabla}\Psi_0 \neq 0$. Then, the velocity of the electron becomes infinite. In addition, the gauge invariance is lost, since the truncated transformation operator does not satisfy the following relation:

$$\{1 + i\gamma_z(\vec{r})B_z\}^{-1}\vec{\nabla}\{1 + i\gamma_z(\vec{r})B_z\} \neq i\vec{\nabla}\gamma_z(\vec{r})B_z.$$

$q\Lambda_{\text{linear}}(\vec{r}) = \gamma_z(\vec{r})B_z$ is the gauge function linear to the magnetic field. The exponential form, $\exp(i\gamma_z B_z)$ is essential to the equality.

The KK theory did not assume a linear response, so that it can be applied to any strength of magnetic field. Furthermore, it is based on the unitary transformation and therefore the electron density is invariant during the energy optimization. The procedure can be continued until the condition $\vec{\nabla}\cdot\vec{J}' = 0$ is perfectly satisfied. After this process, the kinetic energy operator is modified to the following equation:

$$\hat{T}(\vec{A} - \vec{\nabla}\Lambda) = \frac{1}{2}\{-i\vec{\nabla} - q[\vec{A}(\vec{r}) - \vec{\nabla}\Lambda(\vec{r})]\}^2. \qquad (38)$$

Then, the initial wave function is not an eigenfunction of the total Hamiltonian. Although we will not do it in this paper, the normal Hatree-Fock calculation can be repeated again by using the same basis sets to obtain a more accurate wave function. It is also possible to optimize the total energy with respect to $\Lambda(\vec{r})$ and $\Psi(\vec{r})$, simultaneously. Such an approach was reported by Flament, Gervais, and Rerat [9]. They expanded the gauge function to the second power of the coordinates, and obtained $\Lambda(\vec{r}) \approx CB_z xy$ for a H_2 molecule oriented perpendicular to the magnetic field. In their study, it was not clear if the continuity condition was reached. The optimizations both of the wave function and the gauge function may need very large storage space.

Another different formulation was given by Parker [7]. At first, he wrote the transverse current density as the curl of a vector $\vec{k}(\vec{r})$ based on Helmholtz's theorem. Second, the induced current was assumed to be perpendicular to the magnetic field $\vec{B}$ and to be a linear function of $\vec{B}$.

$$\vec{J}(\vec{r}) = \vec{J}_T(\vec{r}) = \vec{\nabla} \times \vec{k}(\vec{r}), \quad \vec{k}(\vec{r}) = \frac{1}{2}f(\vec{r})\rho(\vec{r})\vec{B}. \qquad (39)$$

Moreover, he ignored the paramagnetic current, and wrote as follows:

$$\vec{J}_T(\vec{r}) = -q^2\{\vec{A}(\vec{r}) - \vec{\nabla}\Lambda(\vec{r})\}\rho(\vec{r}). \qquad (40)$$

He calculated the curl of a velocity field, $\vec{v}(\vec{r}) = q^{-1}\rho(\vec{r})^{-1}\vec{J}_T(\vec{r})$ by using the above two equations,

$$\begin{aligned}\vec{\nabla} \times \{\rho(\vec{r})^{-1}\vec{J}_T(\vec{r})\} &= -q^2\vec{\nabla} \times \{\vec{A}(\vec{r}) - \vec{\nabla}\Lambda(\vec{r})\} \\ &= -q^2\vec{B}(\vec{r}) \\ &= \frac{1}{2}\vec{\nabla} \times \{\rho(\vec{r})^{-1}\vec{\nabla} \times [f(\vec{r})\rho(\vec{r})\vec{B}]\}.\end{aligned} \qquad (41)$$

The new quantity $f(\vec{r})$ can be related to our gauge function,

$$\vec{\nabla}\Lambda = \vec{A} + \frac{1}{2}q^{-2}\rho^{-1}\vec{\nabla}(f\rho) \times \vec{B}. \qquad (42)$$

Equation (41) is identical to one of the London's equations for superconductivity [41]. [See Eq. (6).] Therefore, the paramagnetic current is not included in this equation.

