Relativistic Definitions of Atoms in Molecules with the modified Dirac Equation

Andy D. Zapata–Escobar[1] and Alejandro F. Maldonado[1]
Instituto de Modelado e Innovación Tecnológica, IMIT (CONICET-UNNE), Avda Libertad 5460, W3404AAS, Corrientes, Argentina.

(*Electronic mail: danianescobarv@gmail.com, aleoml@yahoo.com.ar)

In quantum chemistry, the region associated with atoms in molecules (AIMs) is determined using the basin definition through the action integral of the total Lagrangian density. This can be associated with different Hamiltonians, such as Schrödinger, Dirac, or the modified Dirac Hamiltonian. The latter two differ only in the associated metric matrix; while for the Dirac Hamiltonian is the 4x4 identity matrix, for the modified Dirac Hamiltonian is a diagonal matrix composed by the 2x2 identity matrix and a 2x2 diagonal matrix with elements $\hat{T}/2mc^2$. It was shown by Cioslowski and Karwowski that when the Dirac Hamiltonian is considered, the total Lagrangian density is zero at every point within the molecular volume, making impossible to partition the molecular electronic structure into basins. Moreover, the nonrelativistic total Lagrangian density derived from the Dirac Hamiltonian is also zero at every point, and a heuristic term must be added to obtain the basin definition in the Quantum Theory of Atoms in Molecules (QTAIM) developed by Bader. In contrast, the total Lagrangian density associated with the modified Dirac Hamiltonian is nonzero at every point within the molecular volume, and the basin can be defined in a relativistic framework. Taking the nonrelativistic limit of this Lagrangian density, the standard nonrelativistic basin definition within the QTAIM approach is recovered.

I. INTRODUCTION

The description of molecules based on their atomic composition is an essential tool for understanding or predicting their properties, grounded in the chemist's intuition and atomic properties. For example, in certain hydrocarbons, it has been experimentally demonstrated that molecular properties can be described as the sum of their constituents.[1–4] However, an extension of the Hohenberg-Kohn theorem to a subdomain shows that the limit of perfect transferability of the properties of atoms or atomic groupings can never be attained.[5]

The Quantum Theory of Atoms in Molecules (QTAIM) is a powerful tool for studying the nature of chemical bonding in molecular systems. The QTAIM approach was developed by Bader in the nonrelativistic regime[6–8] for an isolated system, making possible to define where an atom ends and the next begins as subsystems into a molecule, and also allowing for the description of molecular properties based on atomic electron densities. The QTAIM approach demonstrates that the properties of an atom change in direct response to variations in its charge distribution, and the Schwinger principle of stationary action[9] is used to determine the regions associated with atoms in molecules (AIMs), called basins.[6–8] In the general case, the action integral is altered by generators of infinitesimal unitary transformations acting on both the spacelike and timelike surfaces bounding the space-time volume, whereas for an isolated system, the physics is totally determined by their action on just the spacelike surfaces at the two time endpoints.[10,11] Additionally, these regions are bounded by surfaces of zero flux in the electron density gradient, and the boundary between two basins is established in such a way that a bond critical point (BCP) is on the bond path. Moreover, the properties associated with the electron density at BCP along the bond path can be used to classify the type of interatomic interactions, which are of great importance in chemistry. Several reviews about the QTAIM methodology can be found elsewhere.[11–14]

It is well known that for studies involving molecules containing heavy atoms, relativistic effects are essential for an accurate description.[15,16] Therefore, it is appropriate to extend the QTAIM methodology within a relativistic formalism that allows for the determination of the basin definition, the proper identification of BCPs, and the characterization of the interatomic interactions within this framework. A recent review of the field of relativistic QTAIM was published by Anderson.[17]

Cioslowski and Karwowski presented the first mathematical generalization of QTAIM in the relativistic regime.[18] However, they found that the Hamilton's principle[19] applied to the total Lagrangian density associated with the four-component (4c) Dirac Hamiltonian is zero. Moreover, they discovered that the relativistic definition of AIMs requires the addition of a heuristic term to derive the standard nonrelativistic basin definition. This condition was used to calculate relativistic effects on the energetic stability of Pb_5 clusters.[20]

