Solitons emerge as non-perturbative solutions of non-linear wave equations in classical and quantum theories. These are non-dispersive and localised packets of energy – remarkable properties for solutions of non-linear differential equations. In the presence of such objects, the solutions of Dirac equation lead to the curious phenomenon of ‘fractional fermion number’. Under normal conditions the fermion number takes strictly integral values. In this article, we describe this accidental discovery and its manifestation in polyacetylene chains, which has led to the development of organic conductors.

1. Introduction

The Nobel Prize in Chemistry for the year 2000 was awarded to Alan J Heeger, Alan G MacDiarmid and Hideki Shirakawa for their discovery and development of conducting polymers. Although the Nobel Prize was awarded in chemistry, the theoretical explanation of conducting polymers came from a completely unexpected area: Quantum Field Theory. In 1976 Roman Jackiw and Claudio Rebbi showed that when fermions interact with background fields with a nontrivial topology, like a soliton, the ground state of the fermion-soliton system can have fractional fermion numbers of $\pm \frac{1}{2}$. More interestingly, their work demonstrated how fermion-soliton interactions in the polyacetylene molecule can induce such novel quantum numbers in that system. Jackiw was awarded the Dirac medal of the International Center for Theoretical Physics (ICTP) in 1998 for his many contributions to field theory, including the discovery of fractional fermion number[1]. In the following, we
describe the broad ideas behind fractionization of the fermion number and its manifestation in different physical systems. For a rigorous introduction to fermion number fractionization, albeit at an advanced level, see the review [2].

2. The Dirac Sea

The marriage of quantum mechanics with special relativity gave rise to a number of successes and problems. To start with, for free particles the Schrödinger wave equation, based on the non-relativistic dispersion relation \( E = \frac{p^2}{2m} \) needed to be modified. The Klein–Gordon (KG) equation, which was a wave equation based on the relativistic energy-momentum relation \( E^2 = p^2c^2 + m^2c^4 \), did not correctly describe the spectrum of the hydrogen atom. More importantly the interpretation of \( \Psi^\dagger \Psi \) as a probability density could not hold, since it could assume negative values. This problem was traced to the fact that the KG equation is second order in time. To rectify this, in 1928 Dirac constructed a differential equation which was first order in space and time, as demanded by relativistic covariance. Though the (multi-component) Dirac equation correctly accounted for the half-integral spin of the electron, it was plagued by the existence of an infinite number of unphysical negative energy solutions, as was also the case with the KG equation.

*It is worth emphasizing that one cannot just “discard” the negative energy solutions since both positive and negative energy states are needed to describe a complete set of states, as should be the case for a Hermitian Hamiltonian.* An electron in a positive energy state could, under a perturbation, cascade to states with progressively lower energy, in the process emitting radiation with a continuous spectrum. Hence, atoms would collapse; the Dirac equation could not describe the dynamics of a stable fermionic system. To avoid this fate of

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1. T P Radhakrishnan, Renaissance of the plastic age: Discoverers of conducting polymers honoured with the Millennium Nobel Prize in Chemistry, *Resonance*, Vol.6, No.2, pp.62–70, 2001.

2. Particles carrying half integral spins like electrons, protons, neutrons are known as fermions, whereas particles with integral spin, like photons, pions are known as bosons.

**Keywords**
Soliton, Dirac sea, quantum field theory, polyacetylene.
The “positive electron”, called a positron, was discovered in 1932, confirming Dirac's brilliant hypothesis.

The electrons in atoms, Dirac postulated that all the negative energy states be filled with electrons. The Pauli exclusion principle would then prevent electrons in positive energy states from occupying negative energy states. The infinite ‘sea’ of negative energy electrons, with their infinite charge and mass, called the Dirac sea, was regarded to be the vacuum, i.e., the ground state of the system. The infinite charge and mass of the negative energy electrons was postulated to be unobservable; only a “departure” from the vacuum state, like an electron in one of the positive energy states, was supposed to be observable. If one of the negative energy electrons could gain enough energy (say by an electric field) to cross the energy gap, it would appear as a real electron. The vacancy left behind in the negative energy state has all the properties of a “positive electron” — for example, it would move in the opposite direction, as compared to a negative electron, under the influence of an electric field. The “positive electron”, called a positron, was discovered in 1932, confirming Dirac’s brilliant hypothesis.

