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Viraht Sahni
CUNY Brooklyn College

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New Perspectives on the Schrödinger-Pauli Theory of Electrons:

Part I

Viraht Sahni

Brooklyn College and The Graduate Center of the City

University of New York, New York, New York 10016.

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Abstract

Schrödinger-Pauli (SP) theory is a description of electrons in the presence of a static electromagnetic field in which the interaction of the magnetic field with both the orbital and spin moments is explicitly considered. The theory is described from the new perspective of the individual electron via its equation of motion or ‘Quantal Newtonian’ first law. The law is in terms of ‘classical’ fields whose sources are quantum mechanical expectation values of Hermitian operators taken with respect to the system wave function. The law states that each electron experiences an external and an internal field, the sum of which vanish. The external field is the sum of the electrostatic and a Lorentz field. The internal field is a sum of fields: the electron-interaction, differential density, kinetic, and internal magnetic fields. These fields are respectively representative of a electron correlations due to the Pauli principle and Coulomb repulsion, the electron density, kinetic effects, and the physical current density. The energy can be expressed in integral virial form in terms of these fields. The law leads to the understanding that the Hamiltonian is an exactly known and universal functional of the wave function. This generalizes the SP equation, and proves it to be intrinsically self-consistent. A Quantal density functional (local effective potential) theory of the SP system is developed. Further generalizations of the present work to the temporal case, and relativistic Dirac theory are proposed.

I. INTRODUCTION

The Schrödinger-Pauli theory [1] is a description of a quantum-mechanical system comprised of N electrons in the presence of an external electrostatic field $\mathcal{E}(\mathbf{r}) = -\nabla v(\mathbf{r})/e$ and a magnetostatic field $\mathcal{B}(\mathbf{r}) = \nabla \times A(\mathbf{r})$, where $v(\mathbf{r})$ and $A(\mathbf{r})$ are scalar electrostatic and vector magnetic potentials, in which the interaction of the magnetic field with both the orbital and spin angular momentum is explicitly considered. The purpose of this paper is to describe Schrödinger-Pauli theory of the many-electron system from a new perspective, one that leads to further physical insights into the system, and thereby of our quantum-mechanical understanding of Schrödinger-Pauli theory. The perspective is that of the *individual* electron via its stationary state equation of motion – the ‘Quantal Newtonian’ first law. As a consequence, it is proved that the Hamiltonian is an *exactly known* and *universal* functional of the wave function. This generalizes the Schrödinger-Pauli equation. The generalized form of the equation in turn exhibits its intrinsic self-consistent nature. The electronic system as described by the Schrödinger-Pauli equation is then mapped via quantal density functional theory [2–4] to one of noninteracting fermions possessing the same basic variables of the electronic density $\rho(\mathbf{r})$ and physical current density $\mathbf{j}(\mathbf{r})$, and from which the same total energy can be obtained. The mapping allows for the determination of additional properties of the system not obtainable solely by solution of the Schrödinger-Pauli equation. Hence, the noninteracting fermion model system constitutes an essential complement to the Schrödinger-Pauli theory. The noninteracting fermionic model is also an alternative description of the physical system. It is a local effective potential theory, and as such it is more amenable to numerical solution.

The Schrödinger-Pauli Hamiltonian is descriptive of a wide range of physical phenomenon such as the Zeeman effect (weak, intermediate and high magnetic fields); cyclotron resonance; magnetoresistance; and the magneto-caloric effect [5, 6]. For the two-dimensional electron gas in semiconductor heterostructures, it is applicable to the fractional quantum Hall effect [7–10] at high magnetic fields when the electrons become spin-polarized and the system approaches an incompressible fluid. It is also applicable to the harmonically bound two-dimensional ‘artificial atoms’ or quantum dots [11–14] in such structures. Such ‘artificial atoms’ are of particular interest as the modification of the energy spectrum is discernable at magnetic fields of a few Tesla. These ‘artificial atoms’ have electronic structure similar

to that of natural atoms [11–19]. However, as the size of the quantum dots is an order of magnitude greater than that of natural atoms, the corresponding electronic density is low. As such the electron correlations due to the Pauli exclusion principle and Coulomb repulsion play a more significant role relative to the kinetic energy than in natural atoms. Additionally, the contribution of these correlations to the kinetic energy – the correlation-kinetic energy – becomes significant. The confinement of the electrons in ‘artificial atoms’, and therefore the structure of the electronic density, may also be altered experimentally so as to allow for a study [20–24] of the Wigner [25, 26] high electron correlation regime of the two-dimensional electronic system. Wigner systems are characterized not only by a high value of the electron-interaction energy relative to the kinetic energy, but also by a high correlation-kinetic energy [22–24]. Wigner crystals in such systems can also be created by strong magnetic fields [27]: the electron correlations become significant because the single particle states become degenerate to form Landau levels with the electrons occupying the lowest level. (Three-dimensional spherical quantum dots have also been experimentally obtained [28, 29] and studied [22, 23] in the Wigner regime.) There has also been recent interest, both experimental and theoretical, in studying yrast states for harmonically bound electrons in a magnetic field [14]. These are states of lowest energy for fixed angular momentum.

The new perspective of the quantum system is that of the *individual* electron, in the sea of electrons, as described by its equation of motion, the ‘Quantal Newtonian’ first law for the electron. The law is in terms of ‘classical’ fields that arise from quantal sources. The statement of the law is that the sum of the external $\mathcal{F}^{\text{ext}}(\mathbf{r})$ and internal $\mathcal{F}^{\text{int}}(\mathbf{r})$ fields experienced by *each* electron vanishes. The external field $\mathcal{F}^{\text{ext}}(\mathbf{r})$ is a sum of the external binding electrostatic $\mathcal{E}(\mathbf{r})$ and the Lorentz $\mathcal{L}(\mathbf{r})$ fields. The Lorentz field $\mathcal{L}(\mathbf{r})$ depends upon the cross-product of the physical current density $\mathbf{j}(\mathbf{r})$ and the magnetic field $\mathcal{B}(\mathbf{r})$. (In classical physics, the Lagrangian for a particle of charge q in the potentials $\{v, \mathbf{A}\}$ contains the Lorentz force explicitly [2]. However, in the corresponding Hamiltonian, this term does not appear as it cancels out. Hence, it does not appear in the quantum-mechanical Hamiltonian obtained via the correspondence principle. Thus, in quantum mechanics, it is implicitly understood that electrons in the presence of a magnetic field $\mathcal{B}(\mathbf{r})$ experience a Lorentz force. In the ‘Quantal Newtonian’ first law, the Lorentz field, derived from the Lorentz ‘force’, appears *explicitly*.) The internal field $\mathcal{F}^{\text{int}}(\mathbf{r})$ is a sum of fields, each representative of a property of the system: properties such as the correlations due to the Pauli exclusion

principle and Coulomb repulsion, the kinetic effects, the electron density, and an internal magnetic field component. The ‘sources’ of these fields are quantum-mechanical in that they are expectation values of Hermitian operators taken with respect to the system wave function Ψ . Hence, the perspective hews to the probabilistic interpretation of quantum mechanics. The fields, as obtained from their respective quantal sources, obey equations of classical physics. Therefore, as in classical physics, these fields pervade all space. The description of the quantum mechanical system in terms of these ‘classical’ fields then makes it tangible in the classical sense. In this context, the fields are determinate.

One significant feature of the law is that in addition to the expected external electrostatic and Lorentz fields, each electron also experiences an internal field. And that these fields are representative of the intrinsic properties of the system. Whilst one might expect an internal field representative of Coulombic and Pauli principle electron-electron repulsion, one learns that there exist other components of the internal field. Hence, there exists a field representative of kinetic effects, and one representative of the electron density. And, that there also exists an internal magnetic field component.

The magnetic field contributions to the ‘Quantal Newtonian’ first law are the external Lorentz and internal magnetic fields. Provided the sum of these fields is conservative, i.e. curl-free, then it is possible to define a scalar (path-independent) magnetic potential $v_m(\mathbf{r})$ in a manner similar to the external scalar electrostatic potential $v(\mathbf{r})$. There are other facets of the quantum system that emerge as a consequence of the ‘Quantal Newtonian’ first law, and these will be discussed in the text.

The ‘Quantal Newtonian’ first law is a sum rule. As such it can be employed as a constraint applied to approximate wave functions or as a test of the accuracy of such wave functions.

The non-relativistic Schrödinger-Pauli Hamiltonian \hat{H} for spin $\frac{1}{2}$ particles is the sum of the Feynman [30] kinetic \hat{T}_F , electron-interaction potential \hat{W} , and external electrostatic potential \hat{V} operators. In atomic units (charge of electron $-e$, $e = \hbar = m = 1$) the Hamiltonian is

$$\hat{H} = \hat{T}_F + \hat{W} + \hat{V}, \quad (1)$$

where

$$\hat{T}_F = \frac{1}{2} \sum_k (\boldsymbol{\sigma}_k \cdot \hat{\mathbf{p}}_{k,phys}) (\boldsymbol{\sigma}_k \cdot \hat{\mathbf{p}}_{k,phys}), \quad (2)$$

$$\hat{W} = \frac{1}{2} \sum'_{k,\ell} \frac{1}{|\mathbf{r}_k - \mathbf{r}_\ell|}, \quad (3)$$

$$\hat{V} = \sum_k v(\mathbf{r}_k). \quad (4)$$

Here the physical momentum operator $\hat{\mathbf{p}}_{phys} = (\hat{\mathbf{p}} + \frac{1}{c}\mathbf{A}(\mathbf{r}))$, with $\hat{\mathbf{p}} = -i\nabla$ the canonical momentum operator. The $\boldsymbol{\sigma}$ is the Pauli spin matrix: $\mathbf{s} = \frac{1}{2}\boldsymbol{\sigma}$, with \mathbf{s} the electron spin angular momentum vector operator. On substituting for $\hat{\mathbf{p}}_{phys}$ and $\boldsymbol{\sigma}$ in the kinetic energy operator equation, the Hamiltonian \hat{H} may be written as

$$\hat{H} = \frac{1}{2} \sum_k \left(\hat{\mathbf{p}}_k + \frac{1}{c}\mathbf{A}(\mathbf{r}_k) \right)^2 + \frac{1}{c} \sum_k \boldsymbol{\mathcal{B}}(\mathbf{r}_k) \cdot \mathbf{s}_k + \hat{W} + \hat{V}, \quad (5)$$

which then indicates the interaction of the magnetic field with both the orbital and spin moment of the electrons. (The former interaction becomes evident for the case of a uniform magnetic field. In the symmetric gauge $\mathbf{A}(\mathbf{r}_k) = \frac{1}{2}\mathbf{B} \times \mathbf{r}_k$, the $\mathbf{A}(\mathbf{r}_k) \cdot \hat{\mathbf{p}}_k$ term of the Hamiltonian may be written as $\frac{1}{2}\mathbf{B} \cdot \mathbf{L}_k$, with $\mathbf{L}_k = \mathbf{r}_k \times \hat{\mathbf{p}}_k$ the orbital angular momentum operator. In the symmetric gauge, $\nabla \cdot \mathbf{A}(\mathbf{r}_k) = 0$. Hence, in the Hamiltonian, the $\hat{\mathbf{p}}_k \cdot \mathbf{A}(\mathbf{r}_k)$ term vanishes. The interaction of the magnetic field with the spin moment was originally added *ad hoc* to the Schrödinger equation by Pauli.) It is interesting to note that both interactions arise via the Feynman kinetic energy operator T_F . The spin magnetic moment obtained this way has the correct gyromagnetic ratio $g = 2$. This then is the non-relativistic derivation of the Schrödinger-Pauli Hamiltonian. The Hamiltonian \hat{H} of Eq. (5) may also be derived [30] as the non-relativistic limit of Dirac theory. The corresponding Schrödinger-Pauli equation is then

$$\hat{H}\Psi(\mathbf{X}) = E\Psi(\mathbf{X}), \quad (6)$$

with $\{\Psi(\mathbf{X}), E\}$ the eigenfunctions and eigenvalues; $\mathbf{X} = \mathbf{x}, \dots, \mathbf{x}_N$; $\mathbf{x} = \mathbf{r}\sigma$; and $\mathbf{r}\sigma$ the spatial and spin coordinates.