Anderson and Ayers[21] derived the expression for the basin using the total Lagrangian density associated with the zeroth-order regular approximation (ZORA)[22] Hamiltonian with scalar relativistic (SR) corrections. Furthermore, the nonrelativistic basin definition within the QTAIM approach is obtained when the speed of light tends to infinity. The SR-ZORA basin expression was used by Wang and co-workers[23] to show that scalar relativistic effects are essential for correcting the topological instability observed in the $[Sb_3Au_3Sb_3]^{3-}$ system. In addition, Anderson *et al.*[24] found that relativistic effects can change critical-point properties values up to 30%, compared to the corresponding nonrelativistic values for systems containing very massive atoms, when scalar relativistic corrections are considered. Besides, a few years ago, Anderson and collaborators discovered that when SR-ZORA is applied to QTAIM, the topology of the electron density exhibits extra BCPs between a hydrogen and a gold atom in 1,4-benzenedithiol.[25]

A generalization of the AIM methodology was published by Anderson and Ayers, under which the principle of stationary action for a region leads to open quantum subsystems.[26] They showed that, when a reasonable Lagrangian is selected, it often leads to the integral of the Laplacian of the electron density on the region vanishing as a necessary condition for the zero flux surface. They applied this methodology to the ZORA Hamiltonian with spin-orbit coupling corrections and the decoupled large component of the Dirac wave function and found that it satisfies the atomic Schwinger's principle of stationary action,[9] just as in the nonrelativistic case.

Reiher *et al.*[27] have analyzed the electron densities and their Laplacians obtained from the wave functions associated with the Dirac, ZORA, and Douglas-Kroll-Hess[28] (DKH) Hamiltonians. They found that scalar relativistic effects are sufficient to obtain a reasonable description of the electron density to describe these quantities for three organometallic compounds.[29] In contrast, Galland *et al.*[30,31] used the exact two-component (X2C)[32] wave function to study compounds of astatine with other halogen atoms. They reported that the spin-orbit coupling relativistic effect, included through the density functional theory (DFT), plays a crucial role in analyzing dipole moment orientation, atomic charges, and the Laplacian of the electron density at BCPs. It is also noteworthy that other studies have considered the influence of relativistic effects on the electron density topology, like the Hg-C bond in certain organometallic compounds,[33,34] together with correlation effects at DFT level. Other methods, such as the picture-change error[34,35] or techniques that correct the core electron density modeling when pseudo-potentials, have also been used.[36–38]

In this work, the definition of a basin in the molecular electronic structure using the action integral in both nonrelativistic and relativistic regimes is presented. For the relativistic definition, the Dirac equation[39] with two different metric matrices, which consists of a transformation of the small component of the 4c wave function, is employed. Furthermore, the nonrelativistic basin definition is derived from the relativistic expressions.

In the next section, a formal definition of a basin in the molecular electronic structure using the action integral and the total Lagrangian density is presented. Later, and based on the literature, a brief development of the total Lagrangian density along with the corresponding basin definition for the Schrödinger[40] and Dirac[39] Hamiltonians is presented. Finally, the total Lagrangian density and the corresponding basin definition from the modified Dirac Hamiltonian[41,42] are derived. Additionally, the nonrelativistic expression from a relativistic framework is recovered.

II. BASIN

According to atoms in molecules theory, atoms are regions ($\bar{\Omega}$) within the molecular volume (Ω) that are bounded by surfaces ($\bar{S}$) of zero flux in the electron density gradient.[43,44] These regions are called basins and can be formally defined using the Hamilton's principle.[19] The regions within Ω, where the variation of the action integral (δW) is equal to zero between two fixed time points ($t_1 > t_2$) define $\bar{\Omega}$,

$$\delta W \;=\; \delta \int_{t_1}^{t_2} dt \int_{\bar{\Omega}(t)} \mathscr{L} d^3x = 0 \tag{1}$$

where $\mathscr{L}$ is the total Lagrangian density, which is a function of the molecular wave function (Ψ) and its conjugate ($\Psi^\dagger$). For simplicity and without significant loss of generality, the following arguments are restricted only to one-particle. Additionally, $\mathscr{L}$ depends on both the spatial derivatives ($\boldsymbol{\nabla}$) and the time derivatives ($\partial/\partial t$) of both Ψ and $\Psi^\dagger$.