Finally we will refer to the continuous sets of gauge transformations (CSGT) method proposed by Keith and Bader [10]. This method does not attempt to determine the gauge function. On the contrary, it fixes the origin of the symmetric vector potential to the place where the current density is computed. The idea seemed to be similar to the gauge origin variations in the nuclear magnetic resonance chemical shift calculations. There are the best gauge positions where the computed chemical shifts agree with the experimental ones. With this gauge origin, the current density around the observed nucleus should be computed well. Keith and Bader showed that the current density diagram obtained by this method was far different from those computed using a single fixed gauge origin. They also mentioned that the computed current density was almost divergenceless.

These results are very impressive. However, this method does not determine the gauge function in the whole space. According to their paper, the translation of the gauge origin can be realized by adding the following vector to the vector potential,

$$\delta\vec{A} = -\tfrac{1}{2}\vec{B} \times \vec{d}\{\vec{r}\}. \qquad (43)$$

Because the above vector is not generally irrotational, $\vec{\nabla} \times \delta\vec{A} \neq 0$, it cannot be expressed by the gradient of the scalar gauge function. Therefore, the CSGT obviously is different from the gauge function optimization proposed by Epstein. We felt that this method was logically uncomfortable, although there might be good numerical advantages.

In this paper, we do not attempt to deny or ignore any cited and uncited elaborate works, but we just wanted to explain why we chose the Kenndey-Kobe method. Our view is based on the rather limited knowledge around our hyperbolic cone, we hope that the reader of this article will carefully inspect it from their own independent view.

TABLE I. The anisotropic Gaussian basis sets for a H_2^+ ion in a magnetic field of 1 a.u. The anisotropic Gaussian exponents are obtained by the method described in the previous paper [13]. The exponents $(\zeta_{\perp,k},\zeta_{z,k})$, $k=1-5$, 6–7, and 8–11 are determined for the $1s$, $2p_{-1}$, and $2p_0$ orbitals of an H atom, respectively. The first five Gaussian orbitals are contracted to form a s-type orbital. The fourth and fifth Gaussians are used as one s-type and three p-type orbitals. The exponents 6–11 are used for nine independent p-type orbitals.

k	$\zeta_{\perp,k}$ (a.u.)	$\zeta_{z,k}$ (a.u.)	$c_k(1s)$	$c_k(2sp)$	$c_k(3sp)$
1	55.002246	54.927780	0.004008	0	0
2	8.263733	8.266192	0.030564	0	0
3	1.899472	1.864926	0.147919	0	0
4	0.573247	0.526446	0.448866	1	0
5	0.281788	0.161435	0.468483	0	1
6	1.436977	1.363719	$c_6(4p_x,4p_y)=1$		
7	0.398864	0.306645	$c_7(5p_x,5p_y)=1$		
8	0.254291	0.087103	$c_8(6p_x,6p_y)=1$		
9	0.839704	0.771086	$c_9(7p_z)=1$		
10	0.302631	0.172091	$c_{10}(8p_z)=1$		
11	0.249198	0.051009	$c_{11}(9p_z)=1$		

III. RESULTS

In this paper, we used the wave function of a H_2^+ ion computed at a magnetic field of 1 a.u. (2.35×10^5 T) by the anisotropic GIAO method described in the previous paper [13]. The basis sets used in this study are listed in Table I. In this paper, we will consider a single geometry of the H_2^+ ion; The molecular axis is aligned along the x-axis, while the magnetic field is parallel to the z-axis. The interproton distance is 1.65 a.u. The orbital energy was calculated to be −0.44994 a.u., which agrees with the reported value, −0.448 87 a.u. [42]. Figures 1(a) and 1(b) are the electron density and the initial current density computed from this wave function. This wave function does not satisfy the continuity equation. The divergence of the current density is shown in Fig. 2(a). The divergence takes places along the y and $-y$ directions of electron density maxima.