There are three components to the paper:

1. The first is comprised of the description of the quantum-mechanical system as defined by the Hamiltonian \hat{H} of Eq. (5) in terms of the ‘classical’ fields that satisfy the corresponding ‘Quantal Newtonian’ first law. This description is valid for *arbitrary* state whether ground, excited or degenerate. (The derivation of the law is given in the Appendix.) The description leads to physical insights and understandings, not previously known of the quantum system, and these are then explained.

2. The second is a generalization of the Schrödinger-Pauli equation which shows the Hamiltonian \hat{H} to be a functional of the wave function Ψ , i.e. $\hat{H} = \hat{H}[\Psi]$. Hence, the Schrödinger-Pauli equation can be written in a more general form as

$$\hat{H}[\Psi]\Psi(\mathbf{X}) = E[\Psi]\Psi(\mathbf{X}). \quad (7)$$

In Eq. (7) the fact that the eigenvalues E too are functionals of the wave function Ψ is also explicitly indicated. The generalization of the Schrödinger-Pauli equation is a consequence of the ‘Quantal Newtonian’ first law. It is therefore valid for arbitrary state. As the first law is in terms of fields whose sources are quantum-mechanical expectations of Hermitian operators taken with respect to the wave function Ψ , the functional $\hat{H}[\Psi]$ is *exactly known*. The functional $\hat{H}[\Psi]$ is also *universal* in that it is valid for any electronic system. It is evident from the generalized form of the Schrödinger-Pauli equation that it is intrinsically a self-consistent eigenvalue equation. In the self-consistent procedure, the eigenvalue E at each iteration depends upon the solution of the equation for that iteration. It is for this reason that the eigenvalue E is written as the functional $E[\Psi]$. (The generalized Schrödinger-Pauli equation is akin to the Hartree-Fock theory [31, 32] equations in which the corresponding Hamiltonian \hat{H}^{HF} is a functional of the single-particle spin-orbitals $\phi_i(\mathbf{x})$, i.e. $\hat{H}^{\text{HF}} = \hat{H}^{\text{HF}}[\phi_i(\mathbf{x})]$. The Hartree-Fock theory equations are then $\hat{H}^{\text{HF}}[\phi_i]\phi_i(\mathbf{x}) = \epsilon_i\phi_i(\mathbf{x})$, where the ϵ_i are the eigenvalues. These equations are then solved self-consistently [33]. Such self-consistent equations also arise within all local effective potential theories such as the Optimized Potential Method [34–36], Kohn-Sham [37], and quantal [2–4] density functional theories.)

3. The third component of the paper constitutes the mapping of the interacting system of electrons as defined by the Schrödinger-Pauli equation of Eq. (6) to one of noninteracting fermions possessing the same *basic variables* of the density $\rho(\mathbf{r})$ and physical current density $\mathbf{j}(\mathbf{r})$. The further constraints of the mapping are that of fixed electron number N , and total orbital \mathbf{L} and spin \mathbf{S} angular momentum. (Basic variables in quantum mechanics are gauge invariant properties, knowledge of which uniquely determine the external scalar and vector potentials to within a constant and gradient of a scalar function, respectively.) The mapping is accomplished via quantal density functional theory (QDFT). The mapping is valid for arbitrary state of the interacting system. The state of the model system is also arbitrary provided the constraints are satisfied. The reasons for this mapping are twofold:

(a) The mapping to the model system allows for the determination of properties of the quantum system not obtainable solely via the solution of the Schrödinger-Pauli equation. Such a property is the contribution of electron correlations due to the Pauli exclusion principle and Coulomb repulsion to the kinetic energy – the correlation-kinetic energy. Further, as a consequence of the mapping, it is also possible to separate the contributions to the total energy of the correlations due to the Pauli principle and Coulomb repulsion. (The solution $\Psi(\mathbf{X})$ of the Schrödinger-Pauli Eq. (6,7) accounts for both types of electron correlations, but they are not separable. In quantum chemistry, the separation is accomplished in an approximate manner by performing a Hartree-Fock theory calculation which then leads to the exchange energy – the contribution due to the correlations arising from the Pauli principle. But this latter model differs from the original fully-interacting system as its density $\rho(\mathbf{r})$ and physical current density $\mathbf{j}(\mathbf{r})$ are different. In the QDFT mapping, the model system density and physical current density are the same as that of the interacting electrons.) It is also possible to determine the ionization potential via the mapping to the model system of noninteracting fermions. The highest occupied eigenvalue of the corresponding differential equation is the negative of the ionization potential. (It requires two separate energy calculations to determine the ionization potential within Schrödinger-Pauli theory: one for the charge-neutral and the other for the ionized system.)

(b) The equations governing the model system of noninteracting fermions is easier to solve. The corresponding ‘wave function’ is a Slater determinant of the model fermion spin-orbitals. The QDFT mapping provides the precise *physical* definition of the local effective potential in which all the many-body effects are incorporated. It is the work done by the model fermion in a conservative effective field. This potential then generates the interacting system density $\rho(\mathbf{r})$ and

physical current density $\mathbf{j}(\mathbf{r})$.

The rationale for the choice of the densities $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ as the basic variables in the mapping stems from the ground state theorem of Hohenberg-Kohn (HK) [38] and of its extension by Pan-Sahni (PS) [39] to the presence of a uniform magnetic field. For a system of N electrons in an external electrostatic field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\nabla v(\mathbf{r})/e$, and in a nondegenerate ground state, HK proved that knowledge of the ground state density $\rho(\mathbf{r})$ uniquely determined the external scalar potential $v(\mathbf{r})$ to within a constant. The constraint in the proof is that of fixed electron number N . As the kinetic \hat{T} and electron-interaction \hat{W} potential operators are assumed known, so thus is the Hamiltonian. Solution of the Schrödinger equation then leads to the eigenfunctions and eigenvalues of the system. Hence, the nondegenerate ground state density $\rho(\mathbf{r})$ constitutes a basic variable. What PS proved was that in the added presence of a *uniform* magnetostatic field $\boldsymbol{\mathcal{B}}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$, knowledge of the nondegenerate ground state $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ uniquely determines the potentials $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ to within a constant and gradient of a scalar function, respectively. The constraints in the proof are that of fixed electron number N , orbital \mathbf{L} , and spin \mathbf{S} angular momentum. The PS proof was for both spinless electrons and electrons with spin. Again, with the Hamiltonian now known, the solution of the corresponding Schrödinger and Schrödinger-Pauli equations then leads to the system eigenfunctions and eigenvalues. Hence, in the presence of a magnetostatic field, the nondegenerate ground state $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ constitute basic variables. (The HK and PS proofs differ. There is a fundamental reason for this. In HK the relationship between $v(\mathbf{r})$ and the nondegenerate ground state Ψ is proved to be bijective or one-to-one. In the presence of a magnetic field, however, the relationship between $\{v(\mathbf{r}), \mathbf{A}(\mathbf{r})\}$ and the nondegenerate ground state Ψ is many-to-one and can be infinite-to-one. PS explicitly

account for this many-to-one relationship, and in doing so, the proof follows a different path.) The theorems of HK and PS are ground state theorems. Thus, within HK, the mapping is from an interacting system in a ground state to one of noninteracting fermions also in a ground state possessing the same density $\rho(\mathbf{r})$. This is the mapping performed, for example, in Kohn-Sham density functional theory. However, within QDFT, the mapping to the model system with the same $\rho(\mathbf{r})$ or $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ is possible for ground, excited, and degenerate states of the interacting system [18, 19, 40–43].

To elucidate the ideas underlying the quantal-source-field perspective, the satisfaction of the ‘Quantal Newtonian’ first law, and the intrinsic self-consistent nature of the Schrödinger-Pauli equation, we apply them to the first excited triplet 2^3S state of a quantum dot in a magnetic field in the following paper [44]. The present paper on Schrödinger-Pauli theory is a generalization of work on the Schrödinger theory of electrons [45–47]. As such the description of Schrödinger theory within this new perspective constitutes a special case.

In Sect. II we present the quantal source-field perspective of the Schrödinger-Pauli theory, and describe the new physical insights as obtained from the ‘Quantal Newtonian’ first law. The generalization of the Schrödinger-Pauli equation to exhibit its self-consistent nature is discussed in Sect. III. In Sect. IV the local effective potential quantal density functional theory description of Schrödinger-Pauli theory is developed. Finally, in Sect. V, we summarize the conclusions of the work and propose further generalizations to the time-dependent Schrödinger-Pauli theory, and to relativistic quantum mechanics via the Dirac equation.