$$\mathscr{L} \;=\; \frac{\imath\hbar}{2}\left(\Psi^\dagger \frac{\partial \Psi}{\partial t} - \frac{\partial \Psi^\dagger}{\partial t}\Psi\right) + \bar{\mathscr{L}}(\Psi, \boldsymbol{\nabla}\Psi, \Psi^\dagger, \boldsymbol{\nabla}\Psi^\dagger) \tag{2}$$

The expression for the second term on the right–hand side of Eq. (2) depends on the Hamiltonian ($\hat{H}$) considered.[18,21,43–45] However, it is well known that the Hamiltonian and $\bar{\mathscr{L}}(\Psi, \boldsymbol{\nabla}\Psi, \Psi^\dagger, \boldsymbol{\nabla}\Psi^\dagger)$ are related by the expression,[18,45]

$$\hat{H}\Psi \;=\; \left(\boldsymbol{\nabla}\frac{\partial}{\partial(\boldsymbol{\nabla}\Psi^\dagger)} - \frac{\partial}{\partial \Psi^\dagger}\right)\bar{\mathscr{L}}(\Psi, \boldsymbol{\nabla}\Psi, \Psi^\dagger, \boldsymbol{\nabla}\Psi^\dagger) \tag{3}$$

where Ψ and $\Psi^\dagger$ are generic representations of the wave function such as Schrödinger (ψ),[40] Dirac (Ψ),[39,46] and modified Dirac ($\tilde{\psi}$)[41,42] wave functions, depending on the Hamiltonian considered.

III. SCHRÖDINGER HAMILTONIAN

The dynamics of the electron in the nonrelativistic regime are described by the Schrödinger equation and its conjugate,[40]

$$\imath\hbar\frac{\partial \psi}{\partial t} = \hat{H}^S\psi \qquad -\imath\hbar\frac{\partial \psi^*}{\partial t} = \hat{H}^S\psi^* \tag{4}$$

where $\hbar$ is the reduced Plank's constant. $\hat{H}^S$ is the Schrödinger Hamiltonian, and ψ is the nonrelativistic or one-component (1c) wave function. The $\hat{H}^S$ is composed by the kinetic ($\hat{T}$) and potential ($\hat{V}$) energy operators[19]

$$\hat{H}^S = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V} \tag{5}$$

where m is the electron mass and ∇^2 is the Laplacian.

A. Basin Definition

According to Eq. (5), the second term on the right–hand side of Eq. (2) for the Schrödinger Hamiltonian is given by,[43,44]

$$\bar{\mathscr{L}}^S(\psi, \boldsymbol{\nabla}\psi, \psi^*, \boldsymbol{\nabla}\psi^*) \;=\; -\frac{\hbar^2}{2m}\boldsymbol{\nabla}\psi^* \cdot \boldsymbol{\nabla}\psi - \hat{V}\psi^*\psi \tag{6}$$

When Eq. (6) is substituted into Eq. (3), the Eq. (5) is recovered. On the other hand, given $\bar{\mathscr{L}}^S$ and using Eq. (4), the total Lagrangian density in Eq. (2) for an isolated system is expressed as,

$$\begin{aligned}\mathscr{L}^S &= \frac{1}{2}\left(\psi^*(\hat{H}^s\psi)+(\hat{H}^s\psi^*)\psi\right)\\ &\quad -\frac{\hbar^2}{2m}\boldsymbol{\nabla}\psi^*\cdot\boldsymbol{\nabla}\psi-\hat{V}\psi^*\psi\\ &= -\frac{\hbar^2}{4m}\nabla^2(\psi^*\psi) \qquad (7)\end{aligned}$$

Then, by substituting Eq. (7) into Eq. (1) and applying the divergence theorem, an atom or basin in the nonrelativistic regime is defined by the region within the molecular volume, bounded by a surface of zero flux in the electron density gradient ($\boldsymbol{\nabla}\rho=\boldsymbol{\nabla}(\psi^*\psi)$), which is orthogonal to the normal vector ($\boldsymbol{n}$) of $\bar{S}$[43,44]

$$\boldsymbol{\nabla}\rho\cdot\boldsymbol{n} = 0 \qquad (8)$$

for any point on $\bar{S}$.