Next, we performed the FEM calculations of the gauge function by using the above electron density and current density as inputs. We optimized $\Lambda(\vec{r})$ inside of a spheroidal region, where the surface of the spheroid was determined from the condition, $\rho(\vec{r})=\varepsilon$. ε is a small cutoff parameter. The spheroid was divided to 56 tetrahedrons, further each tetrahedron was divided to 27 tetrahedrons. A total of 1512 tetrahedrons were obtained. We used the second-order shape

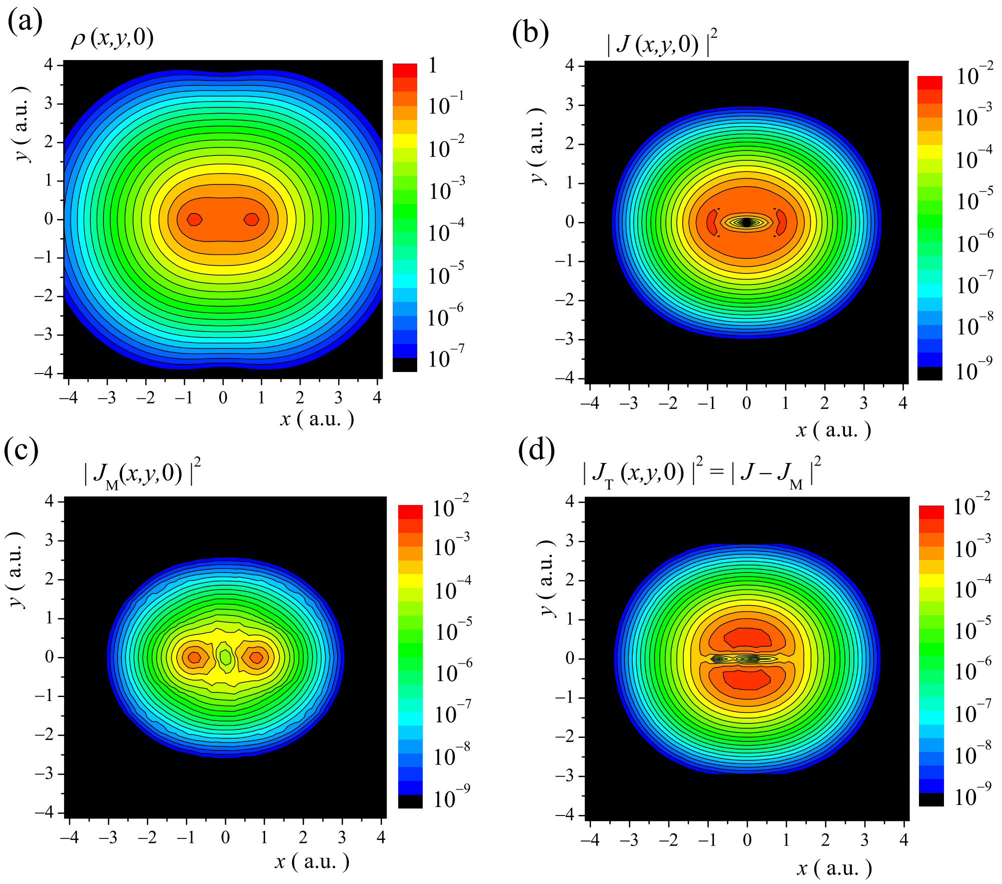

FIG. 1. (Color online) (a) The electron density and [(b)–(d)] the square of the current densities of a H_2^+ ion in a magnetic field of 1 a.u. (2.35×10^5 T) applied perpendicular to the molecular axis. The other conditions are given in the text. (b) The current density was computed from the wave function and the symmetric vector potential; $\vec{A}=\frac{1}{2}\vec{B}\times\vec{r}$. (c) The mixed current density was calculated by the FEM gauge function optimization. (d) The transverse current density was obtained by subtracting (c) from (b).