II. DESCRIPTION IN TERMS OF QUANTAL SOURCES AND FIELDS: THE ‘QUANTAL NEWTONIAN’ FIRST LAW

In this section the quantum-mechanical system defined by the Schrödinger-Pauli Hamiltonian is described in terms of ‘classical’ fields as experienced by each electron. These fields arise from quantal sources that are expectation values of Hermitian operators, or of complex operators whose real and imaginary parts are Hermitian, taken with respect

to the system wave function $\Psi(\mathbf{X})$. Knowledge of the structure of the quantal sources is then predictive of the structure of the corresponding fields. The fields satisfy the ‘Quantal Newtonian’ first law – the equation of motion of the individual electron. The description is valid for arbitrary state. Further, the total energy E of the system, and its components can also be expressed in integral virial form in terms of these fields. The fields can be separated into two categories: an external $\mathcal{F}^{\text{ext}}(\mathbf{r})$ and an internal $\mathcal{F}^{\text{int}}(\mathbf{r})$ field. To define these fields, the Hamiltonian \hat{H} of Eq. (5) is rewritten as

$$\begin{aligned} \hat{H} = \hat{T} + \frac{1}{c} \int \hat{\mathbf{j}}_p(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} + \frac{1}{2c} \int \hat{\mathbf{j}}_d(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} \\ + \frac{1}{c} \int \hat{\mathbf{j}}_m(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} + \hat{W} + \hat{V}. \end{aligned} \quad (8)$$

In the above equation, \hat{T} is the canonical kinetic energy operator:

$$\hat{T} = \frac{1}{2} \sum_k \hat{p}_k^2, \quad (9)$$

and where the paramagnetic $\hat{\mathbf{j}}_p(\mathbf{r})$, diamagnetic $\hat{\mathbf{j}}_d(\mathbf{r})$, and magnetization $\hat{\mathbf{j}}_m(\mathbf{r})$ current density operators are defined as

$$\hat{\mathbf{j}}_p(\mathbf{r}) = \frac{1}{2} \sum_k [\hat{\mathbf{p}}_k \delta(\mathbf{r}_k - \mathbf{r}) + \delta(\mathbf{r}_k - \mathbf{r}) \hat{\mathbf{p}}_k], \quad (10)$$

$$\hat{\mathbf{j}}_d(\mathbf{r}) = \frac{1}{c} \hat{\rho}(\mathbf{r}) \mathbf{A}(\mathbf{r}), \quad (11)$$

and

$$\hat{\mathbf{j}}_m(\mathbf{r}) = -c \nabla \times \hat{\mathbf{m}}(\mathbf{r}). \quad (12)$$

In turn the electronic density $\hat{\rho}(\mathbf{r})$ and magnetization density $\hat{\mathbf{m}}(\mathbf{r})$ operators of these equations are defined as

$$\hat{\rho}(\mathbf{r}) = \sum_k \delta(\mathbf{r}_k - \mathbf{r}), \quad (13)$$

and

$$\hat{\mathbf{m}}(\mathbf{r}) = -\frac{1}{c} \sum_k \mathbf{s}_k \delta(\mathbf{r}_k - \mathbf{r}). \quad (14)$$

The physical current density operator $\hat{\mathbf{j}}(\mathbf{r})$ is then obtained via its definition [48] as

$$\hat{\mathbf{j}}(\mathbf{r}) = c \frac{\partial \hat{H}}{\partial \mathbf{A}(\mathbf{r})} = \hat{\mathbf{j}}_p(\mathbf{r}) + \hat{\mathbf{j}}_d(\mathbf{r}) + \hat{\mathbf{j}}_m(\mathbf{r}). \quad (15)$$

In terms of the current density $\hat{\mathbf{j}}(\mathbf{r})$, the Hamiltonian \hat{H} of Eq. (8) may be written as

$$\hat{H} = \hat{T} + \frac{1}{c} \int \hat{\mathbf{j}}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} - \frac{1}{2c^2} \int \hat{\rho}(\mathbf{r}) A^2(\mathbf{r}) d\mathbf{r} + \hat{W} + \hat{V}, \quad (16)$$

which then emphasizes the significance of both the electronic and physical current densities to the quantum system.

A. *External Field $\mathcal{F}^{\text{ext}}(\mathbf{r})$*

The external field $\mathcal{F}^{\text{ext}}(\mathbf{r})$ experienced by each electron is the sum of the binding electrostatic $\mathcal{E}(\mathbf{r})$ and Lorentz $\mathcal{L}(\mathbf{r})$ fields:

$$\mathcal{F}^{\text{ext}}(\mathbf{r}) = \mathcal{E}(\mathbf{r}) - \mathcal{L}(\mathbf{r}) = -\nabla v(\mathbf{r}) - \mathcal{L}(\mathbf{r}), \quad (17)$$

where the Lorentz field $\mathcal{L}(\mathbf{r})$ is defined in terms of the Lorentz ‘force’ $\boldsymbol{\ell}(\mathbf{r})$ and electronic density $\rho(\mathbf{r})$ (charge) as

$$\mathcal{L}(\mathbf{r}) = \frac{\boldsymbol{\ell}(\mathbf{r})}{\rho(\mathbf{r})}, \quad (18)$$

with

$$\boldsymbol{\ell}(\mathbf{r}) = \mathbf{j}(\mathbf{r}) \times \mathcal{B}(\mathbf{r}). \quad (19)$$

The electronic $\rho(\mathbf{r})$ and physical current $\mathbf{j}(\mathbf{r})$ densities are, respectively, the expectation values of the operators $\hat{\rho}(\mathbf{r})$ and $\hat{\mathbf{j}}(\mathbf{r})$:

$$\rho(\mathbf{r}) = \langle \Psi(\mathbf{X}) | \hat{\rho}(\mathbf{r}) | \Psi(\mathbf{X}) \rangle, \quad (20)$$

and

$$\mathbf{j}(\mathbf{r}) = \langle \Psi(\mathbf{X}) | \hat{\mathbf{j}}(\mathbf{r}) | \Psi(\mathbf{X}) \rangle. \quad (21)$$

B. *Internal Field $\mathcal{F}^{\text{int}}(\mathbf{r})$*

The internal field $\mathcal{F}^{\text{int}}(\mathbf{r})$ is a sum of components each descriptive of a property of the system: an electron-interaction field $\mathcal{E}_{\text{ee}}(\mathbf{r})$ representative of electron correlations due to the Pauli exclusion principle and Coulomb repulsion; a kinetic field $\mathcal{Z}(\mathbf{r})$ from which the kinetic energy density and kinetic energy can be obtained; the differential density field $\mathcal{D}(\mathbf{r})$ representative of the electron density; and finally an internal magnetic field component $\mathcal{I}_m(\mathbf{r})$. Thus,

$$\mathcal{F}^{\text{int}}(\mathbf{r}) = \mathcal{E}_{\text{ee}}(\mathbf{r}) - \mathcal{Z}(\mathbf{r}) - \mathcal{D}(\mathbf{r}) - \mathcal{I}_m(\mathbf{r}). \quad (22)$$

The component fields and their respective quantal sources are defined next.

The electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$ in terms of the electron-interaction ‘force’ $\mathbf{e}_{ee}(\mathbf{r})$ and density $\rho(\mathbf{r})$ (charge) is

$$\mathcal{E}_{ee}(\mathbf{r}) = \frac{\mathbf{e}_{ee}(\mathbf{r})}{\rho(\mathbf{r})}, \quad (23)$$

where $\mathbf{e}_{ee}(\mathbf{r})$ is obtained via Coulomb’s law from its *nonlocal* (dynamic) quantal source, the pair-correlation function $P(\mathbf{r}\mathbf{r}')$:

$$\mathbf{e}_{ee}(\mathbf{r}) = \int \frac{P(\mathbf{r}\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'. \quad (24)$$

with $P(\mathbf{r}\mathbf{r}')$ the expectation value

$$P(\mathbf{r}\mathbf{r}') = \langle \Psi(\mathbf{X}) | \hat{P}(\mathbf{r}\mathbf{r}') | \Psi(\mathbf{X}) \rangle, \quad (25)$$

of the pair-correlation operator

$$\hat{P}(\mathbf{r}\mathbf{r}') = \sum_{k,\ell}' \delta(\mathbf{r}_k - \mathbf{r}) \delta(\mathbf{r}_\ell - \mathbf{r}'). \quad (26)$$

The electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$ may equivalently be thought of as arising via Coulomb’s law from the quantal source of the pair-correlation density $g(\mathbf{r}\mathbf{r}') = P(\mathbf{r}\mathbf{r}')/\rho(\mathbf{r})$. The pair-correlation density can be separated into its *local* $\rho(\mathbf{r}')$ and *nonlocal* $\rho_{xc}(\mathbf{r}\mathbf{r}')$ components: $g(\mathbf{r}\mathbf{r}') = \rho(\mathbf{r}') + \rho_{xc}(\mathbf{r}\mathbf{r}')$, where $\rho_{xc}(\mathbf{r}\mathbf{r}')$ is the quantum-mechanical Fermi-Coulomb hole charge distribution. Thus, the field $\mathcal{E}_{ee}(\mathbf{r})$ may be written as a sum of its Hartree $\mathcal{E}_H(\mathbf{r})$ and Pauli-Coulomb $\mathcal{E}_{xc}(\mathbf{r})$ components:

$$\mathcal{E}_{ee}(\mathbf{r}) = \mathcal{E}_H(\mathbf{r}) + \mathcal{E}_{xc}(\mathbf{r}), \quad (27)$$

where

$$\mathcal{E}_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}', \quad (28)$$

and

$$\mathcal{E}_{xc}(\mathbf{r}) = \int \frac{\rho_{xc}(\mathbf{r}\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'. \quad (29)$$

Note that in traditional quantum mechanics, it is not possible to further split the Fermi-Coulomb hole into its Fermi $\rho_x(\mathbf{r}\mathbf{r}')$ and Coulomb $\rho_c(\mathbf{r}\mathbf{r}')$ components. In other words, it is not possible to separate the correlations due to the Pauli exclusion principle and Coulomb

repulsion. This separation will be accomplished in Sect. IV via quantal density functional theory.

The kinetic field $\mathcal{Z}(\mathbf{r})$ is defined in terms of the kinetic ‘force’ $\mathbf{z}(\mathbf{r})$ and the density $\rho(\mathbf{r})$ as

$$\mathcal{Z}(\mathbf{r}) = \frac{\mathbf{z}(\mathbf{r})}{\rho(\mathbf{r})}. \quad (30)$$

The kinetic ‘force’ is obtained from its *nonlocal* (dynamic) quantal source, the single-particle density matrix $\gamma(\mathbf{r}\mathbf{r}')$ as follows:

$$z_\alpha(\mathbf{r}) = 2 \sum_{\beta} \nabla_{\beta} t_{\alpha\beta}(\mathbf{r}; \gamma), \quad (31)$$

where the second-rank kinetic energy tensor $t_{\alpha\beta}(\mathbf{r}; \gamma)$ is

$$t_{\alpha\beta}(\mathbf{r}; \gamma) = \frac{1}{4} \left[\frac{\partial^2}{\partial r'_{\alpha} \partial r''_{\beta}} + \frac{\partial^2}{\partial r'_{\beta} \partial r''_{\alpha}} \right] \gamma(\mathbf{r}'\mathbf{r}'') \Big|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}. \quad (32)$$

The quantal source $\gamma(\mathbf{r}\mathbf{r}')$ is the expectation value

$$\gamma(\mathbf{r}\mathbf{r}') = \langle \Psi(\mathbf{X}) | \hat{\gamma}(\mathbf{r}\mathbf{r}') | \Psi(\mathbf{X}) \rangle, \quad (33)$$

with the complex density matrix operator $\hat{\gamma}(\mathbf{r}\mathbf{r}')$ being [49, 50]

$$\hat{\gamma}(\mathbf{r}\mathbf{r}') = \hat{A} + i\hat{B}, \quad (34)$$

$$\hat{A} = \frac{1}{2} \sum_k [\delta(\mathbf{r}_k - \mathbf{r}) T_k(\mathbf{a}) + \delta(\mathbf{r}_k - \mathbf{r}') T_k(-\mathbf{a})], \quad (35)$$

$$\hat{B} = -\frac{i}{2} \sum_k [\delta(\mathbf{r}_k - \mathbf{r}) T_k(\mathbf{a}) - \delta(\mathbf{r}_k - \mathbf{r}') T_k(-\mathbf{a})], \quad (36)$$

with $T_k(\mathbf{a})$ a translation operator such that $T_k(\mathbf{a})\psi(\dots \mathbf{r}_k, \dots) = \psi(\dots \mathbf{r}_k + \mathbf{a}, \dots)$ and $\mathbf{a} = \mathbf{r}' - \mathbf{r}$. The operators \hat{A} and \hat{B} are each Hermitian.