The zero flux surface condition is universal, since it applies equally to an isolated atom or to an atom bound in a molecule, as the atomic values for a given property should yield the molecular average for that property when summed over all the atoms in a molecule.[8]

IV. DIRAC HAMILTONIAN

In the relativistic regime, the electronic structure of atoms and molecules is described by a four-component (4c) wave function (Ψ), which is the solution of the Dirac equation[39,46]

$$\imath\hbar\frac{\partial\Psi}{\partial t}=\hat{H}^D\Psi;\ \ \Psi=\begin{bmatrix}\Psi^L\\ \Psi^S\end{bmatrix} \qquad (9)$$

The 4c wave function can be written in terms of two-component (2c) wave functions called large and small components represented by Ψ^L and Ψ^S respectively, and the corresponding Dirac Hamiltonian is given by

$$\hat{H}^D=c\boldsymbol{\alpha}\cdot\hat{\boldsymbol{p}}+\beta mc^2+\hat{V} \qquad (10)$$

where c is the speed of light in vacuum, m is the electron mass, $\hat{\boldsymbol{p}}$ is the linear momentum vector operator, and $\hat{V}$ is the potential energy operator. Finally, $\boldsymbol{\alpha}$ and β are 4x4 matrices

$$\boldsymbol{\alpha}=\begin{bmatrix}0_2 & \boldsymbol{\sigma}\\ \boldsymbol{\sigma} & 0_2\end{bmatrix};\ \ \beta=\begin{bmatrix}1_2 & 0_2\\ 0_2 & -1_2\end{bmatrix} \qquad (11)$$

which contain the Pauli matrices ($\boldsymbol{\sigma}$), the 2x2 identity matrix, and the null matrix.

A. Basin Definition

The time independent part of the total Lagrangian density in Eq. (2) associated to the Dirac Hamiltonian is given by

$$\begin{aligned}\bar{\mathscr{L}}^D(\Psi,\boldsymbol{\nabla}\Psi,\Psi^\dagger,\boldsymbol{\nabla}\Psi^\dagger) &= \frac{\imath\hbar c}{2}\left(\Psi^\dagger\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}\Psi-\boldsymbol{\nabla}\Psi^\dagger\cdot\boldsymbol{\alpha}\Psi\right)\\ &\quad -(\beta mc^2+\hat{V})\Psi^\dagger\Psi \qquad (12)\end{aligned}$$

and, when Eq. (12) is substituted into Eq. (3), the Dirac Hamiltonian of Eq. (10) is recovered. For an isolated system, the total Lagrangian density given by Eq. (2) is equal to zero, in agreement with results obtained by Cioslowski and Karwowski.[18]

$$\begin{aligned}\mathscr{L}^D &= \frac{1}{2}\left(\Psi^\dagger(\hat{H}^D\Psi)+(\hat{H}^D\Psi)^\dagger\Psi\right)+\\ &\quad \frac{\imath\hbar c}{2}\left(\Psi^\dagger\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}\Psi-\boldsymbol{\nabla}\Psi^\dagger\cdot\boldsymbol{\alpha}\Psi\right)\\ &\quad -(\beta mc^2+\hat{V})\Psi^\dagger\Psi\\ &= \frac{\imath\hbar}{2}\boldsymbol{\nabla}\cdot(\Psi^\dagger c\boldsymbol{\alpha}\Psi-\Psi^\dagger c\boldsymbol{\alpha}\Psi)=0 \qquad (13)\end{aligned}$$

The terms in parentheses cancel because they represent the difference between two relativistic current electron densities ($\boldsymbol{j}=\Psi^\dagger c\boldsymbol{\alpha}\Psi$), which have the same magnitudes but opposite directions. Thus, Eq. (1) vanishes at every point within the molecular volume, making impossible to define the regions associated with each atom that composes the molecule. As the total Lagrangian density is zero for the Dirac Hamiltonian, the nonrelativistic limit taken to obtain the nonrelativistic basin definition is also zero, making impossible to recover the definition given by Eq. (8) in that framework. The nonrelativistic Bader definition can be recaptured only by adding a heuristic term, as pointed out by Cioslowski and Karwowski.[18]

V. MODIFIED DIRAC HAMILTONIAN

The modified Dirac equation[41] is obtained by decoupling the time independent Dirac equation of the Hamiltonian given in Eq. (10) and using the 4c wave function defined in Eq. (9). After the shift of the energy in -2mc^2 to align the zero of the Dirac spectrum with the Schrödinger one,[42] the Dirac equation can be written as

$$\begin{aligned}c(\boldsymbol{\sigma}\cdot\boldsymbol{p})\Psi^S+\hat{V}\Psi^L &= E\Psi^L\\ c(\boldsymbol{\sigma}\cdot\boldsymbol{p})\Psi^L+(\hat{V}-2mc^2)\Psi^S &= E\Psi^S \qquad (14)\end{aligned}$$