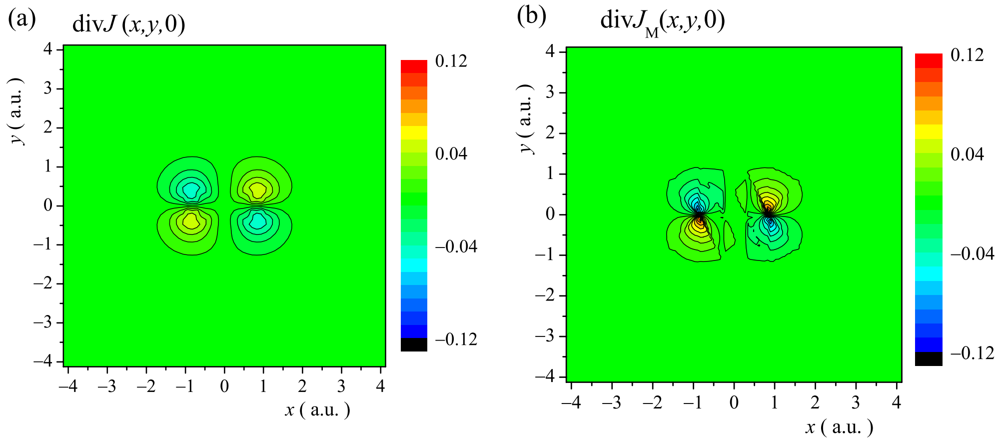

FIG. 2. (Color online) The divergence of the current density of a H_2^+ ion calculated from (a) the wave function and that computed from (b) the FEM gauge function.

functions to expand the gauge function inside of each tetrahedron. The total number of grid points became 2683. The numerical integrations were performed by using the Hammer formula [39] to obtain the matrix elements, $K_{i,j}$, and the vector components $g_i = g_{1,i} - g_{2,i}$. The 15 points formula and the 7 points formula were used for the volume integrals and for the surface integrals, respectively. Table II shows the maximum value of x coordinate in the sphero-cylinder and the gauge energy as a function of the cutoff parameter ε. E_G became the lowest at $\varepsilon = 10^{-5}$.

Figure 3(a) shows the optimum gauge function $\Lambda(\vec{r})$ obtained for $\varepsilon = 10^{-5}$. $\Lambda(\vec{r})$ was determined in the ellipse, while it was assumed to be zero at the outside. The general functional form of $\Lambda(\vec{r})$ resembles the solution, $\Lambda \propto xy$, which corresponds to the exact solution for an anisotropic harmonic oscillator, or Larsen's result for an H_2^+ ion in a strong magnetic field. We also plotted the square of the gradient vector in Fig. 3(b). If we assume $\Lambda \approx xy$, circular contours are expected, because $|\vec{\nabla}\Lambda|^2 \approx x^2 + y^2$. The deviation from this function is readily seen in Fig. 3(b). Therefore, the optimized gauge function is different from the simple second-order polynomial, xy.

In the next step, we computed the mixed current density $\vec{J}_M(\vec{r})$ by using Eq. (21). The square $|\vec{J}_M(\vec{r})|^2$ is plotted in Fig. 1(c). We also computed the transverse current density by subtracting the mixed one from the initial current density of Fig. 1(b). There is a distinct difference between the current density before and after the gauge optimization. The initial current density does not vanish at the positions of protons. However, the transverse current density plotted in Fig. 1(d) becomes almost zero at these positions.

TABLE II. The Gauge energy E_G and the maximum x coordinate as a function of the cutoff parameter ε for the electron density $[\rho(\vec{r}) \geq \varepsilon]$, which defines the region used by the FEM calculations.