The marriage of special relativity and quantum mechanics inherently describes a multiparticle theory — a single particle interpretation of the Dirac equation would not be consistent. This led to the birth of relativistic quantum field theory, where the one particle wave function \( \Psi \) is interpreted as an operator acting on the Hilbert space of quantum states (number states or Fock states which contain a given number of particles with fixed momenta), which obeys the appropriate equation of motion. It was found that spin zero particles obeyed the KG equation and spin half particles, the Dirac equation. \( \Psi \) is expanded in terms of plane wave solutions of the appropriate equation of motion, with the expansion coefficients being “annihilation” \( (a_p) \) and “creation” \( (a_p^\dagger) \) operators acting on the number states of the Hilbert
Particle and antiparticle states are interpreted as excitations of the vacuum by suitable creation operators acting on the vacuum state.
The Dirac sea does have real and observable effects such as the Casimir effect and the Klein paradox.

The Dirac sea

KG and Dirac field operators is that, while the former obey the commutation relation (2), the latter obey an *anticommutation* relation. This also holds true for the corresponding creation and annihilation operators:

\[ \{a_\mathbf{p}, a_\mathbf{k}^\dagger\} = a_\mathbf{p}a_\mathbf{k}^\dagger + a_\mathbf{k}^\dagger a_\mathbf{p} = (2\pi)^3 \delta^{(3)}(\mathbf{p} - \mathbf{k}) \] (Spin half field).

It is this anticommutation relation which results in the observed fact that spin \( \frac{1}{2} \) fields (and generally all fields with half integer spin) obey Fermi statistics (which states that two fermions cannot occupy the same state or mode).

Since \( \Psi \) is no longer a wave function, but an operator, it is not necessary that its norm be positive definite. Interpreting the vacuum of a fermionic system as an infinite sea of filled electrons did not seem to be necessary in this framework.

However, as we will show, the Dirac sea does have real and observable effects. The reader may be aware of two other manifestations of the vacuum – that of the Casimir effect and the Klein paradox. In this article, we outline the relatively less well known phenomenon of fractional fermion number, which can be interpreted as a result of nontrivial changes in the structure of the Dirac sea. While the same results can be more rigorously derived using the formalism of quantum field theory, the Dirac sea picture has the advantage of making a connection with nonrelativistic quantum mechanics, where the wave function \( \Psi^\dagger \Psi \) is interpreted as a probability or number density of particles.

3. The Fermion Number

If a Lagrangian with Dirac fermions is invariant under a global \( U(1) \) phase transformation \( (\Psi \rightarrow e^{i\alpha}\Psi) \), by Noether’s theorem there exists a conserved current associated with it. The corresponding conserved charge,
To properly define the fermion number we have to subtract the contribution of the vacuum state.

\[ N = \int d^3x \Psi^\dagger(x) \Psi(x). \]  \hspace{1cm} (6)

In terms of the creation and annihilation operators this is written as

\[ N = \int \frac{d^3p}{(2\pi)^3} \sum_s \left( a_{p_s}^\dagger a_{p_s} + b_{-p_s}^s b_{-p_s}^s \right), \]  \hspace{1cm} (7)

where \( a_{p_s}^\dagger \) and \( b_{p_s}^s \) are the creation operators of the fermion and antifermion respectively and \( s = 1, 2 \) are the two spin states of the fermion/antifermion. Because of the anticommutation relations of the \( b \) and \( b^\dagger \) (similar to (3)), we get an infinite contribution when the \( b \) is taken to the right of \( b^\dagger \), since both are evaluated at the same momentum mode. This infinite contribution to the fermion number is simply the contribution of the Dirac sea. To properly define the fermion number we have to \textit{subtract} the contribution of the vacuum state; this can simply be achieved by the following commutator [2]:

\[ N = \frac{1}{2} \int d^3x \left[ \Psi^\dagger, \Psi \right]. \]  \hspace{1cm} (8)

This is the \textit{regularised} or \textit{normal ordered} form of the number operator. One can show, through a careful analysis, that the fermion number of the ground state (vacuum) is simply \(-\frac{1}{2}\) times the difference between the number of positive and negative energy states of the Dirac spectrum (called the “Spectral asymmetry”). We see that, roughly, the fermion number operator goes like \( \Psi^\dagger \Psi \sim |\Psi|^2 \), just as in non-relativistic quantum mechanics where \( |\Psi|^2 \) gives the probability density of finding the particle in a certain region.