Defining a pseudo-large component (ϕ^L) as

$$\Psi^S = \frac{(\boldsymbol{\sigma}\cdot\boldsymbol{p})}{2mc}\phi^L \qquad (15)$$

and multiplying the second row of Eq. (14) by $(\boldsymbol{\sigma}\cdot\boldsymbol{p})/2mc$, and substituting the pseudo-large component in the same equation, the modified Dirac equation is obtained,

$$\begin{aligned}\hat{T}\phi^L+\hat{V}\Psi^L &= E\Psi^L\\ \hat{T}\Psi^L+\left[\frac{1}{4m^2c^2}(\boldsymbol{\sigma}\cdot\boldsymbol{p})\hat{V}(\boldsymbol{\sigma}\cdot\boldsymbol{p})-\hat{T}\right]\phi^L &= E\frac{\hat{T}}{2mc^2}\phi^L \qquad (16)\end{aligned}$$

where $\hat{T}$ is the nonrelativistic kinetic energy operator. Then, the time independent modified Dirac equation is written as

$$\tilde{H}^{MD}\tilde{\psi}=E\tilde{\boldsymbol{G}}\tilde{\psi} \qquad (17)$$

where the modified wave function ($\tilde{\psi}$) is composed of a large component and a pseudo-large component

$$\tilde{\psi} \;=\; \begin{bmatrix} \Psi^L \\ \phi^L \end{bmatrix} \tag{18}$$

with a change of metric defined from Eq. (16) as

$$\tilde{\boldsymbol{G}} \;=\; \begin{bmatrix} 1_2 & 0_2 \\ 0_2 & \hat{T}/2mc^2 \end{bmatrix} \tag{19}$$

Applying the Dirac's relation

$$(\boldsymbol{\sigma}\cdot\boldsymbol{p})\hat{V}(\boldsymbol{\sigma}\cdot\boldsymbol{p}) \;=\; (\boldsymbol{p}\hat{V})\cdot\boldsymbol{p} + \imath\boldsymbol{\sigma}\cdot((\boldsymbol{p}\hat{V})\times\boldsymbol{p}) \tag{20}$$

it is possible to separate the Dirac Hamiltonian ($\tilde{H}^{MD}$) in the spin-free ($\tilde{H}^{sf}$) and spin-dependent ($\tilde{H}^{sd}$) terms as

$$\begin{aligned} \tilde{H}^{MD} \;&=\; \tilde{H}^{sf} + \tilde{H}^{sd} \\ &=\; \begin{bmatrix} \hat{V} & \hat{T} \\ \hat{T} & \frac{(\boldsymbol{p}\hat{V})\cdot\boldsymbol{p}}{4m^2c^2} - \hat{T} \end{bmatrix} + \begin{bmatrix} 0_2 & 0_2 \\ 0_2 & \frac{\imath\boldsymbol{\sigma}((\boldsymbol{p}\hat{V})\times\boldsymbol{p})}{4m^2c^2} \end{bmatrix} \end{aligned} \tag{21}$$

which is useful to study scalar and spin-dependet terms separately, although this will not be done in this work. Since no approximations have been made in deriving of the modified Dirac equation from the Dirac equation using the pseudo-large component, the modified Dirac Hamiltonian given by Eq. (21) yields the same results as those obtained from the Dirac Hamiltonian of Eq. (10).[41,42] On the other hand, for convenience and without any approximation, instead of using the $\tilde{H}^{sf}$ and $\tilde{H}^{sd}$ Hamiltonians, it is possible to separate the nonrelativistic kinetic energy and the potential energy operators in the matrices $\boldsymbol{\Lambda}$ and $\boldsymbol{\Omega}$ defined as

$$\boldsymbol{\Lambda} = \begin{bmatrix} 0_2 & 1_2 \\ 1_2 & -1_2 \end{bmatrix};\; \boldsymbol{\Omega} = \begin{bmatrix} \hat{V} & 0_2 \\ 0_2 & \frac{(\boldsymbol{\sigma}\cdot\boldsymbol{p})\hat{V}(\boldsymbol{\sigma}\cdot\boldsymbol{p})}{4m^2c^2} \end{bmatrix} \tag{22}$$

with which Eq. (17) can be written as

$$\boldsymbol{\Lambda}\hat{T}\tilde{\psi} + \boldsymbol{\Omega}\tilde{\psi} \;=\; E\tilde{\boldsymbol{G}}\tilde{\psi} \tag{23}$$

The modified Dirac equation written in terms of the matrices $\boldsymbol{\Lambda}$ and $\boldsymbol{\Omega}$ will be useful to obtain an expression for the basin analogous to the nonrelativistic case.