ε (a.u.)	$x_{\max}$ (a.u.)	$-E_G(\Lambda_{\text{opt}})$ (a.u.)
1×10^{-4}	3.10	7.04×10^{-3}
1×10^{-5}	3.61	7.32×10^{-3}
1×10^{-6}	4.12	7.25×10^{-3}
1×10^{-7}	4.65	7.12×10^{-3}
1×10^{-8}	5.14	7.02×10^{-3}

We calculated the divergence of the current density from the optimum gauge function. It is shown in Fig. 2(b). The perfect agreement between Figs. 2(a) and 2(b) is still not achieved. In the present paper, we used the second-order shape functions. Therefore, the gradient $\vec{\nabla}\Lambda(\vec{r})$ becomes a linear function of $\vec{r}$. This approximation may not be enough. We have to use higher-order shape functions to improve the accuracy.

IV. DISCUSSION

In the previous section, we have found that the accurate current density obtained by the gauge optimization satisfies the following condition:

$$\vec{J}_T(\vec{R}_{N,i}) \approx 0. \tag{44}$$

$\vec{R}_{N,i}$ is the position of the ith nucleus. We will show here the above condition can be derived from the KK equation in a few limiting cases. Kato derived the following nuclear cusp condition of a wave function from the singularity of the Coulomb interactions [34],

$$[\vec{\nabla}\Psi](\vec{R}_{N,i}) = -Z_{N,i}\frac{\vec{r}_{N,i}}{|\vec{r}_{N,i}|}\Psi(\vec{R}_{N,i}), \quad \vec{r}_{N,i} = \vec{r} - \vec{R}_{N,i}. \tag{45}$$

Let us find here the condition derived from Eq. (44). Equation (44) can be rewritten as follows:

$$\vec{J}(\vec{R}_{N,i}) = q\{\mathrm{Im}[\Psi^*\vec{\nabla}\Psi] - q\vec{A}\rho\}(\vec{R}_{N,i}) = 0. \tag{46}$$

If we combine this equation with Eq. (45), the gradient of a wave function must satisfy the following condition at nuclear positions,

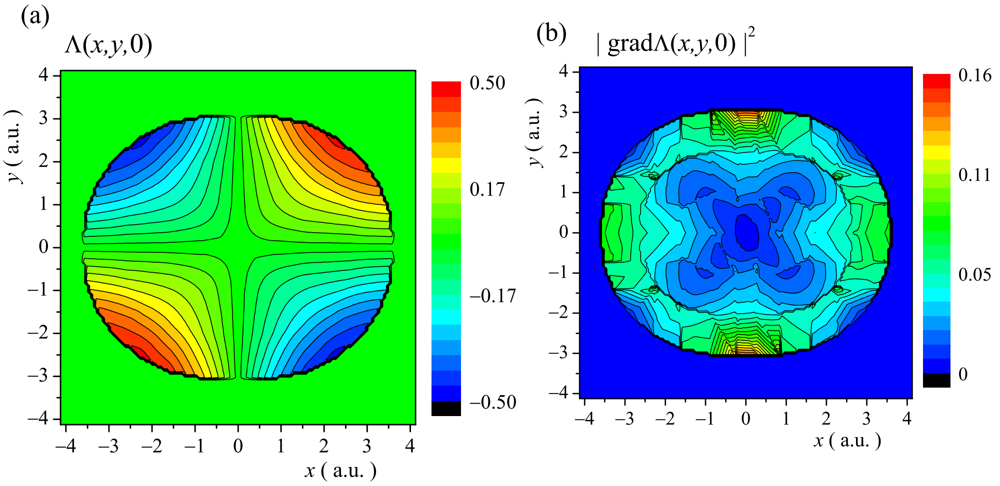

FIG. 3. (Color online) The gauge function $\Lambda(\vec{r})$ and the square of its gradient $|\vec{\nabla}\Lambda(\vec{r})|^2$ obtained by the FEM gauge function optimization. The function $\Lambda(\vec{r})$ was computed in the ellipsoid, where the density is larger than 1×10^{-5}.

$$[\vec{\nabla}\Psi](\vec{R}_{N,i}) = \left\{ -\frac{Z_{N,i}\vec{r}_{N,i}}{|\vec{r}_{N,i}|} + iq\vec{A}_{N,i} \right\}\Psi(\vec{R}_{N,i}), \quad \vec{A}_{N,i} = \vec{A}(\vec{R}_{N,i}). \tag{47}$$

This condition may remind us of the gauge invariant atomic orbitals. However, if they are used to construct a molecular orbital, it does not satisfy Eq. (47) because of the significant overlaps of the neighboring atomic orbitals.