The differential density field $\mathcal{D}(\mathbf{r})$ whose quantal source is the *local* electron density $\rho(\mathbf{r})$, is defined in terms of the corresponding ‘force’ $d(\mathbf{r})$ and density $\rho(\mathbf{r})$ as

$$\mathcal{D}(\mathbf{r}) = \frac{d(\mathbf{r})}{\rho(\mathbf{r})}, \quad (37)$$

where

$$d(\mathbf{r}) = -\frac{1}{4} \nabla \nabla^2 \rho(\mathbf{r}). \quad (38)$$

The magnetic field contribution $\mathcal{I}_m(\mathbf{r})$ to the internal field in terms of the ‘force’ $\mathbf{i}_m(\mathbf{r})$ and the density $\rho(\mathbf{r})$ is

$$\mathcal{I}_m(\mathbf{r}) = \frac{\mathbf{i}_m(\mathbf{r})}{\rho(\mathbf{r})}, \quad (39)$$

where

$$i_{m,\alpha}(\mathbf{r}) = \sum_{\beta} \nabla_{\beta} I_{\alpha\beta}(\mathbf{r}), \quad (40)$$

and the second-rank tensor $I_{\alpha\beta}(\mathbf{r})$ is

$$I_{\alpha\beta}(\mathbf{r}) = [j_{\alpha}(\mathbf{r})A_{\beta}(\mathbf{r}) + j_{\beta}(\mathbf{r})A_{\alpha}(\mathbf{r})] - \rho(\mathbf{r})A_{\alpha}(\mathbf{r})A_{\beta}(\mathbf{r}), \quad (41)$$

with $\mathbf{j}(\mathbf{r})$ the quantal source of the field.

The individual components of the internal field $\mathcal{F}^{\text{int}}(\mathbf{r})$ are in general not conservative. However, as shown below, their sum taken together with the Lorentz field is conservative. Under conditions of certain symmetry, the individual components can each be separately conservative.

C. ‘Quantal Newtonian’ First Law

The equation of motion or ‘Quantal Newtonian’ first law is satisfied by *each electron* of the physical system defined by the Schrödinger-Pauli equation of Eq. (6). The law states that the sum of the external $\mathcal{F}^{\text{ext}}(\mathbf{r})$ and internal $\mathcal{F}^{\text{int}}(\mathbf{r})$ fields experienced by each electron vanishes:

$$\mathcal{F}^{\text{ext}}(\mathbf{r}) + \mathcal{F}^{\text{int}}(\mathbf{r}) = 0. \quad (42)$$

The law is derived employing the continuity condition

$$\nabla \cdot \mathbf{j}(\mathbf{r}) = 0. \quad (43)$$

Thus, the quantal source-field perspective of the Schrödinger-Pauli theory is consistent with Schrödinger’s [51] insight that satisfaction of this condition is the explanation of the lack of radiation in a stationary state. The ‘Quantal Newtonian’ first law is valid for arbitrary state. It is also gauge invariant.

D. Total Energy and Components

The terms of the total energy E – the canonical kinetic T , the electron-interaction E_{ee} , and its Hartree E_H and Pauli-Coulomb E_{xc} components, – can each be expressed in integral virial form in terms of the corresponding fields $\mathbf{Z}(\mathbf{r})$, $\mathbf{E}_{ee}(\mathbf{r})$, $\mathbf{E}_H(\mathbf{r})$, $\mathbf{E}_{xc}(\mathbf{r})$. With the exception of $\mathbf{E}_H(\mathbf{r})$ which is conservative, these expressions are valid irrespective of whether the fields are conservative. Thus,

$$T = -\frac{1}{2} \int \rho(\mathbf{r}) \mathbf{r} \cdot \mathbf{Z}(\mathbf{r}) d\mathbf{r}, \quad (44)$$

$$E_{ee} = \int \rho(\mathbf{r}) \mathbf{r} \cdot \mathbf{E}_{ee}(\mathbf{r}) d\mathbf{r}, \quad (45)$$

$$E_H = \int \rho(\mathbf{r}) \mathbf{r} \cdot \mathbf{E}_H(\mathbf{r}) d\mathbf{r}, \quad (46)$$

$$E_{xc} = \int \rho(\mathbf{r}) \mathbf{r} \cdot \mathbf{E}_{xc}(\mathbf{r}) d\mathbf{r}. \quad (47)$$

The contribution of the conservative external electrostatic field $\mathbf{E}(\mathbf{r}) = -\nabla v(\mathbf{r})$ to the energy E_{el} can be written directly in terms of the potential $v(\mathbf{r})$ as

$$E_{es} = \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}. \quad (48)$$

Note that $v(\mathbf{r})$ is path-independent. The energy can also be written in integral virial form, but the coefficient of the expression depends upon the degree of the homogeneous function $v(\mathbf{r})$. Hence, for the Coulombic potential for which the degree is -1 , the expression is

$$E_{es} = \int \rho(\mathbf{r}) \mathbf{r} \cdot \mathbf{E}(\mathbf{r}) d\mathbf{r}. \quad (49)$$

For the magnetic field contribution to the energy, *i.e.* the contribution of the Lorentz $\mathcal{L}(\mathbf{r})$ and internal magnetic $\mathcal{I}_m(\mathbf{r})$ field components, define the field

$$\mathcal{M}(\mathbf{r}) = -[\mathcal{L}(\mathbf{r}) + \mathcal{I}_m(\mathbf{r})]. \quad (50)$$

If the field $\mathcal{M}(\mathbf{r})$ is conservative, *i.e.* $\nabla \times \mathcal{M}(\mathbf{r}) = 0$, then one can define a magnetic scalar potential $v_m(\mathbf{r})$ as

$$\mathcal{M}(\mathbf{r}) = -\nabla v_m(\mathbf{r}). \quad (51)$$

This implies that $v_m(\mathbf{r})$ is path-independent. The magnetic contribution E_{mag} to the energy is then

$$E_{mag} = \int \rho(\mathbf{r}) v_m(\mathbf{r}) d\mathbf{r}. \quad (52)$$

The E_{mag} can also be written in integral virial form depending on the degree of the homogeneous function $v_m(\mathbf{r})$. If $v_m(\mathbf{r})$ is of degree 2 as for the harmonic oscillator, then

$$E_{\text{mag}} = -\frac{1}{2} \int \rho(\mathbf{r}) \mathbf{r} \cdot \mathcal{M}(\mathbf{r}) d\mathbf{r}. \quad (53)$$

In the general case when $\nabla \times \mathcal{M}(\mathbf{r}) \neq 0$, the expression is

$$E_{\text{mag}} = \int \rho(\mathbf{r}) \mathbf{r} \cdot \mathcal{M}(\mathbf{r}) d\mathbf{r}. \quad (54)$$

The total energy E may then be expressed as

$$E = T + E_{ee} + E_{es} + E_{\text{mag}} \quad (55)$$

$$= T + E_H + E_{xc} + E_{es} + E_{\text{mag}}. \quad (56)$$

It is evident from the above that the quantum-mechanical system defined via the Schrödinger-Pauli equation can be alternatively described from the perspective of the individual electron. This description is in terms of ‘classical’ fields experienced by each electron, with the fields arising from quantal sources. The fields satisfy the ‘Quantal Newtonian’ first law or equation of motion for each electron. The total energy E and its components can also be expressed in terms of these fields.

E. Further Physical and Mathematical Insights

In addition to the above new perspective, further understandings of the Schrödinger-Pauli system may be gleaned from the ‘Quantal Newtonian’ first law. These are as follows:

(i) The Hamiltonian of a system of classical particles in an electrostatic and magnetostatic field contains both a scalar and vector potential representative respectively of these fields. From the correspondence principle, these same potentials appear in the quantum-mechanical Hamiltonian. Hence, it is understood that each electron of the quantum system in such fields experiences a force due to the electrostatic field, and a Lorentz force due to the magnetic field. Whilst the electrostatic force is explicit via the scalar potential, the Lorentz force does not appear explicitly in the quantum-mechanical Hamiltonian. The ‘Quantal Newtonian’ first law now makes the existence of both forces acting on each electron *explicit* via the external field $\mathcal{F}^{\text{ext}}(\mathbf{r})$ which is the sum of the electrostatic $\mathcal{E}(\mathbf{r})$ and Lorentz $\mathcal{L}(\mathbf{r})$ fields, the latter involving the Lorentz force.

(*ii*) As is the case for classical particles interacting via Newton's third law forces, and the resulting Newton's first law for each particle, each electron of the quantum system is observed via the 'Quantal Newtonian' first law to also experience an internal field $\mathcal{F}^{\text{int}}(\mathbf{r})$. The components of this field are representative of fundamental properties of the quantum system: electron correlations due to the Pauli exclusion principle and Coulomb repulsion, $\mathcal{E}_{\text{ee}}(\mathbf{r})$; kinetic effects, $\mathcal{Z}(\mathbf{r})$; electron density, $\mathcal{D}(\mathbf{r})$; and an internal magnetic field component, $\mathcal{I}_m(\mathbf{r})$. The existence of the internal field $\mathcal{F}^{\text{int}}(\mathbf{r})$ and of its property related components would be unknown but for the 'Quantal Newtonian' first law.

(*iii*) In summing the 'Quantal Newtonian' first law over all the electrons, the contribution of the internal field $\mathcal{F}^{\text{int}}(\mathbf{r})$ vanishes, leading to Ehrenfest's [52] theorem for a stationary state: $\int \rho(\mathbf{r})\mathcal{F}^{\text{ext}}(\mathbf{r})d\mathbf{r} = 0$.