We can show, using the notion of \( |\Psi|^2 \) as the number or probability density, in a heuristic way that a \textit{fractional} fermion number may result. Consider fermions interacting with a background field. We denote the energy

\[ \text{To properly define the fermion number we have to \textit{subtract} the contribution of the vacuum state.} \]
The fermion number is measured relative to the free vacuum (which consists of all the negative energy states being occupied in the Dirac sea picture).

eigenfunction as $\Psi_E$ in the presence of the field and $\phi_E$ for the free Dirac field, in which case the $\phi_E$ are just plane waves. (Note that both $\Psi_E$ and $\phi_E$ are spinors as they are solutions of the matrix Dirac equation). The background field would distort the fermion spectrum as compared to the free case and, in general, there could also be bound states in between the mass gap. As mentioned before, we define the regularised fermion number by subtracting the contribution of the free Dirac vacuum; the fermion number is measured relative to the free vacuum (which, we recall, consists of all the negative energy states being occupied in the Dirac sea picture). Interpreting $|\Psi|^2$ as a number density, as in non-relativistic quantum mechanics, the vacuum fermion number density of the interacting fermion system is given by

$$
\rho(x) = \sum_{-\infty}^{0} dE |\Psi_E|^2 - \int_{-\infty}^{0} dE |\phi_E|^2
$$

$$
= \sum_{-\infty}^{0} dE |\Psi_E|^2 - \frac{1}{2} \int_{-\infty}^{\infty} dE |\phi_E|^2
$$

$$
= \sum_{-\infty}^{0} dE |\Psi_E|^2 - \frac{1}{2} \sum_{-\infty}^{\infty} dE |\Psi_E|^2
$$

$$
= -\frac{1}{2} \sum_{0}^{\infty} dE |\Psi_E|^2 + \frac{1}{2} \sum_{-\infty}^{0} dE |\Psi_E|^2.
$$

The integral/sum is over all the states with negative energy, with an integral over the continuum states and summation over the bound states, if any, in the case of $\Psi_E$. Of course, the free Dirac field $\phi_E$ has no bound states and thus no summation is required. The second step follows because the free Dirac spectrum is symmetric with respect to the energy and thus an integral over the negative energy states is simply one half the integral over all states. The third step is because of the completeness relation – the total number of states is the same regardless of the presence or absence of an interaction. Hence, assuming the states are normalized to
Whenever we have degenerate vacua, as in the double well case, there also exist solutions of the scalar field, called solitons, which interpolate between the two vacua. Perturbations around the vacua would never reveal the presence of the solitons, which are thus inherently non-perturbative objects. Whenever fermions interact with such solitons, the corresponding Dirac equation has a zero energy solution in the middle of the mass gap, a nontrivial result which can be proved generally. This is the soliton sector. For a lucid introduction to solitons and their many applications, including fermion fractionization, see [3, 4]. To compute the fermion number in this sector the exact form of the zero energy eigenmode

\[ \langle N \rangle_0 = \int d^3x \rho(x) \]

\[ = -\frac{1}{2} \left[ \int_0^{\infty} dE - \int_{-\infty}^{0} dE \right] \]

The integral above counts the number of states within the specified energy interval; the quantity in brackets is thus the spectral density.

3.1 Zero Modes

An interesting situation arises when a fermion soliton system has a zero energy solution. For simplicity consider fermions interacting with a classical background scalar field with a double well potential structure in one spatial dimension. When the scalar field is at either of the two minima of the double well, from (8), the fermion number operator is

\[ N = \int \frac{dk}{2\pi} \left[ b_k^\dagger b_k - d_k^\dagger d_k \right] \]

One can show that, as a result of the anticommutation property of the $b$ and $d$ operators (5), $N$ has only integral eigenvalues.

Whenever we have degenerate vacua, as in the double well case, there also exist solutions of the scalar field, called solitons.
The fermion number of \( \pm \frac{1}{2} \) for the two degenerate vacua is an eigenvalue of the number operator, not just an expectation value.

is not required. We have to take into account this extra eigenmode solution when expanding \( \Psi \) in a complete set of states:

\[
\Psi_S(x) = \int \frac{dk}{2\pi} \left[ b_k \tilde{u}_k(x) + \tilde{d}^\dagger_k \tilde{v}_k(x) \right] + a \eta_0(x). \tag{12}
\]

Here \( \eta_0 \) is the zero energy eigenfunction and \( a \) is the corresponding expansion coefficient. The state \( \eta_0 \) is charge self-conjugate, i.e., under the charge conjugation operator it goes into itself. The \( k \neq 0 \) constraint means that the integral/sum is over all the non-zero energy states. Substituting this in (8) one can show that the fermion number operator is

\[
N_S = \int \frac{dk}{2\pi} \left[ b_k b^\dagger_k - \tilde{d}^\dagger_k d_k \right] + a^\dagger a - \frac{1}{2}. \tag{13}
\]