Next, we will solve the KK equation near a nucleus. The wave function usually does not have a node at nuclear positions. Therefore, the phase of wave function can be set to zero or included in the scalar gauge function $\Lambda(\vec{r})$. We can also fix the vector potential to $\vec{A}(\vec{r})=\frac{1}{2}\vec{B}\times\vec{r}$. The electron density around a nucleus can be expanded by using Eq. (45),

$$\rho^{-1}\vec{\nabla}\rho = -2Z_N\vec{e}_{\vec{r}_N} + \vec{\hat{\rho}}^{(1)}_N + 2\hat{\rho}^{(2)}_N\cdot\vec{r}_N + \cdots, \quad \vec{e}_{\vec{r}_N} = \vec{r}_N/|\vec{r}_N|. \tag{48}$$

We consider a particular nucleus and omitted the index i in Eq. (45). The terms after the second are due to the (C^∞) continuous part of the density gradient, $\vec{\nabla}\rho_c = \vec{\nabla}\rho + 2Z_N\vec{e}_{\vec{r}_N}\rho(\vec{R}_N)$.

$$\vec{\hat{\rho}}^{(1)}_N = [\rho^{-1}\vec{\nabla}\rho_c](\vec{R}_N),$$

$$\hat{\rho}^{(2)}_N = (2!)^{-1}[\rho^{-1}\vec{\nabla}\otimes\vec{\nabla}\rho_c](\vec{R}_N). \tag{49}$$

At first, we consider the first term of Eq. (48) and rewrite the KK equation as follows:

$$\rho^{-1}\vec{\nabla}\{\rho(\vec{\nabla}\Lambda - \vec{A})\} = \vec{\nabla}^2\Lambda - 2Z_N\vec{e}_{\vec{r}_N}\cdot(\vec{\nabla}\Lambda - \vec{A}) = 0. \tag{50}$$

The vector potential can be expressed as the sum, $\vec{A}(\vec{r}) = \vec{A}(\vec{r}_N) + \vec{A}_N$, where $\vec{e}_{\vec{r}_N}\cdot\vec{A}(\vec{r}_N)=0$ is satisfied for the first component. Therefore, Eq. (50) can be rewritten as follows:

$$\vec{\nabla}^2\Lambda - 2Z_N\vec{e}_{\vec{r}_N}\cdot(\vec{\nabla}\Lambda - \vec{A}_N) = 0. \tag{51}$$

The solution of Eq. (51) is given by the following equation:

$$\Lambda(\vec{r}) = \Lambda_0 + \vec{A}_N\cdot\vec{r}_N. \tag{52}$$

Λ_0 is an arbitrary constant. This solution satisfies $\vec{\nabla}^2\Lambda=0$ and $\vec{\nabla}\Lambda - \vec{A}_N=0$, simultaneously. If we consider $q\Lambda(\vec{r})$ as the phase of the corrected wave function, Eq. (52) leads to Eq. (47). Therefore, the current density must vanish at nuclear positions. Actually, Eq. (50) can be applied to a hydrogenlike atom, where the electron density is given by $\rho(\vec{r}) = N\exp(-2Z_N r_N)$.

