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Electron exchange-correlation in quantum mechanics

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It is shown that Fermi-Dirac statistics is guaranteed by the Dirac current, from which spin-dependent quantum velocity fields and spin-dependent quantum trajectories can be inferred. Pauli's exclusion principle is demonstrated using the spin-dependent quantum trajectories. The Dirac current, unlike the Schroedinger current, is nonzero for stationary bound states due to the permanent magnetic moment of the electron. It is of order c^0 in agreement with observation that Fermi-Dirac statistics is independent of electronic velocity. In summary the physical basis for exchange-correlation is found in Dirac's equation, although Schroedinger's equation may be used to evaluate the Dirac current in the nonrelativistic regime of electronic velocity.

In his little volume from the Benjamin lecture notes and reprint series Richard Feynman [1] raises the point if spin is a relativistic requirement and then answers negatively because the Klein-Gordon equation is a valid relativistic equation for a particle without spin. The answer is not totally correct. The Lorentz-invariant equations of motion (EOM) for a spin-0 particle can be written as the scalar product of its covariant and contravariant four-momenta operating on a scalar wave function,

$$(\frac{1}{c}(i\hbar\frac{\partial}{\partial t} - e\Phi), i\hbar\vec{\nabla})\cdot(\frac{1}{c}(i\hbar\frac{\partial}{\partial t} - e\Phi), -i\hbar\vec{\nabla})\psi = mc\psi, \qquad (1)$$

where $e\Phi$ is a scalar potential. The Lorentz-invariant EOM for a spin-1/2 particle – Dirac's equation - can be written as the scalar product of Dirac's four-vector and the electron's four-momentum operating on a four-component vector wave function,

$$(\gamma_0, \vec{\gamma})\cdot(\frac{1}{c}(i\hbar\frac{\partial}{\partial t} - e\Phi), i\hbar\vec{\nabla})\psi_D = mc\psi_D, \qquad (2)$$

where the first four-vector on the left side of Eq. (2) contains Dirac's beta ($\beta = \gamma_0$) and gamma ($\vec{\gamma} = \beta\vec{\alpha} = \begin{matrix} 0 & \sigma \\ -\sigma & 0 \end{matrix}$) matrices. The scalar product of two four-vectors is always Lorentz invariant; therefore a second step is required to prove the covariance of the four-component vector wave function ψ_D [2].

But it is possible to prove the Lorentz invariance of the spin-1/2 EOM in a single step by writing it as a pair of coupled equations formed by successively taking the scalar products of the electron's mass-renormalized four-momenta $(\frac{i\hbar\partial}{c\partial t} - \frac{e}{c}\Phi \pm mc, i\hbar\vec{\nabla})$ and four-vectors $(\chi, \vec{\sigma}\xi)$ and $(\xi, \vec{\sigma}\chi)$ for upper and lower signs respectively which we introduced in an earlier paper [3] and called four-spinors. We obtain the pair of Lorentz invariants,

$$(i\hbar\frac{\partial}{\partial t} - e\Phi + mc^2)\chi + i\hbar c\vec{\sigma}\cdot\vec{\nabla}\xi = 0 \qquad (3a)$$

$$(i\hbar\frac{\partial}{\partial t} - e\Phi - mc^2)\xi + i\hbar c\vec{\sigma}\cdot\vec{\nabla}\chi = 0 \ , \qquad (3b)$$

which are identically Dirac's equations, where $\psi_D = \begin{matrix}\xi \\ \chi\end{matrix}$ and the wave-function components in ψ_D are respectively Dirac's large and small two-component spinors formed in the usual way from linear combinations of the products of spherical harmonics and alpha or beta spin eigen-functions. Hence we may revise Feynman's answer here by saying that spin is indeed a relativistic requirement in the sense that spin guarantees the Lorentz invariance of a particle EOM having a vector rather than a scalar wave function

How is it then that Fermi-Dirac statistics is obeyed in the permutation symmetry for the exchange of identical electrons in nonrelativistic

quantum theory, in which Pauli's spin vector does not even appear? The answer is found in the Dirac current,

$$\vec{j} = c\psi_D^+ \vec{\alpha} \psi_D \ , \tag{4}$$

which is of order c^0, since c in Eq. (4) is cancelled by the c^{-1} dependence of the small component of the wave function, putting the current squarely in the nonrelativistic regime. A finite current is a physical consequence of the existence of the electron's permanent magnetic moment. The current vanishes in Schroedinger theory for the bound stationary states of an atom because Schroedinger theory has omitted the physics of the electron's magnetic moment.

