

Electron–electron interactions in the chemical bond: “1/3” Effect in the bond length of hydrogen molecule

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Abstract. The prominent “1/3” effect observed in the Hall effect plateaus of two-dimensional electron gas (2DEG) systems has been postulated to indicate 1/3 fractional charge quasiparticle excitations arising from electron–electron interactions. Tunneling shot-noise experiments on 2DEF exhibiting fractional quantum Hall effect (FQHE) shows evidence for tunnelling of particles with e and $e/3$ charges for a constant band mass. A “1/3” effect in the hydrogen molecule is seen in as much as its internuclear distance, $d_{H-H} = D^- + D^+$, with $|D^+/D^-| = 1/3$. This is examined in terms of electron–electron interactions involving electron- and hole quasiparticles, (e^-) and (h^+), equivalent to those observed in FQHE shot-noise experiments. The (e/m) ratio of the (e^-) and (h^+) quasiparticles is kept at 1:–3. Instead of a 2DEG, these particles are treated as being in flat Bohr orbits. A treatment in the language of charge-flux tube composites for the hydrogen atom as well as the hydrogen molecule is attempted. Such treatment gives important insights into changes in chemical potential and bond energy on crossing a phase boundary during the atom-bond transition as well as on models for FQHE itself.

Keywords. Electron–electron interactions; quantum Hall effect; hydrogen-molecule bond length.

1. Introduction

Breakthroughs in physics wield considerable influence on theoretical understanding of the main results of the ultimate experimental science dealing with the making and breaking, and the rearranging of chemical bonds. The last such influence^{1,2} was in the late 1920s (Schrödinger equation) and early 1930s (Thomas–Fermi theory). Since that time the opacity of Schrödinger “equators” or exchange-correlation functionals to working bench-chemists^{3–5} (including this author) remains – even if very able computational programmes are able to reproduce the effect of accumulated empirical experience (and errors) of chemists almost instantaneously without feeling. The “recent progress towards better approximations ... is leading to increasingly complicated wave functions whose conceptual meaning is becoming less and less lucid”³. In this article we shall discuss the possible relation that a recent “breakthrough in physics” could have on the understanding of the chemical bond.

One of the more dramatic, if less publicized (relative to, say, high-temperature superconductivity or colossal magnetoresistance or buckyballs), developments in recent times is the consequences of the discovery of the quantum Hall effect (QHE) in two-dimensional (2D) systems⁶. Chief among these is the discovery⁷ of the “1/3” fractional quantum Hall effect (FQHE), Laughlin’s postulate⁸ of a fundamental fractionally charged

excitation or fractional charges, $e^* = \pm e/3$, and their recent experimental verification⁹. Until this time, the quantization of charge in integral units of the electron charge, e , has been one of the basic features in the extra-nuclear, non-quarkian world. Since the FQHE has been shown to be exact in the low-temperature and macroscopic limit, it has been concluded that the measurement of a fractional charge reveals it to be as fundamental a quantum of nature as particles with integral charge – with a difference. The elementary charged excitations, the quasiholes and quasiparticles with fractional charge *do not exist in the absence of the electron–electron interaction*¹⁰. They then represent the fundamental quanta of interactions in an electron gas in solids much as quarks seem to have done for nucleons.

It may be pertinent to inquire into the possible existence of such states at the smallest scale of electron–electron interactions in anisotropic systems – that of the prototype chemical bond in hydrogen molecule. On the basis of what is known so far, it would seem that looking for the equivalence of a fractional charge in the interactions of a chemical bond is far fetched at best. The so-called “exotic” quantum liquid state that gives rise to FQHE is presumed to be a many-electron state in low-dimensions that yields accurate results only in the macroscopic limit and in the presence of an applied external magnetic field. Yet Laughlin’s wave function for such states involves summations which do not lose their validity when a pair of electrons are involved. Moreover, a “1/3” effect manifests¹¹ itself – even if seemingly from numerological considerations only at first – in the interatomic distance, d_{H-H} , of the hydrogen molecule with $d_{H-H} = D^- + D^+$ and $|D^+/D^-| = 1/3$ (see later). It is this that we investigate.