When the C^∞ continuous part of the electron density is included, Eq. (51) becomes

$$\vec{\nabla}^2\Lambda + \rho^{-1}\vec{\nabla}\rho_c\cdot[\vec{\nabla}\Lambda - \vec{A}_N - \vec{A}(\vec{r}_N)] - 2Z_N\vec{e}_{\vec{r}_N}\cdot(\vec{\nabla}\Lambda - \vec{A}_N) = 0. \tag{53}$$

There is no simple solution to the above equation. To reveal whether Eq. (47) is satisfied for general forms of a wave function or not, we must solve the KK equation for the wave functions having cusps. For example, the wave function of an H_2^+ ion expressed by the Slater-type atomic orbitals.

If the electron density is expanded around general point $\vec{P}$, we obtain the following equation:

$$\rho^{-1}\vec{\nabla}\rho = \vec{\hat{\rho}}^{(1)}_R + 2\hat{\rho}^{(2)}_P\cdot\vec{r}_P + \cdots, \quad \vec{r}_P = \vec{r} - \vec{P}. \tag{54}$$

By considering only the first term, we obtain the following KK equation:

$$\vec{\nabla}^2\Lambda + \vec{\hat{\rho}}^{(1)}_P\cdot\vec{\nabla}\Lambda = \vec{\hat{\rho}}^{(1)}_P\cdot\vec{A}_P + \tfrac{1}{2}\vec{r}_P\cdot(\vec{\hat{\rho}}^{(1)}_P\times\vec{B}). \tag{55}$$

The solution should consist of an infinite series of $\vec{r}_P$, since the part $\vec{\nabla}^2\Lambda + \vec{\hat{\rho}}^{(1)}_P\cdot\vec{\nabla}\Lambda$ connects polynomials with different orders. In the next paper, we will solve the case that $\rho(\vec{r})$ is C^∞ continuous in $\mathbb{R}^3$.

We can also investigate the solution near the electron density maximum of Gaussian wave functions. The first term of Eq. (54) is zero. The electron density becomes as follows.:

$$\rho^{-1}\vec{\nabla}\rho = 2\hat{\rho}^{(2)}_G\cdot\vec{r}_G + \cdots, \quad \vec{r}_G = \vec{r} - \vec{G}. \tag{56}$$

The Kennedy-Kobe equation is given in the following form:

$$\vec{\nabla}^2\Lambda + 2\vec{r}_G \cdot \hat{\rho}_G^{(2)} \cdot (\vec{\nabla}\Lambda - \vec{A}_G - \vec{A}(\vec{r}_G)) = 0. \tag{57}$$

The above equation is identical to that of anisotropic harmonic oscillator with the electron density of $\rho(\vec{r}_G) \propto \exp[-\vec{r}_G \cdot (-\hat{\rho}_G^{(2)}) \cdot \vec{r}_G]$. The solution has already been described by Parker [7], Kennedy and Kobe [8], and is given by the following equation:

$$\Lambda = \Lambda_0 + \vec{A}_G \cdot \vec{r}_G + \Lambda_2^{xy} x_G y_G + \Lambda_2^{yz} y_G z_G + \Lambda_2^{zx} z_G x_G. \tag{58}$$

The symmetric tensor Λ_2 is determined, so that the following gauge-corrected vector potential, $\vec{A}'$ becomes perpendicular to the density gradient,

$$\vec{A}' = \vec{A} - \vec{\nabla}\Lambda = \vec{A}(\vec{r}_G) - \vec{\nabla}\Lambda_2. \tag{59}$$

Here we adapt the following notation of the second-derivative matrix,

$$-\hat{\rho}_G^{(2)} = 2\begin{bmatrix} \alpha_x & 0 & 0 \\ 0 & \alpha_y & 0 \\ 0 & 0 & \alpha_z \end{bmatrix}. \tag{60}$$

The xy component in Eq. (58) is given by

$$\Lambda_2^{xy} = -\frac{\alpha_x - \alpha_y}{2(\alpha_x + \alpha_y)} B_z. \tag{61}$$

The other components are obtained by the cyclic permutations, $(x,y,z) \to (z,x,y)$. The current density at the Gaussian maximum is determined by the first-order term of Eq. (58). Therefore, the current density vanishes at the Gaussian maxima.

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