A. Basin Definition

To derive a relativistic QTAIM, an appropriate Lagrangian density must be proposed for the modified Dirac Hamiltonian. The expression of the second term on the right–hand side of Eq. (2) can be written as,

$$\bar{\mathscr{L}}^{MD}(\tilde{\psi}, \boldsymbol{\nabla}\tilde{\psi}, \tilde{\psi}^\dagger, \boldsymbol{\nabla}\tilde{\psi}^\dagger) = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}\tilde{\psi}^\dagger\boldsymbol{\Lambda}\cdot\boldsymbol{\nabla}\tilde{\psi} - \tilde{\psi}^\dagger\boldsymbol{\Omega}\tilde{\psi} \tag{24}$$

This can be corroborated when Eq. (24) is substituted in the right-hand side of the Eq. (3); then the modified Dirac Hamiltonian is recovered

$$\begin{aligned} \boldsymbol{\nabla}\frac{\partial}{\partial(\boldsymbol{\nabla}\tilde{\psi}^\dagger)}\left[-\frac{\hbar}{2m}\boldsymbol{\nabla}\tilde{\psi}^\dagger\boldsymbol{\Lambda}\cdot\boldsymbol{\nabla}\tilde{\psi} - \tilde{\psi}^\dagger\boldsymbol{\Omega}\tilde{\psi}\right] \;&=\; -\frac{\hbar^2}{2m}\boldsymbol{\Lambda}\nabla^2\tilde{\psi} \\ -\frac{\partial}{\partial\tilde{\psi}^\dagger}\left[-\frac{\hbar}{2m}\boldsymbol{\nabla}\tilde{\psi}^\dagger\boldsymbol{\Lambda}\cdot\boldsymbol{\nabla}\tilde{\psi} - \tilde{\psi}^\dagger\boldsymbol{\Omega}\tilde{\psi}\right] \;&=\; \boldsymbol{\Omega}\tilde{\psi} \end{aligned}$$

then,

$$\begin{gathered} \left(\boldsymbol{\nabla}\frac{\partial}{\partial(\boldsymbol{\nabla}\tilde{\psi}^\dagger)} - \frac{\partial}{\partial\tilde{\psi}^\dagger}\right)\bar{\mathscr{L}}^{MD} \;= \\ -\frac{\hbar^2}{2m}\boldsymbol{\Lambda}\nabla^2\tilde{\psi} + \boldsymbol{\Omega}\tilde{\psi} = \boldsymbol{\Lambda}\hat{T}\tilde{\psi} + \boldsymbol{\Omega}\tilde{\psi} \end{gathered} \tag{25}$$

For the total Lagrangian density, Eq. (2) must be modified in order to take into account the change of the metric used in the modified Dirac equation, giving

$$\mathscr{L}^{MD} = \frac{\imath\hbar}{2}\left(\tilde{\psi}^\dagger\frac{\partial\tilde{\boldsymbol{G}}\tilde{\psi}}{\partial t} - \frac{\partial\tilde{\boldsymbol{G}}\tilde{\psi}^\dagger}{\partial t}\tilde{\psi}\right) + \bar{\mathscr{L}}^{MD}(\tilde{\psi}, \boldsymbol{\nabla}\tilde{\psi}, \tilde{\psi}^\dagger, \boldsymbol{\nabla}\tilde{\psi}^\dagger) \tag{26}$$