(*iv*) The external scalar potential $v(\mathbf{r})$ which appears in the quantum-mechanical Hamiltonian represents the potential energy of each electron in the presence of the field of the positively charged nucleus in atoms, molecules, and solids. It could represent the potential due to the field of the positive jellium background model of solids (metals) employed to study the uniform electron gas or the study of the metal-vacuum interface [3, 53], or the fractional quantum Hall effect [9, 10]. The potential, furthermore, is path-independent. The 'Quantal Newtonian' first law, however, provides a deeper physical understanding of this potential in terms of the properties of the system. Further, it affords an interpretation of the potential in the rigorous classical sense. It follows from the 'Quantal Newtonian' first law of Eq. (41) that *the potential $v(\mathbf{r})$ is the work done to move an electron from some reference point at infinity to its position at \mathbf{r} in the force of a conservative field $\mathcal{F}(\mathbf{r})$:*

$$v(\mathbf{r}) = \int_{\infty}^{\mathbf{r}} \mathcal{F}(\mathbf{r}') \cdot d\ell', \quad (57)$$

where $\mathcal{F}(\mathbf{r}) = \mathcal{F}^{\text{int}}(\mathbf{r}) - \mathcal{L}(\mathbf{r}) = \mathcal{E}_{\text{ee}}(\mathbf{r}) - \mathcal{Z}(\mathbf{r}) - \mathcal{D}(\mathbf{r}) - \mathcal{I}_m(\mathbf{r}) - \mathcal{L}(\mathbf{r})$. As the field $\mathcal{F}(\mathbf{r})$ is conservative, the $\nabla \times \mathcal{F}(\mathbf{r}) = 0$. Hence, the work done is *path-independent*, and therefore $v(\mathbf{r})$ constitutes a potential energy. It is reiterated that the 'Quantal Newtonian' first law is valid for arbitrary state. Hence, the potential function $v(\mathbf{r})$ as expressed in Eq. (57) remains the same irrespective of the state of the system.

(*v*) In the Hamiltonian of Eq. (6), the potential energy function $v(\mathbf{r})$ binding the electrons is assumed analytically known. It could be Coulombic ($-Ze^2/r$), harmonic ($\frac{1}{2}kr^2$), screened-Coulomb Yukawa ($-Ze^2\exp(-\lambda r/r)$), etc. The 'Quantal Newtonian' first

law written as in Eq. (57) then shows that this analytical function $v(\mathbf{r})$ depends on all the components of the internal field $\mathcal{F}^{\text{int}}(\mathbf{r})$ of the system and the Lorentz field $\mathcal{L}(\mathbf{r})$. Thus, the potential $v(\mathbf{r})$ is inherently related to and constructed via the properties of the system. Further, if the various internal fields are separately conservative, then the function $v(\mathbf{r})$ is comprised of a sum of constituent functions, each representative of a property of the system, with each being the work done in the corresponding field.

(*vi*) Provided the sum of the Lorentz $\mathcal{L}(\mathbf{r})$ and internal magnetic $\mathcal{I}_m(\mathbf{r})$ fields is conservative, it is then possible to define a scalar potential $v_m(\mathbf{r})$ representative of all the magnetic effects of the system. This potential is the work done in the sum of the fields $\mathcal{L}(\mathbf{r})$ and $\mathcal{I}_m(\mathbf{r})$. This work done is path-independent.

(*vii*) The ‘Quantal Newtonian’ first law also provides a deeper mathematical understanding of the potential $v(\mathbf{r})$. As the components of the conservative field $\mathcal{F}(\mathbf{r})$ of Eq. (57) are obtained from quantal sources that are expectation values of Hermitian operators taken with respect to the wave function Ψ , the field $\mathcal{F}(\mathbf{r})$ is a functional of Ψ , *i.e.* $\mathcal{F}(\mathbf{r}) = \mathcal{F}[\Psi](\mathbf{r})$. This functional is *exactly known* since the individual component fields are explicitly defined. This in turn means that the scalar potential energy $v(\mathbf{r})$ as defined by Eq. (57) is an *exactly known* functional of the wave function $\Psi : v(\mathbf{r}) = v[\Psi](\mathbf{r})$. We emphasize that this functional dependence is valid for *arbitrary* state. (That the external potential $v(\mathbf{r})$ is a functional of the *ground state* wave function Ψ_g was originally proved by Hohenberg and Kohn [38] for the case when the only external field present was the electrostatic binding field $\mathcal{E}(\mathbf{r})$. The explicit functional dependence of $v(\mathbf{r})$ on Ψ_g was, however, not given.)

III. GENERALIZATION OF THE SCHRÖDINGER-PAULI EQUATION

Another consequence of the ‘Quantal Newtonian’ first law is the generalization of the Schrödinger-Pauli equation. This generalized form of the equation exhibits its intrinsic self-consistent nature. In the previous section, it was shown that the scalar potential $v(\mathbf{r})$ was a known functional of the wave function Ψ . Substituting the functional $v[\Psi](\mathbf{r})$ into the Schrödinger-Pauli equation Eq. (6), the equation can then be written as

$$\left[\frac{1}{2} \sum_k (\hat{\mathbf{p}}_k + \frac{1}{c} \mathbf{A}(\mathbf{r}_k))^2 + \frac{1}{c} \sum_k \mathbf{B}(\mathbf{r}_k) \cdot \mathbf{s}_k + \frac{1}{2} \sum'_{k,\ell} \frac{1}{|\mathbf{r}_k - \mathbf{r}_\ell|} + \sum_k v[\Psi](\mathbf{r}_k) \right] \Psi(\mathbf{X}) = E[\Psi] \Psi(\mathbf{X}), \quad (58)$$

or, on employing Eq. (57), as

$$\left[\frac{1}{2} \sum_k (\hat{\mathbf{p}}_k + \frac{1}{c} \mathbf{A}(\mathbf{r}_k))^2 + \frac{1}{c} \sum_k \mathbf{B}(\mathbf{r}_k) \cdot \mathbf{s}_k + \frac{1}{2} \sum'_{k,\ell} \frac{1}{|\mathbf{r}_k - \mathbf{r}_\ell|} + \sum_k \int_{-\infty}^{\mathbf{r}_k} \mathcal{F}[\Psi](\mathbf{r}) \cdot d\boldsymbol{\ell} \right] \Psi(\mathbf{X}) = E[\Psi] \Psi(\mathbf{X}). \quad (59)$$

Thus, the Hamiltonian is a functional of the wave function $\Psi : \hat{H} = \hat{H}[\Psi]$, and the Schrödinger-Pauli equation can then be written in its generalized form as in Eq. (7). The Hamiltonian functional $\hat{H}[\Psi]$ is exactly known. It is valid for *arbitrary state*. It is also *universal* in that it is applicable to any electronic system defined by this Hamiltonian.

The generalized form of the Schrödinger-Pauli equation makes evident that its solution Ψ may be obtained self-consistently. One begins with an appropriate approximate wave function Ψ to first determine the corresponding quantal sources and fields, and the potential $v(\mathbf{r})$, and thereby the approximate Hamiltonian $\hat{H}[\Psi]$. The Schrödinger-Pauli equation Eq. (7 or 59) is then solved to obtain the next approximation to the wave function Ψ and energy E , from which the corresponding sources and fields and potential $v(\mathbf{r})$ then lead to the next approximate $\hat{H}[\Psi]$. For this new approximate $\hat{H}[\Psi]$, the Schrödinger-Pauli equation is again solved for the next approximate wave function Ψ and energy E . And this procedure is continued till the input wave function Ψ to $\hat{H}[\Psi]$ is the same Ψ as that generated by this $\hat{H}[\Psi]$ via solution of the Schrödinger-Pauli equation. Note that the meaning of the functional $v[\Psi]$ is that for each new Ψ , one obtains a new $v[\Psi](\mathbf{r})$, and therefore the Hamiltonian functional $\hat{H}[\Psi]$ changes with each new iterative Ψ . This then allows for the self-consistent procedure. The understanding that the Schrödinger-Pauli equation is intrinsically self-consistent is new.

In its generalized form, the Schrödinger-Pauli equation has additional attributes, and leads to further insights:

(a) In traditional quantum mechanics, the potential $v(\mathbf{r})$ is considered as being *extrinsic* to the system of N electrons, and as such is assumed to be a *known but independent*

input to the Hamiltonian \hat{H} . In other words, it does not depend on any other terms of the Hamiltonian \hat{H} . From the generalized form of the equation, it becomes evident that the potential $v[\Psi](\mathbf{r})$ is in fact *intrinsic* to the physical system being related to it via the internal field components (see Eq. (57)). It is thereby (self-consistently) *dependent* on all the properties of the system via the other operators of the Hamiltonian \hat{H} .

(b) On achieving self-consistency, the wave function $\Psi(\mathbf{X})$, the eigen energy E , and the potential $v[\Psi](\mathbf{r})$ or equivalently the Hamiltonian $\hat{H}[\Psi]$, are determined. This is of particular significance in those cases for which the potential $v(\mathbf{r})$ may be *unknown*. Due to the advances in semiconductor technology, it has been possible to create 2-dimensional ‘artificial atoms’ or quantum dots. When such quantum dots were initially developed, the form of the binding potential of the electrons was not known. Later, via experimentation and theoretical work at the Hartree level [13, 14, 54], it was determined that the potential was harmonic. This is now accepted to be the case. Had the generalized form of the Schrödinger-Pauli equation existed at that time, the fact of a harmonic binding potential $v(\mathbf{r})$ for quantum dots could have been arrived at via its self-consistent solution. In the future, when new electronic devices are created, the corresponding binding potential could thus be obtained.

(c) The self-consistent procedure could also be employed to determine the wave function $\Psi(\mathbf{X})$ and energy E even for the common case when the potential $v(\mathbf{r})$ is known. Starting with an accurate approximate wave function Ψ , the corresponding approximate $v[\Psi](\mathbf{r})$ could be determined. Of course, this would not correspond to the known $v(\mathbf{r})$ function. But the solution of the resulting Schrödinger-Pauli equation with this approximate $v[\Psi](\mathbf{r})$ would be an improvement to the original wave function. Continuing with the self-consistency procedure would lead to the exact $\{\Psi(\mathbf{X}), E\}$. On achieving self-consistency, the known function $v(\mathbf{r})$ would be reproduced.

(d) It is worth comparing the self-consistent procedure of the generalized Schrödinger-Pauli equation with that of the variational principle for the *ground* state energy [55]. Starting with an approximate parameterized wave function correct to $O(\delta)$, the variational principle leads to a rigorous upper bound to the energy that is correct to $O(\delta^2)$. However, all other properties of the system are obtained correct to only $O(\delta)$. Thus, the variationally obtained wave function is accurate only in the region of space contributing to the energy. On the other hand, the self-consistently obtained solution is accurate through-

out space, and hence all properties are accurate to the same degree of numerical accuracy as required. For *excited* states, the application of the variational principle requires that the approximate wave function be orthogonal to the exact ground state wave function. The generalized Schrödinger-Pauli equation is valid for both ground and excited states. The corresponding excited state wave function obtained self-consistently will automatically be orthogonal to the ground and other states of the system.