We point out first of all in this communication that in the atomic non-interacting limit, the analysis of integral QHE involving magnetic fields may be extended to the isolated hydrogen atom. The results of the Bohr model for the hydrogen atom are reproduced once we introduce one magnetic flux into the first Bohr orbit, the size of which is determined by purely electrostatic interactions. We then consider the origin of the bonding “1/3” effect in terms of fractional charges or their mass equivalents. This leads to the requirement that equilibrium ground states be described in terms of an universal chemical potential, $\mu_{\text{miv}} = 0$ proposed earlier^{11a}. Our results suggest that we may not require more than the simple two-body effects in the chemical bond to understand some many-body FQHE observations. In making this analysis we shall resort to the simplest analysis based on the novel application^{11a} of the Bohr model to the bonding quasiparticles of the hydrogen molecule. The immediate advantage of this study is that we consolidate on our earlier understanding of the chemical bond in the hydrogen molecule as an universal prototype for the description of all chemical single bonds. Further, there are some important irrefutable conclusions (even if unemphasised) which may help us to understand better the “emergent phenomenon” of the atom-bond transition in terms of spin and charge and their composites^{12–14}.

2. Landau levels and the Bohr radius

According to the currently accepted theories⁶ of QHE, the energy spectrum of a two-dimensional electron gas (2DEG) in the presence of a strong perpendicular magnetic field, B , consists of highly degenerate Landau levels. The solution of the Schrödinger equation for a 2D gas of electrons in a strong perpendicular magnetic field, B , gives eigenvalues of an harmonic oscillator,

$$\mathbf{e}_i = \left(n + \frac{1}{2}\right) \hbar \mathbf{w}_c, \quad (1)$$

where $n=0, 1, 2, 3\dots$ correspond to the different Landau levels. $\mathbf{w}_c (= eB/m)$ is the cyclotron frequency which has no dependence on the size of the Landau levels. The degeneracy of the Landau levels per unit area is given by B/\mathbf{f}_o where $\mathbf{f}_o = h/e$ is the flux quantum. The Hall conductance shows plateaus at ve^2/h with very high accuracy at magnetic fields corresponding to the filling factor, ν , of the Landau level. In FQHE, the filling factor ν is a fraction. The “1/3” effect arises from the observation that prominent plateaus are observed at $\nu = 1/3$. The first shot-noise experiments^{9,14} demonstrated that the ratio of the magnitude of charge on the electron and the fractionally charged quasiparticle is 3:1.

Since the electron’s trajectory in the presence of an external magnetic field is in spiral orbits perpendicular to the direction of the field, Laughlin’s single particle wave functions^{8b} are necessarily eigenfunctions of orbital angular momentum. In the localized electron limit, one obtains a real-space picture of Landau levels as two-dimensional rings with quantized energy levels¹⁵. In the limit of the ground state ($n = 0$ in (1)), the scheme for the Landau levels resembles the Bohr model¹⁶ of two-dimensional planetary orbit, in a more than trivial way. Although the Bohr model was derived at the beginning of the last century simply from the orbit of a negatively charged electron bound to a positively charged core, one perhaps obtains new insights by re-examining the model in terms of the electron spin. We consider a flat Bohr orbit containing one flux and one electron. For a magnetic field, B , and a circular coil area, A , the total magnetic flux, $\Phi = BA$. If the radius of the coil is \mathbf{I} so that $A = \mathbf{pI}^2$, and $\Phi = S\mathbf{f}_o$ for a total number, $n_\Phi = S$, of flux quantum, $\mathbf{f}_o = h/e$, we obtain¹⁷,

$$B = n_\Phi h/e \mathbf{pI}^2 = 2n_\Phi (\hbar/e\mathbf{I}^2). \quad (2)$$

We identify the magnetic length¹⁸, \mathbf{I} , with the first Bohr radius, a_H , such that $A = \mathbf{p}a_H^2$, and the magnetic field corresponding to the first Bohr orbit, $B_{\text{Bohr}}^1 = hS/e\mathbf{p}a_H^2$. The interaction energy¹⁹, $\mathbf{e}_o = B_{\text{Bohr}}^1 \mathbf{m}$, of the magnetic field B_{Bohr}^1 , aligned antiparallel with the magnetic dipole of the electron of one Bohr magneton, \mathbf{m} , is given by