Then, substituting Eq. (24) in Eq. (26) and taking into account that the time dependent modified Dirac equations are

$$\imath\hbar\frac{\partial\tilde{\boldsymbol{G}}\tilde{\psi}}{\partial t} = \tilde{H}^{MD}\tilde{\psi} \qquad -\imath\hbar\frac{\partial\tilde{\boldsymbol{G}}\tilde{\psi}^\dagger}{\partial t} = (\tilde{H}^{MD}\tilde{\psi})^\dagger \tag{27}$$

the total Lagrangian density of the modified Dirac Hamiltonian for an isolated system is

$$\begin{aligned} &\mathscr{L}^{MD} = \\ &\frac{1}{2}\left(\tilde{\psi}^\dagger\boldsymbol{\Lambda}\hat{T}\tilde{\psi} + \tilde{\psi}^\dagger\boldsymbol{\Omega}\tilde{\psi} + (\hat{T}\tilde{\psi}^\dagger)\boldsymbol{\Lambda}\tilde{\psi} + (\boldsymbol{\Omega}\tilde{\psi})^\dagger\tilde{\psi}\right) \\ &-\frac{\hbar^2}{2m}\boldsymbol{\nabla}\tilde{\psi}^\dagger\boldsymbol{\Lambda}\cdot\boldsymbol{\nabla}\tilde{\psi} - \tilde{\psi}^\dagger\boldsymbol{\Omega}\tilde{\psi} = \\ &-\frac{\hbar^2}{4m}\nabla^2(\tilde{\psi}^\dagger\boldsymbol{\Lambda}\tilde{\psi}) \end{aligned} \tag{28}$$

When this expression is substituted into Eq. (1) and the divergence theorem is applied, the region associated with each basin within the molecular volume is enclosed by the surface $\bar{S}$, and the gradient of the modified Dirac electron density ($\boldsymbol{\nabla}\rho^{MD} = \boldsymbol{\nabla}(\tilde{\psi}^\dagger\boldsymbol{\Lambda}\tilde{\psi})$) is orthogonal to the normal vector for any point on $\bar{S}$

$$\boldsymbol{\nabla}\rho^{MD}\cdot\boldsymbol{n} = 0 \tag{29}$$

Eq. (29) represents the relativistic counterpart of Eq. (8). Furthermore, Eq. (29) indicates that when the small component Ψ^S of the Dirac equation is transformed into the pseudo-large component ϕ^L (Eq. (15)), the definitions of the basin and electron density also change. Moreover, it is expected that this dependence on the metric matrix also alters the nonrelativistic expression derived from the relativistic regime, giving the correct nonrelativistic basin definition.

B. Nonrelativistic Limit

In the nonrelativistic limit, *i.e.*, setting the speed of light $c \to \infty$, the pseudo-large component of the modified wave function becomes the large component of the 4c Dirac wave function.[41,42] After transformation of the 4c Dirac equation to a 2c nonrelativistic Schrödinger equation written in terms of spin-orbitals, the large component corresponds to the nonrelativistic wave function in that limit. Thus, in the nonrelativistic limit, Eq. (28) becomes

$$\lim_{c\to\infty} \mathscr{L}^{MD} = -\frac{\hbar^2}{4m}\nabla^2(\psi^\dagger\psi) \tag{30}$$

which is the same as Eq. (7) (in a 2c form) when the Schrödinger Hamiltonian is considered. This result confirms that the nonrelativistic expression can be obtained without adding any heuristic term to the total relativistic Lagrangian density, and it only depends on the metric matrix used in the Dirac equation, *i.e.*, on the transformation that has been applied to Ψ^S.

VI. CONCLUSION

In this work, the total Lagrangian density, along with the corresponding basin definition, is derived for the modified Dirac Hamiltonian. Additionally, the nonrelativistic expression is derived within the relativistic framework by taking the proper nonrelativistic limit.

As observed in the work by Cioslowski and Karwowski, the total Lagrangian density associated with the Dirac Hamiltonian for an isolated system is zero at every point within the molecular volume. However, instead of adding a heuristic term to the total Lagrangian density, a transformation of the small component of the 4c wave function leads to a change in the metric matrix associated with the Dirac equation. This change of metric is sufficient to obtain a total Lagrangian density that is not necessarily zero at every point of the molecular volume, thus providing a proper definition of the basin in the relativistic framework. From the total Lagrangian density associated with the modified Dirac Hamiltonian, the standard nonrelativistic basin definition can also be derived taking the nonrelativistic limit.

The relativistic basin definition could lead to studying the QTAIM topology of heavy-atom containing molecules at four-component level instead of approximated two-component methodologies. However, in order to use the current definition of the relativistic basin, it is necessary the proper implementation of certain equations in a computational code, and some efforts are being made in that direction.

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