(e) In the Schrödinger theory [30] of electrons in the presence of electrostatic $\mathcal{E}(\mathbf{r})$ and magnetostatic $\mathcal{B}(\mathbf{r})$ fields, one hews to the philosophy that electromagnetic interactions occur by the substitution $\hat{\mathbf{p}} \rightarrow \hat{\mathbf{p}} + (e/c)\mathbf{A}$. Thus, it is the vector potential $\mathbf{A}(\mathbf{r})$ and not the magnetic field $\mathcal{B}(\mathbf{r})$ that appears in the corresponding Schrödinger equation. This fundamental difference between classical and quantum physics then explains, for example, the Aharonov-Bohm effect [56]. The magnetic field $\mathcal{B}(\mathbf{r})$ appears in the Schrödinger equation only after a choice of gauge for the vector potential $\mathbf{A}(\mathbf{r})$. In the Schrödinger-Pauli equation (Eq. (6)), the magnetic field $\mathcal{B}(\mathbf{r})$ appears explicitly as a consequence of the use of the Feynman kinetic energy operator \hat{T}_F : It is the term corresponding to the interaction between the magnetic field and the spin angular momentum operator. The generalized form of the Schrödinger-Pauli equation further shows that the magnetic field $\mathcal{B}(\mathbf{r})$ also appears in the term involving $v[\Psi](\mathbf{r})$ via the conservative field $\mathcal{F}(\mathbf{r})$ which includes the Lorentz field $\mathcal{L}(\mathbf{r})$ (see Eqs. 57-59).

IV. QUANTAL DENSITY FUNCTIONAL THEORY

In this section the system of electrons described by the Schrödinger-Pauli Hamiltonian of Eq. (5) is mapped via quantal density functional theory (QDFT) [2, 3] to one of noninteracting fermions possessing the same electronic $\rho(\mathbf{r})$ and physical current $\mathbf{j}(\mathbf{r})$ density. The additional constraints on the model system are that it also possesses the same number N of fermions, and the same total orbital \mathbf{L} and spin \mathbf{S} angular momentum. It is assumed that the model fermions are subject to the same electrostatic $\mathcal{E}(\mathbf{r}) = -\nabla v(\mathbf{r})/e$ and magnetostatic $\mathcal{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ fields as the electrons of the interacting system. It is further assumed that such a model system can exist.

The key to the mapping from the interacting to the noninteracting fermion model system is to determine the *local* electron-interaction potential $v_{ee}(\mathbf{r})$ in which the many-

body effects are incorporated. This potential then generates the single-particle orbitals $\phi_i(\mathbf{x})$ of the Slater determinant $\Phi\{\phi_i(\mathbf{x})\}$ that lead to the same electronic and physical current density. For the QDFT model system with the constraints as described above, the only electron correlations that must be *explicitly* accounted for in $v_{ee}(\mathbf{r})$ are those due to the Pauli exclusion principle and Coulomb repulsion, and Correlation-Kinetic effects [57].

It is reiterated that a principal purpose of the mapping to the model system is to determine the Correlation-Kinetic energy T_c , and to separate the Pauli-Coulomb E_{xc} (quantum-mechanical exchange-correlation) energy into its Pauli E_x (exchange) and Coulomb E_c (correlation) energy components.

Consider a system of N noninteracting fermions possessing the same potential energies $\{v, \mathbf{A}\}$ as that of the interacting electrons. The Schrödinger-Pauli Hamiltonian \hat{H}_s of the model fermions (the S system) is (see also Eq. (16))

$$\hat{H}_s = \hat{T} + \frac{1}{c} \int \hat{\mathbf{j}}_s(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} - \frac{1}{2c^2} \int \hat{\rho}(\mathbf{r}) A^2(\mathbf{r}) d\mathbf{r} + \hat{V}_s, \quad (60)$$

where the local potential operator \hat{V}_s is

$$\hat{V}_s = \sum_k v_s(\mathbf{r}_k) = \sum_k \left[v(\mathbf{r}_k) + v_{ee}(\mathbf{r}_k) \right], \quad (61)$$

and $v_{ee}(\mathbf{r})$ the *local* electron-interaction potential in which all the many-body effects are incorporated. As the configuration of the model fermions is as yet unspecified, the S system current density operator $\hat{\mathbf{j}}_s(\mathbf{r})$ is

$$\hat{\mathbf{j}}_s(\mathbf{r}) = \hat{\mathbf{j}}_p(\mathbf{r}) + \hat{\mathbf{j}}_d(\mathbf{r}) + \hat{\mathbf{j}}_{m,s}(\mathbf{r}), \quad (62)$$

with the paramagnetic $\hat{\mathbf{j}}_p(\mathbf{r})$ and diamagnetic $\hat{\mathbf{j}}_d(\mathbf{r})$ current density operators defined as in Eqs. (10) and (11). The magnetization current density operator $\hat{\mathbf{j}}_{m,s}(\mathbf{r}) = -c \nabla \times \hat{\mathbf{m}}_s(\mathbf{r})$ with the magnetization density operator $\hat{\mathbf{m}}_s(\mathbf{r}) = (-\frac{1}{c}) \sum_k \mathbf{s}_{k,s} \delta(\mathbf{r}_k - \mathbf{r})$, and $\mathbf{s}_{k,s}$ the spin vector of the k -th model fermion.

For *arbitrary state* of the interacting system, the mapping to the model system is to be such that it possesses the same basic variables $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ and satisfies the same constraints on N, \mathbf{L} , and \mathbf{S} . With the orbital angular momentum \mathbf{L} being the same, the equivalence of the spin \mathbf{S} angular momentum requires that $\mathbf{s}_{k,s} = \mathbf{s}_k$. (This means that the configuration of the model fermions is either the same as that of the interacting electrons, or a different configuration but one possessing the same \mathbf{L} and \mathbf{S} . Thus, for example, it is

possible to map an interacting two-electron system in an excited singlet state to a S system in its ground state.) The equivalence of the spin vectors implies that $\hat{\mathbf{m}}_s(\mathbf{r}) = \mathbf{m}(\mathbf{r})$ so that $\hat{\mathbf{j}}_{m,s}(\mathbf{r}) = \hat{\mathbf{j}}_m(\mathbf{r})$. It follows that the operator $\hat{\mathbf{j}}_s(\mathbf{r}) = \hat{\mathbf{j}}(\mathbf{r})$. Hence, the S system Hamiltonian \hat{H}_s of Eq. (60) may be written as

$$\hat{H}_s = \hat{T} + \frac{1}{c} \int \hat{\mathbf{j}}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} - \frac{1}{2c^2} \int \hat{\rho}(\mathbf{r}) A^2(\mathbf{r}) + \hat{V}_s. \quad (63)$$

The corresponding local effective potential differential equation for the orbitals $\phi_i(\mathbf{x})$ of the Slater determinant wave function $\Phi\{\phi_k\}$ of the model fermions (assuming additionally that $c = 1$) is

$$\left[\frac{1}{2} (\hat{\mathbf{p}} + \mathbf{A}(\mathbf{r}))^2 + \mathbf{B} \cdot \mathbf{s} + v(\mathbf{r}) + v_{ee}(\mathbf{r}) \right] \phi_k(\mathbf{x}) = \epsilon_k \phi_k(\mathbf{x}); \quad k = 1, \dots, N. \quad (64)$$

The S system properties of the density $\rho_s(\mathbf{r})$, Dirac density matrix $\gamma_s(\mathbf{r}\mathbf{r}')$, pair-correlation density $g_s(\mathbf{r}\mathbf{r}')$, and the current density $\mathbf{j}_s(\mathbf{r})$ are then, respectively, the expectation values of the corresponding Hermitian operators taken with respect to the Slater determinant wave function $\Phi\{\phi_i\}$. Thus $\rho_s(\mathbf{r}) = \langle \Phi\{\phi_k\} | \hat{\rho}(\mathbf{r}) | \Phi\{\phi_k\} \rangle = \sum_{\sigma,k} \phi_k^*(\mathbf{r}\sigma) \phi_k(\mathbf{r}\sigma)$; $\gamma_s(\mathbf{r}\mathbf{r}') = \langle \Phi\{\phi_k\} | \hat{\gamma}(\mathbf{r}\mathbf{r}') | \Phi\{\phi_k\} \rangle = \sum_{\sigma,k} \phi_k^*(\mathbf{r}\sigma) \phi_k(\mathbf{r}'\sigma)$; $g_s(\mathbf{r}\mathbf{r}') = \frac{1}{\rho_s(\mathbf{r})} \langle \Phi\{\phi_k\} | \hat{P}(\mathbf{r}\mathbf{r}') | \Phi\{\phi_k\} \rangle$; $\mathbf{j}_s(\mathbf{r}) = \langle \Phi\{\phi_k\} | \hat{\mathbf{j}}(\mathbf{r}) | \Phi\{\phi_k\} \rangle$. Note that $g_s(\mathbf{r}\mathbf{r}') = \rho(\mathbf{r}') + \rho_x(\mathbf{r}\mathbf{r}')$, where the Fermi hole is defined as $\rho_x(\mathbf{r}\mathbf{r}') = -|\gamma_s(\mathbf{r}\mathbf{r}')|^2 / 2\rho_s(\mathbf{r})$.

With the requirement that the S system density $\rho_s(\mathbf{r})$ and current density $\mathbf{j}_s(\mathbf{r})$ are the same as $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ of the interacting system, the ‘Quantal Newtonian’ first law as satisfied by each model fermion is then

$$\mathcal{F}^{\text{ext}}(\mathbf{r}) + \mathcal{F}_s^{\text{int}}(\mathbf{r}) = 0. \quad (65)$$

The law is derived (see Appendix) employing the continuity condition $\nabla \cdot \mathbf{j}(\mathbf{r}) = 0$. As the potentials $\{v, \mathbf{A}\}$ and the densities $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ of the S system are the same as those of the interacting system, the external field $\mathcal{F}^{\text{ext}}(\mathbf{r})$ experienced by the model fermions is the same as for the electrons (see Eq. (17)). The internal field $\mathcal{F}_s^{\text{int}}(\mathbf{r})$ of these fermions is obtained as

$$\mathcal{F}_s^{\text{int}}(\mathbf{r}) = -\nabla v_{ee}(\mathbf{r}) - \mathcal{Z}_s(\mathbf{r}) - \mathcal{D}(\mathbf{r}) - \mathcal{I}_m(\mathbf{r}), \quad (66)$$

where $\mathcal{Z}_s(\mathbf{r}), \mathcal{D}(\mathbf{r}), \mathcal{I}_m(\mathbf{r})$ are the corresponding kinetic, differential density, and internal magnetic fields. The S system kinetic field $\mathcal{Z}_s(\mathbf{r})$ is defined in a manner similar to the

kinetic field $\mathcal{Z}(\mathbf{r})$ of the interacting system (see Eq. (30)):

$$\mathcal{Z}_s(\mathbf{r}) = \frac{\mathbf{z}_s(\mathbf{r})}{\rho(\mathbf{r})}, \quad (67)$$

where the kinetic ‘force’ $\mathbf{z}_s(\mathbf{r})$ is obtained from its *nonlocal* quantal source, the Dirac density matrix $\gamma_s(\mathbf{r}\mathbf{r}')$ (defined earlier) as

$$z_{s,\alpha}(\mathbf{r}) = 2 \sum_{\beta} \nabla_{\beta} t_{s,\alpha\beta}(\mathbf{r}; \gamma_s), \quad (68)$$

where the second rank tensor $t_{s,\alpha\beta}(\mathbf{r}; \gamma_s)$ is

$$t_{s,\alpha\beta}(\mathbf{r}; \gamma_s) = \frac{1}{4} \left[\frac{\partial^2}{\partial r'_{\alpha} \partial r''_{\beta}} + \frac{\partial^2}{\partial r'_{\beta} \partial r''_{\alpha}} \right] \gamma_s(\mathbf{r}'\mathbf{r}'') \Big|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}. \quad (69)$$

The fields $\mathcal{D}(\mathbf{r})$ and $\mathcal{I}_m(\mathbf{r})$ are defined as for the interacting system. As the densities $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r})\}$ of the interacting and S systems are the same, so are these corresponding fields (see Eqs. (37) and (39)).