The term \( a^\dagger a \) counts the number of electrons in the zero energy state. Since the state has zero energy, the energy of the system does not change if it is occupied by a fermion or not. Hence the ground state is doubly degenerate. If the state \( \eta_0 \) is not occupied the fermion number is \( -\frac{1}{2} \), corresponding to the c-number piece in (13). If \( \eta_0 \) is occupied, then the fermion number is \( -\frac{1}{2} + 1 = +\frac{1}{2} \).

We emphasize that the fermion number of \( \pm \frac{1}{2} \) for the two degenerate vacua is an eigenvalue of the number operator, not just an expectation value. Expectation values can, in general, be fractional in quantum mechanics. For example, a particle tunnelling back and forth in a double well potential spends half its time in either well; the probability of finding it in a given well is one half.

Though the eigenvalue of \( \pm \frac{1}{2} \) is surprising, it is even more amazing that this relativistic field theory model of fermion-soliton interaction finds an application in a “down to earth” condensed matter system – the polyacetylene molecule! In the following we outline this interesting phenomenon.
4. Solitonic Excitations in Polyacetylene

Polyacetylene is a one dimensional array of carbon atoms which can form one of the two degenerate ground states: A (⋯212121⋯) and B (⋯121212⋯) as shown in Figure 1, where ‘1’ and ‘2’ stand for single and double bonds in the configuration of A and B. The degeneracy arises from a spontaneous breaking of the left-right symmetry in the one dimensional chain O, and manifests itself in an alteration of the bonding pattern, as illustrated in the two ground states A and B. The left-right symmetric state with respect to any carbon atom in a long chain of carbon atoms is very much unstable. This instability of the carbon atoms is called ‘Peierls instability’. It is a generic tendency of all systems to remain in a state having minimum energy configuration. Therefore, the system slips into any one of the degenerate ground states A or B. These states are called conjugated chains of polyacetylene having alternate single and double bonds. These states are energetically stable with a large band gap of the order of 1.5 eV and thus behave as semiconductors. However, polyacetylene can be transformed into a conductor by doping it with either an electron donor or an electron acceptor. This is reminiscent of doping of silicon based semiconductors where silicon is doped with either arsenic or boron. However, while the doping of silicon produces a donor energy level close to the valence band, this is not the case with polyacetylene. In the latter case the doping leads to the formation of a defect called soliton (a non-trivial twist of the conjugated chain) in the alternate bonding pattern

Figure 1. Schematic representation of the unstable carbon chain O, the two degenerate ground states A and B, and the soliton state S in poly-acetylene chain. The black dots represent the carbon atoms while the single and double lines represent single and double bonds among the carbon atoms in polyacetylene.
of carbon atoms as shown in the third chain S (⋯121121⋯) of Figure 1. This results in the creation of a new localized electronic state in the middle of the energy gap. At high doping levels, the charged solitons interact with each other to form a soliton band which can eventually merge with the band edge to create true metallic conductivity and thus polyacetylene behaves as a ‘conducting polymer’.

Let us try to understand how a solitonic state in polyacetylene is achieved. A polyacetylene chain is a non-conducting plastic. It is then oxidized or reduced to make it conducting by using an appropriate agent. In case of oxidation an electron is removed from a carbon atom by using an oxidizing agent like iodine. On the other hand, in case of reduction an electron is supplied to the chain by using a reducing agent like sodium. In either case a mobile charge carrier is created in the carbon chain. For the rest of the discussion let us consider the case of oxidation (it is similar for reduction). Here a hole is created in the electronic structure into which an electron from a neighbouring atom can jump, whereupon a new hole is formed and so on. A hole, i.e., lack of an electron, corresponds to a positive charge and thus its movement along the chain gives rise to a net current. In other words the π-bond in the carbon chain moves from one end to the other. This makes the non-conducting plastic a conducting one. The positively charged chain, formed after oxidation, is usually called ‘polaron’. By further oxidation if the second lone-pair electron of the polaron is removed, then this state is called ‘bipolaron’ or ‘soliton’. This is equivalent to removing a π-bond from the polyacetylene chain. Since the π-bond between two carbon atoms is shared by two electrons with same charge and opposite spin, the soliton state has net spin zero but is charged. This is an unusual behavior; in most physical systems spin and charge always come together. This phenomenon in the conducting polyacetylene poly-
mer is called spin-charge separation.