As we show in the body of the paper it is possible to infer spin-dependent quantum velocity fields and quantum trajectories from the Dirac current for a single-electron Dirac equation. This equation is coupled to the single-electron Dirac equations of the other electrons through the electron-electron Coulomb interaction, which depends on the three spatial coordinates of the reference Dirac equation and on the time through the trajectories of the other electrons. These spin-dependent quantum trajectories show the following properties. If two electrons with the same spin state are assigned the same spatial orbital at initial time,

then their trajectories remain identical for all times, which means that the electrons do not correlate. On the other hand if the two electrons are assigned opposite spin states in the same spatial orbital at initial time, then after a transient they correlate. The correlation is demonstrated (Fig. 1) in two trajectories which exhibit periodic excursions of two electrons to the opposites sides of a point nucleus The physics of correlation – the two interacting electrons mutually recoil to a maximum distance from each other – cannot be captured by standard mean-field theories, in which partial screening of the nucleus and electronic exchange omit the instantaneous response of a reference electron interacting with the other electrons. The physical description of the response requires the entire spectrum of states of the Hamiltonian.

Two electrons in the same spin state but with an assignment of different spatial orbitals at initial time also correlate. Thus Pauli's exclusion principle, which is the rule used in nonrelativistic quantum theory to guarantee Fermi-Dirac statistics, is manifestly observed in the quantum trajectories inferred from Dirac's current. Exchange as guaranteed by the odd permutation symmetry of Slater's determinantal

wave function on the exchange of identical electrons is not a physical effect: if electron correlation is correctly described, it is sufficient to write the total wave function as a simple, unsymmetrized product of atomic orbitals. This point was understood in the early days of quantum mechanics, as discussed in Riley, Schulman, and Musher [4], although virtually all practical applications proceeded from the symmetrization of a product of atomic orbitals.

The observation that Fermi-Dirac statistics is independent of electronic velocity but yet depends fundamentally on the spin-1/2 nature of an individual electron demonstrates the governance of the Dirac's equation even in the nonrelativistic regime in the physics of exchange-correlation and Fermi-Dirac statistics, although to out knowledge practical calculations demonstrating this governance appear not to exist. We may of course evaluate the current using Schroedinger wave functions if we are otherwise in the nonrelativistic regime with respect to electronic velocity. We develop the details of the present theory and present our numerical results in the remainder of the paper.

In Eq. (4) on eliminating the small component in favor of the large component, on assuming the Schroedinger form for the large component

$\psi_S(\vec{r},t)$, and on assuming that $mc^2 >> Z/r$, we obtain the following contributions diagonal in the spin eigenfunctions,

$$j_n(\vec{r},t) = \frac{\hbar}{m}[\mathrm{Im}\,\psi_S^*(\vec{r},t)\vec{\nabla}\psi_S(\vec{r},t) \pm \hat{i}\,\mathrm{Re}\,\psi_S^*(\vec{r},t)\frac{\partial}{\partial y}\psi_S \mp \hat{j}\,\mathrm{Re}\,\psi_S^*\frac{\partial}{\partial x}\psi_S(\vec{r},t)] \ , \qquad (5)$$

for upper (lower) signs for diagonal spin-up (spin-down) contributions. The first term on the right side of Eq. (5) is the Schroedinger current, which vanishes for bound stationary eigenstates. The next two terms for unit vectors in the x and y directions are Dirac contributions which are transverse to the quantization axis.

Velocity and position fields can be inferred from Eq. (5),

$$\vec{\upsilon}(\vec{r},t) = \frac{\vec{j}_n(\vec{r},t)}{\psi_S^*(\vec{r},t)\psi_S(\vec{r},t)} \qquad (6a)$$

$$\vec{s}(\vec{r},t) = \int_0^t dt'\,\vec{\upsilon}(\vec{r},t') \ . \qquad (6b)$$

The trajectory itself is calculated from the expectation value of the position field,

$$\vec{r}(t) = \int d\vec{r}\,\psi_S^*(\vec{r},t)\vec{s}(\vec{r},t)\psi_S(\vec{r},t) \ . \qquad (7)$$

Notice that the wave function density in the denominator of Eq. (6a) Is not cancelled by the wave function density in Eq. (7) due to the temporal integration in Eq. (6b), which archives the history of the

trajectory operator $\bar{s}(\vec{r},t)$ from t'=0 to t'=t.

A time-dependent Schroedinger equation for is written for each electron as follows,

$$(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + \sum_{j\neq i}\frac{e^2}{|\vec{r}-\vec{r}_j(t)|} - i\hbar\frac{\partial}{\partial t})\psi_i(\vec{r},t) = 0 \ , \qquad (8)$$

where the sum runs over all of the other electrons. These Schroedinger equations are solved in the time and Cartesian coordinates using the implicit PDE solver described in a previous publication [5]. Notice that the Schroedinger term in Eq. (4) does not vanish when Eq. (4) is evaluated using the time-dependent wave functions (hereafter called the spectral wave functions) calculated from Eq. (8) since these are superpositions of eigenstates [6]. Although the interelectronic interaction in Eq. (8) is time dependent, we nevertheless find that a solution has a stationary spectrum of states from which we can calculate eigenfunctions by inverse temporal Fourier transformation [6]. These eigenfunctions are then used in Eq. (7) to calculate new trajectories – hereafter called eigentrajectories. Then the many-electron energy is calculated from the expectation value of the Hamiltonian using an unsymmetrized product of the eigenfunctions. The physics of exchange-correlation is captured in the calculation of the interelectronic potential

whose use in the Schroedinger equation causes the spectral suppression of states which violate Pauli's exclusion principle such that a symmetrization of a product wave function to evaluate the the Hamiltonian is unnecessary.