Equating the ‘Quantal Newtonian’ first laws for the interacting and model systems (Eqs. (42) and (65)) then leads to the definition of the *local* electron-interaction potential $v_{ee}(\mathbf{r})$ of the S system differential equation (Eq. (64)). *The potential $v_{ee}(\mathbf{r})$ is the work done to move the model fermion from some reference point at infinity to its position at \mathbf{r} in the force of a conservative effective field $\mathcal{F}^{\text{eff}}(\mathbf{r})$:*

$$v_{ee}(\mathbf{r}) = - \int_{\infty}^{\mathbf{r}} \mathcal{F}^{\text{eff}}(\mathbf{r}') \cdot d\ell', \quad (70)$$

where

$$\mathcal{F}^{\text{eff}}(\mathbf{r}) = \mathcal{E}_{ee}(\mathbf{r}) + \mathcal{Z}_{t_c}(\mathbf{r}), \quad (71)$$

with the electron-interaction field $\mathcal{E}_{ee}(\mathbf{r})$ given by Eq. (23), and the correlation-kinetic field $\mathcal{Z}_{t_c}(\mathbf{r})$ defined as

$$\mathcal{Z}_{t_c}(\mathbf{r}) = \mathcal{Z}_s(\mathbf{r}) - \mathcal{Z}(\mathbf{r}). \quad (72)$$

Since the $\nabla \times \mathcal{F}^{\text{eff}}(\mathbf{r})$ vanishes, the potential $v_{ee}(\mathbf{r})$ is *path-independent*. Further, in the self-consistent determination of $v_{ee}(\mathbf{r})$, it follows from Eq. (71) that the only correlations that must be accounted for are those due to the Pauli exclusion principle, Coulomb repulsion, and correlation-kinetic effects.

The total energy E of the interacting system can be expressed in terms of the S system properties. Splitting the kinetic energy T into its noninteracting T_s and correlation-kinetic T_c components, the energy $E = \langle \Psi(\mathbf{X}) | \hat{H} | \Psi(\mathbf{X}) \rangle$ (assuming $c = 1$) may be written

as (see Eq. (16))

$$E = T_s + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})d\mathbf{r} - \frac{1}{2} \int \rho(\mathbf{r})A^2(\mathbf{r})d\mathbf{r} + E_{ee} + T_c. \quad (73)$$

By multiplying the S system differential equation Eq. (64) by $\phi_k^*(\mathbf{x})$, summing over all the model fermions, and integrating over all space, the noninteracting kinetic energy T_s is obtained as

$$T_s = \sum_k \epsilon_k - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} - \int \rho(\mathbf{r})v_{ee}(\mathbf{r})d\mathbf{r} - \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \rho(\mathbf{r})A^2(\mathbf{r})d\mathbf{r}. \quad (74)$$

In substituting Eq. (74) into Eq. (73) the expression for E becomes

$$E = \sum_k \epsilon_k - \int \rho(\mathbf{r})v_{ee}(\mathbf{r})d\mathbf{r} + E_{ee} + T_c, \quad (75)$$

where

$$T_c = \frac{1}{2} \int \rho(\mathbf{r})\mathbf{r} \cdot \mathbf{Z}_{t_c}(\mathbf{r})d\mathbf{r}. \quad (76)$$

Thus, the correlation-kinetic energy T_c – the contribution of electron correlations to the kinetic energy – is explicitly defined. This is a property of the electronic system not obtainable solely by solution of the Schrödinger-Pauli equation.

Finally, via the mapping to the model S system, it is possible to split the Pauli-Coulomb energy E_{xc} of Eq. (47) into its Pauli E_x and Coulomb E_c components. Defining the Coulomb hole $\rho_c(\mathbf{r}\mathbf{r}')$ as the difference between the Fermi-Coulomb $\rho_{xc}(\mathbf{r}\mathbf{r}')$ and Fermi $\rho_x(\mathbf{r}\mathbf{r}')$ hole charges where $\rho_x(\mathbf{r}\mathbf{r}')$ is determined from $\gamma_s(\mathbf{r}\mathbf{r}')$ as mentioned earlier: $\rho_c(\mathbf{r}\mathbf{r}') = \rho_{xc}(\mathbf{r}\mathbf{r}') - \rho_x(\mathbf{r}\mathbf{r}')$, the Pauli-Coulomb field $\mathcal{E}_{xc}(\mathbf{r})$ of Eq. (29) may be written as a sum of its Pauli $\mathcal{E}_x(\mathbf{r})$ and Coulomb $\mathcal{E}_c(\mathbf{r})$ components:

$$\mathcal{E}_{xc}(\mathbf{r}) = \mathcal{E}_x(\mathbf{r}) + \mathcal{E}_c(\mathbf{r}), \quad (77)$$

where

$$\mathcal{E}_x(\mathbf{r}) = \int \frac{\rho_x(\mathbf{r}\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}', \quad (78)$$

and

$$\mathcal{E}_c(\mathbf{r}) = \int \frac{\rho_c(\mathbf{r}\mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}'. \quad (79)$$

The corresponding Pauli E_x and Coulomb E_c energies are then, respectively,

$$E_x = \int \rho(\mathbf{r})\mathbf{r} \cdot \mathcal{E}_x(\mathbf{r})d\mathbf{r}, \quad (80)$$

and

$$E_c = \int \rho(\mathbf{r}) \mathbf{r} \cdot \boldsymbol{\mathcal{E}}_c(\mathbf{r}) d\mathbf{r}. \quad (81)$$

The total energy E of the interacting system may thus be written in terms of its components as (see Eq. (56))

$$E = T_s + E_H + E_x + E_c + T_c + E_{es} + E_{\text{mag}}. \quad (82)$$

(Note that T_s may be determined either via the field $\boldsymbol{\mathcal{Z}}_s(\mathbf{r})$ through its integral virial expression, or as the expectation value $\langle \Phi\{\phi_k\} | \hat{T} | \Phi\{\phi_k\} \rangle$). It is emphasized that the components of the energy E are properties of the *same* physical system.

The fact that the energy E can be so expressed in terms of these individual components shows the significance of the QDFT mapping to the model system. As such the mapping constitutes an essential complement to Schrödinger-Pauli theory. The mapping to the model system possessing the same basic variables of the density and physical current density provides a deeper insight into the physical system.

The second principal reason for the development of a local effective potential theory such as the QDFT described above, or Kohn-Sham density functional theory, or the Optimized Potential Method, is the easier numerical solution of the corresponding single-particle differential or integro-differential equation. These theories, of course, lead to properties of the interacting system. The QDFT differential equation Eq. (64) is designed to deliver the interacting system density $\rho(\mathbf{r})$, and the current density $\mathbf{j}(\mathbf{r})$. From these properties may be determined all single-particle operator expectation values, the Lorentz ‘force’ and field, and the internal magnetic ‘force’ and field. The highest occupied eigenvalue of the differential equation is the negative of the ionization potential. The total energy E is in turn determined via Eq. (75). In the application of local effective potential theories, approximations must of course be made. For a description of approximation methods within QDFT, such as those of many-body perturbation theory, the Møller-Plesset perturbation theory, or approximations based on electron correlations, the reader is referred to Ref. [3].

V. SUMMARY OF NEW UNDERSTANDINGS AND FUTURE WORK

In this paper, the Schrödinger-Pauli theory of electrons in a static electromagnetic field is described from a new perspective, one that leads to further insights into the quantum-mechanical description of the physical system, and thereby into the quantum mechanics of

electronic structure. The perspective is that of the *individual electron* via its equation of motion, the ‘Quantal Newtonian’ first law. The law is in terms of ‘classical’ fields that pervade all space. The fields arise from quantal sources that are expectation values of Hermitian operators taken with respect to the system wave function Ψ . Hence, the perspective hews to the Copenhagen probabilistic interpretation of the wave function via these quantal sources. The fields obey the equations of classical physics, and are therefore determinate. This determinism is in the same sense as those of the classical electrostatic field between two charges or magnetostatic field between two magnetic poles. In this context, the new perspective is simultaneously probabilistic and deterministic.

As is the case for classical particles in an external field and interacting via Newton’s third law forces, the ‘Quantal Newtonian’ first law is comprised of the vanishing sum of the external $\mathcal{F}^{\text{ext}}(\mathbf{r})$ and internal $\mathcal{F}^{\text{int}}(\mathbf{r})$ fields experienced by each electron. The external field $\mathcal{F}^{\text{ext}}(\mathbf{r})$ is comprised of the sum of the electrostatic $\mathcal{E}(\mathbf{r})$ and Lorentz $\mathcal{L}(\mathbf{r})$ fields. The latter arises from its quantal source, the physical current density $\mathbf{j}(\mathbf{r})$ via the Lorentz ‘force’. In the Schrödinger-Pauli differential equation, the presence of the scalar potential $v(\mathbf{r})$ implies the existence of the electrostatic field $\mathcal{E}(\mathbf{r})$. However, the fact that each electron experiences a Lorentz ‘force’ or field, though implicitly understood to be the case, is not explicitly represented by a term in the Schrödinger-Pauli differential equation or in the Schrödinger equation for electrons in the presence of a magnetic field. Such a term appears *explicitly* in the ‘Quantal Newtonian’ first law. Hence, the ‘Quantal Newtonian’ first law makes explicit our understanding that in the presence of a magnetic field, each electron experiences a Lorentz field $\mathcal{L}(\mathbf{r})$ and ‘force’.

The ‘Quantal Newtonian’ first law also informs that each electron experiences an internal field $\mathcal{F}^{\text{int}}(\mathbf{r})$ comprised of a sum of fields each representative of a property of the system. Thus, the electron-interaction $\mathcal{E}_{\text{ee}}(\mathbf{r})$, differential density $\mathcal{D}(\mathbf{r})$, and kinetic $\mathcal{Z}(\mathbf{r})$ fields are representative of the electron-correlations due to the Pauli exclusion principle and Coulomb repulsion, the electronic density, and kinetic effects, respectively. There is also a magnetic field component $\mathcal{I}_m(\mathbf{r})$ to the internal field. The fact that each electron is furthermore subject to these property-related fields is also not evident from Schrödinger-Pauli theory as presently understood.

The external magnetic field $\mathcal{B}(\mathbf{r})$ thus gives rise in quantum mechanics to both the Lorentz field $\mathcal{L}(\mathbf{r})$ as well as an internal magnetic field $\mathcal{I}_m(\mathbf{r})$ as experienced by each

electron. Interestingly, if the sum of these fields is conservative, then it is possible to describe the contributions of the magnetic field to the quantum system by a scalar (path-independent) magnetic potential $v_m(\mathbf{r})$ similar to the external scalar electrostatic potential $v(\mathbf{r})$.