5. Charge Fractionization in Polyacetylene

We have seen that in order to get fractional fermion numbers, there must be a distortion in the Dirac spectrum ($\eta \neq 0$), or zero modes or an asymmetrical number of bound states must be present. As we have seen, this can happen when fermions interact with topological objects like solitons.

The necessary ingredients for fermion number fractionization come together in polyacetylene [6]. They are: (i) phonon fields, the lattice vibrations, which measure the displacement, and (ii) left and right moving electrons which interact with the phonon fields.

Let us try to understand the phenomenon of charge fractionization in polyacetylene chain in a simple manner. We need to consider a defect obtained by removing a $\pi$-bond from the conjugated chain $B$ ($\cdots 12121212 \cdots$) at the fourth link in the form of $\cdots 12111212 \cdots$. By exchanging bonds between fifth and sixth links we arrive at $\cdots 12112112 \cdots$. This is nothing but the $B + 2S$ state shown in Figure 2. This displays the original defect (i.e., $B+2S$) as two more elementary ones. Indeed the elementary defect $B+S$ ($\cdots 12112121 \cdots$) if continued without further disruption of the order, is a soliton interpolating between the ground state $B$ ($\cdots 12121212 \cdots$) on the left and $A$ ($\cdots 21212121 \cdots$) on the right. The fact that by removing one $\pi$-bond we produced two defects, strongly

![Figure 2. Schematic representation of the unstable carbon chain O, the two degenerate ground states A and B, the soliton states B+S and B+2S in polyacetylene chain. The black dots represent carbon atoms while the single and double lines represent single and double bonds among the carbon atoms in polyacetylene.](image-url)
The spin and charge get separated, showing an indirect signature of charge fractionization in the polyacetylene chain.

suggests that each defect would carry a charge $e$ with spin zero since the $\pi$-bond is formed out of two electrons with opposite spin. Thus we don’t get any fractional charge but we find something unusual, i.e., the spin and charge get separated, showing an indirect signature of charge fractionization in the polyacetylene chain.

Intuitively, all this seems mysterious. Though we have given an explanation of how fractional charges can come about in a field theoretic formalism, we know that electrons cannot break or split in half. Any physical system (polyacetylene in our example) is composed of an integral number of electrons, protons, etc. No matter what interactions an electron experiences, it does not physically split into fragments. We have also seen that there is irrefutable experimental evidence, in the case of polyacetylene, for charge fractionization. How, then, does fractional charge arise?

These questions were analysed by Rajaraman and Bell [4, 5]. Rather than going through their careful analysis, which is beyond the scope of this article, we will just present their answer. Unlike field theoretic models, with continuum (and thus infinite) degrees of freedom, the physical polyacetylene molecule is a finite-sized system. They have clearly shown that as long as the system is of finite size, there are no fractional eigenvalues of the charge. However, because of the zero modes, there is a redistribution of the charge, such that a fractional value can be found localised in a finite domain within the system. The remaining part has been shown to be stuck to the edges (i.e., the boundaries) of the system, such that the total charge remains integral. An experimentalist measuring the charge, will thus find a fractional charge near the localisation point.

Electrons confined in two dimensions and placed in a magnetic field perpendicular to the plane is another physical system which exhibits fractional quantum numbers.
At low temperatures this system exhibits a phenomenon called the quantum Hall effect, where the measured Hall voltage can be fractional. The excitations in this system can carry fractional spin and statistics. They are neither bosons nor fermions but somewhere in between! They have been formally christened as “anyons”.

5. Summary

In summary, we have shown, in a very simple setting, how the vacuum of a system of fermions can play an important part in generating novel phenomena like fractional fermion number. Exotic ideas derived from theoretical physics and mathematics may not be far removed from reality. The close interaction between theoreticians and experimentalists may lead to their physical realization on surprisingly down-to-earth systems as the example of polyacetylene reveals. Although fractional fermion number was first realized in polyacetylene chain through solitonic excitation, it is no longer confined to it. It is observed in many different areas in condensed matter physics. In particular, fractional quantum Hall effect and fractional charge in shot noise experiments are prime among them. Many other related concepts like anyons, fractional statistics and spin are still to be confirmed by experiment. The recent discovery of new materials like graphene having a two dimensional structure and making of Bose–Einstein condensates have opened the lower dimensional world for deeper exploration.

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