Our results are presented in Fig. 1 and Table 1. Fig. 1 shows late-time trajectories calculated using the the spectral wave functions, eigentrajectories calculated using the eigenfunctions "filtered" [6] from the spectral wave functions, and the energy obtained as the expectation value of the two-electron Hamiltonian. Notice that the maximum excursions about the nucleus of the spectral trajectories are much larger than those of the eigentrajectories, which reflects the excited-state content of the spectral wave functions. The envelop of the spectral trajectories gradually increases with time, reflecting their continuum-state content.

The ground-state binding energy is overestimated by a few percent (Table 1). We believe that that this is due to the difficulty of completely eliminating dissipative or non-energy-conserving errors in the temporal integration of the trajectories, which appears to be especially troubling in the Schroedinger contributions to the current, which are small compared

to the transverse contributions and numerically noisy, as observed from the z-component. Non-energy conserving errors in the integration of the trajectories lead to an overestimation of the binding energy through erroneously large excursions from the nucleus, which lead to an underestimation of the interelectronic potential. The flatness of the envelops of the eigentrajectories in Fig. 1 shows that non-energy conserving errors in the integration of the trajectories have been reduced to an acceptable level.

The Schroedinger x- and y-contributions are also included in the transverse trajectories but appear to be negligible compared to the Dirac contributions. The Schroedinger contributions are possibly unphysical as suggested by their increasing smallness with increasing refinement of the temporal mesh. Notice also that a scheme of solution iterating on the current would eventually extinguish the Schroedinger contributions, which are zero for bound Schroedinger eigenstates.

Notice that the spectral trajectories are strongly correlated over most of the times shown in Fig. 1. This is due solely to the equal and opposite Dirac contributions to the current [Eq. (5)] for alpha and beta spin states, since each electron is assigned the same spatial orbital at initial time. The

singlet excited state (Table 1) is similarly calculated using equal and opposite Dirac contributions and the same spatial orbital at initial time for both electrons except that in this case one of the electrons is assigned to the first-excited member of the spectrum of states generated from the time-dependent Schroedinger equation belonging to the electron which is assigned to the excited orbital. The triplet state is calculated using identical Dirac contributions to the current appropriate for parallel spin states but with widely different orbitals assigned to the two electrons at initial time, as well as assignment of one of the electrons to the first excited member of the Schroedinger spectrum belonging to the electron which is assigned to the excited state. We believe that a perfect calculation in the triplet case would depend on choosing the initial orbital of one of the electrons such that all spectral members lying below the orbital excited state are totally rather than just partially suppressed. Yes it is possible to introduce a physically incorrect electron distinguishability in the choices of initial conditions. Yet it appears that most of any bias which might exist through the choice of initial conditions is reduced to an acceptable level over time as the trajectories correlate, although injudicious initial conditions can be a source of error.

In conclusion we have demonstrated that Fermi-Dirac statistics has a relativistic physical basis in the Dirac Hamiltonian and current notwithstanding that otherwise we may be in the nonrelativistic regime of electronic velocity. We believe that the present theory elucidates the physics of how the spin-1/2 nature of an individual electron affects the motion in the aggregate of many electrons. Finally the theory offers a new computational methodology in which the replacement of the physically correct electron-electron interaction with a mean-field model interaction is eliminated.

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Table 1. Energy levels for He in a. u.

	Present Theory	Variational [7]
1^1S	-3.00250	-2.90372
8001 temporal grid points for 0<t<100 a. u.		
2^1S	-2.14353	-2.14597
8001 temporal grid points for 0<t<200 a. u.		
2^3S	-2.17339	-2.17523
4001 temporal grid points for 0<t<200 a. u.		

The ground-state calculation uses a 32^3 spatial mesh for a square computational box with edge length of 9.4981 a. u. The excited-state calculations use a 32^3 spatial mesh for a square computational box with edge length 15.0773 a. u.

Figure captions

Fig. 1. He ground-state trajectories and energy. $R \equiv$ spectral trajectories (large-amplitude trajectories) in the y direction for the alpha (solid) and beta (dashed) spin states (calculated from Eqs. (6) and Eq. (7) using spectral wave functions); radial eigentrajectories (small-amplitude trajectories) for the alpha (solid) and beta (dashed) spin states (calculated from Eqs. (6) using spectral wave functions and from Eq, (7) using eigenfunctions); energy (flat solid curve near -3 a. u.)