Another new understanding arrived at via the ‘Quantal Newtonian’ first law is that the Schrödinger-Pauli Hamiltonian \hat{H} is a functional of the wave function Ψ , i.e. $\hat{H} = \hat{H}[\Psi]$. This functional is *exactly known* and *universal*. With the Schrödinger-Pauli equation now written as $\hat{H}[\Psi]\Psi = E[\Psi]\Psi$, it becomes evident that the equation is intrinsically self-consistent. This then allows for the self-consistent determination of the wave function Ψ and eigen energy E . It also allows for the determination of the external scalar potential $v(\mathbf{r})$ for new physical systems that may be created in the future for which the binding potential is unknown. The traditional approach to Schrödinger-Pauli theory, (with the binding potential $v(\mathbf{r})$ known), has been the direct solution of the differential equation for the wave function Ψ . The issue of whether the Schrödinger-Pauli differential equation was a self-consistent one did not arise. On the other hand, all single-particle formalisms such as Hartree, Hartree-Fock, and local effective potential theories, which are derivatives of the Schrödinger-Pauli theory, are intrinsically self-consistent. We now understand that the fundamental equation on which these theories are founded – the Schrödinger-Pauli equation – is itself self-consistent.

In order to obtain additional properties, the (interacting) physical system is mapped via the quantal source-field perspective of QDFT to one of noninteracting fermions possessing the same basic variables of the electronic density $\rho(\mathbf{r})$ and physical current density $\mathbf{j}(\mathbf{r})$, and the same electron number N , orbital \mathbf{L} and spin \mathbf{S} angular momentum. The additional properties obtained thereby are the correlation contribution to the kinetic energy - the correlation-kinetic energy T_c ; the contribution of the electron correlations due to the Pauli exclusion principle to the energy – the Pauli energy E_x ; the correlation contribution to the energy beyond the Hartree energy E_H due to Coulomb repulsion – the Coulomb energy E_c ; the ionization potential or electron affinity. In this manner, the QDFT mapping constitutes an essential complement to Schrödinger-Pauli theory. The model system can also be thought of as being an independent local effective potential theory in which each model fermion experiences the same effective field, and therefore the same effective potential. This allows for an easier numerical solution of the corresponding differential equation.

A generalization of the stationary-state Schrödinger-Pauli theory as described above would be the extension to the temporal case. Hence, in addition to the external

binding electrostatic field $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\nabla v(\mathbf{r})/e$, the electrons would be subject to a time-dependent electromagnetic field: $\mathbf{E}(\mathbf{y}) = -\nabla\phi(\mathbf{y}) - (1/c)\partial\mathbf{A}(\mathbf{y})/\partial t$; $\mathbf{B}(\mathbf{y}) = \nabla \times \mathbf{A}(\mathbf{y})$, with $\mathbf{y} = (\mathbf{r}, t)$. This would then lead to the time-dependent equation of motion for each electron or equivalently the ‘Quantal Newtonian’ second law. The law would then give rise to further insights into time-dependent Schrödinger-Pauli theory as in the present work. One could go beyond the Born-Oppenheimer approximation by assuming a time-dependent binding potential $\boldsymbol{\mathcal{E}}(\mathbf{y}) = -\nabla v(\mathbf{y})/e$.

The stationary-state Schrödinger-Pauli equation can be derived as the non-relativistic limit of the time-independent Dirac equation. For a particle of charge q and mass m in a static electromagnetic field defined by the potentials $\{v, \mathbf{A}\}$, the Dirac equation for the 2-component spinors $\psi(\mathbf{r})$ and $\eta(\mathbf{r})$ which make up the four-component spinor $\chi(\mathbf{r})$, the solution to the Dirac equation, reduces to the coupled equations :

$$E\psi(\mathbf{r}) = c\hat{\mathbf{p}}_{\text{phys}} \cdot \boldsymbol{\sigma}\eta(\mathbf{r}) + (qv + mc^2)\psi(\mathbf{r}), \quad (83)$$

$$E\eta(\mathbf{r}) = c\hat{\mathbf{p}}_{\text{phys}} \cdot \boldsymbol{\sigma}\psi(\mathbf{r}) + (qv - mc^2)\eta(\mathbf{r}). \quad (84)$$

In the non-relativistic limit, the small component $\eta(\mathbf{r})$ can be written in terms of the large component $\psi(\mathbf{r})$. Substituting this expression for $\eta(\mathbf{r})$ into Eq. (83) then leads to the Schrödinger-Pauli equation for the particle. It is first proposed to further generalize the ideas presented in this paper to the above Dirac equation, and then to extend them to the many particle case.

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APPENDIX A: DERIVATION OF THE ‘QUANTAL NEWTONIAN’ FIRST LAW FOR SCHRÖDINGER-PAULI THEORY

Consider first a system of N *spin-less electrons* in an external electrostatic $\boldsymbol{\mathcal{E}}(\mathbf{r}) = -\nabla v(\mathbf{r})/e$ and magnetostatic $\boldsymbol{\mathcal{B}}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ field. The Schrödinger-Pauli theory equation for the system is

$$\hat{H}_{\text{spin-less}} \Psi = E \Psi, \quad (\text{A1})$$

where the Hamiltonian $\hat{H}_{\text{spin-less}}$ (charge of electron $-e$, $|e| = \hbar = m = 1$)

$$\hat{H}_{\text{spin-less}} = \hat{T}_A + \hat{W} + \hat{V}, \quad (\text{A2})$$

with

$$\hat{T}_A = \frac{1}{2} \sum_k \left(\hat{\mathbf{p}}_k + \frac{1}{c} \mathbf{A}(\mathbf{r}_k) \right)^2; \quad \hat{W} = \frac{1}{2} \sum'_{k,\ell} \frac{1}{|\mathbf{r}_k - \mathbf{r}_\ell|}; \quad \hat{V} = \sum_k v(\mathbf{r}_k), \quad (\text{A3})$$

the physical kinetic, electron-interaction, and scalar potential operators, respectively.

A method [2, 18, 58–60] for deriving the ‘Quantal Newtonian’ first law in general is to write the wave function as $\Psi = \Psi^R + i\Psi^I$, where Ψ^R and Ψ^I are the real and imaginary parts, substitute it into the corresponding differential equation, perform the various derivatives, employ the equation of continuity, and after considerable algebra [18], arrive at the law. The law for the spin-less electron is the vanishing of the sum of an external $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r})$ and internal $\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r})$ fields.

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) + \boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}) = 0. \quad (\text{A4})$$

where

$$\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}(\mathbf{r}) - \boldsymbol{\mathcal{L}}(\mathbf{r}), \quad (\text{A5})$$

$$\boldsymbol{\mathcal{F}}^{\text{int}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{\text{ee}}(\mathbf{r}) - \boldsymbol{\mathcal{D}}(\mathbf{r}) - \boldsymbol{\mathcal{Z}}(\mathbf{r}) - \boldsymbol{\mathcal{I}}_m(\mathbf{r}). \quad (\text{A6})$$

The various fields in Eqs. (A4) - (A6) have the same nomenclature and definitions in terms of their respective quantal sources as given in the text. There is, however, a fundamental difference between the law for spin-less electrons Eq. (A4) and that for electrons with spin Eq. (42). This occurs in the Lorentz $\boldsymbol{\mathcal{L}}(\mathbf{r})$ and internal magnetic $\boldsymbol{\mathcal{I}}_m(\mathbf{r})$ field components. The quantal source of these fields – the physical current density $\mathbf{j}(\mathbf{r})$ – is, in this case, a sum of the paramagnetic $\mathbf{j}_p(\mathbf{r})$ and diamagnetic $\mathbf{j}_d(\mathbf{r})$ components.

For electrons with spin, (the Schrödinger-Pauli equation), one could employ the same methodology as described above to arrive at the corresponding ‘Quantal Newtonian’ first law of Eq. (42). Instead of providing this derivation, the law can be more easily derived via comparison by writing the Hamiltonian $\hat{H}_{\text{spin-less}}$ in terms of the current density $\mathbf{j}(\mathbf{r})$. Thus,

$$\hat{H}_{\text{spin-less}} = \hat{T} + \frac{1}{c} \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) d\mathbf{r} - \frac{1}{2c^2} \int \rho(\mathbf{r}) A^2(\mathbf{r}) d\mathbf{r} + \hat{W} + \hat{V}, \quad (\text{A7})$$

with \hat{T} the canonical kinetic energy operator and $\mathbf{j}(\mathbf{r}) = \mathbf{j}_p + \mathbf{j}_d(\mathbf{r})$. However, Eq. (A7) is of the same form as the Hamiltonian \hat{H} of the Schrödinger-Pauli equation Eq. (16). The only difference between these two equations is that in the latter, the current density $\mathbf{j}(\mathbf{r}) = \mathbf{j}_p + \mathbf{j}_d(\mathbf{r}) + \mathbf{j}_m(\mathbf{r})$. Thus, the resulting ‘Quantal Newtonian’ first law Eq. (42) is also of the same form as Eq. (A4) but with the added contribution of the magnetization current density $\mathbf{j}_m(\mathbf{r})$ in the Lorentz $\mathcal{L}(\mathbf{r})$ and internal magnetic $\mathcal{I}_m(\mathbf{r})$ field components. Thus, the ‘Quantal Newtonian’ first law of Schrödinger-Pauli theory is derived.

The ‘Quantal Newtonian’ first law of Eq. (65) for the model noninteracting fermionic system possessing the same $\{\rho(\mathbf{r}), \mathbf{j}(\mathbf{r}), N, \mathbf{L}, \mathbf{S}\}$ as that of the interacting Schrödinger-Pauli system can be derived by writing the single-particle orbitals $\phi_j(\mathbf{r}) = \phi_j^R(\mathbf{r}) + i\phi_j^I(\mathbf{r})$, where $\phi_j^R(\mathbf{r})$ and $\phi_j^I(\mathbf{r})$ are the real and imaginary parts, substituting in the differential equation Eq. (64), and employing the continuity condition.

It can also be obtained by recognizing that the Schrödinger theory and Schrödinger-Pauli theory Hamiltonians \hat{H}_s of the model noninteracting fermionic system (See Eq. (60)) are of the same form. The difference between the two lies in the fact that in addition to the paramagnetic $\mathbf{j}_p(\mathbf{r})$ and diamagnetic $\mathbf{j}_d(\mathbf{r})$ components, there is the presence of the magnetization current density $\mathbf{j}_{m,s}(\mathbf{r})$ in the physical current density $\mathbf{j}(\mathbf{r})$, and thus in the Hamiltonian \hat{H}_s , of the latter. Of course the corresponding differential equations, their solutions $\phi_j(\mathbf{r})$ and the resulting fields of the two model systems differ. But the form of the ‘Quantal Newtonian’ first law is the same.

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