$$\mathbf{e}_o = B_{\text{Bohr}}^1 \mathbf{m} = -\hbar^2 S/ma_H^2 = -me^4 S/\hbar^2 = E_H, \quad (3)$$

when²⁰ $S = 1/2$ and E_H is the total energy (potential + kinetic) of the hydrogen atom in the Bohr model. The energy $\hbar^2/2m_o a_H^2$ is the kinetic energy ($= \mathbf{e}_T$) of the electron so that the potential energy ($= \mathbf{e}_V$) may be equated to an energy $-\hbar^2/m_o a_H^2$ such that the energy $B_{\text{Bohr}}^1 \mathbf{m} = -\hbar^2/2m_o a_H^2$ ($= \mathbf{e}_T + \mathbf{e}_V$) satisfies the virial theorem. The magnetic interaction energy, $B_{\text{Bohr}}^1 \mathbf{m}$, thus satisfies the virial theorem. This result does not seem to be trivial and has not been noticed in the literature – advanced or elementary – by the author (admittedly inexperienced).

The value of the Bohr radius, a_H , used in (3) is obtained *a priori* from the Bohr model using an electrostatic Coulomb interaction potential energy term. *The consequence of the above seems to be that the Bohr radius is a fundamental magnetic length of an electron orbit containing one flux quantum per unit area so as to interact with one Bohr magneton to give one fundamental and maximum unit of interaction energy involving one electron.* In the hydrogen atom this interaction energy is the self energy of the electron’s dipole moment with the field produced by its orbit. It does not seem that the quantized Bohr radius can be obtained from the magnetic interaction energy terms alone unless one introduces the concept of quantized magnetic flux.

The concept of interaction between an orbiting charge and magnetic flux in a tube giving rise to quantization is central to the ideas of the charge-flux-tube composite introduced by Wilczek^{21,22}. The flux tube is visualized as a solenoid with its axis (z axis) perpendicular to the plane of the orbit (x - y plane) of an orbiting charge, q . When there is no magnetic field due to a current in the solenoid, the orbital magnetic moment, $l_z = \text{integer}$. The electron and the “flux tube” to which it is bound are the “composite particle”. When the magnetic field of the solenoid is switched on with a magnetic flux, \mathbf{f} , by passing a current through it, the angular momentum is quantized in terms of $l_z = \text{integer} - q\mathbf{f}2\mathbf{p}$. The phase change on interchange of flux-tube/charged-particle composite is given by $e^{iq\mathbf{f}}$. If the composite is a flux tube + electron, the phase factor is unity with $l_z = (\text{integer} - q\mathbf{f}2\mathbf{p}) = \text{integer}$ (when $q=e$, and $\mathbf{f} = \mathbf{f}_0 = h/e$, a quantum of flux), and the composite behaves as a fermion. When $l_z = (\text{integer} - q\mathbf{f}2\mathbf{p}) = (\text{integer} + \frac{1}{2})$ the composite is a boson. The important quantity²³ is the ratio, $n_e/n_\Phi = \nu$, of the flux quanta to the total number of electrons. The charge-flux-tube composite is now recognized to be almost ubiquitous in important areas of low-dimensional condensed matter of science ever since Jain¹² introduced it in the context of FQHE. It does not seem to have pervaded the low-dimensional regime of chemical bonding and flat Bohr orbits as yet. We shall point out the possible relevance of such charge-flux-tube composite in the context of electron–electron interactions in the chemical bond (see §§5 & 6).

3. Fractional charge and “fractional” Bohr radius

Since the cyclotron frequency, ω_c , of (1) depends on the ratio (e/m), one of the ways by which a fractional charge may become apparent is through the equivalence of the ratios e^*/e (for the same mass) $= \nu = m_o/m^*$ (for the same charge). Electron–electron interactions effectively change the electrostatic potentials thereby changing the effective mass of the participating charges, nuclear as well as extra-nuclear. One may incorporate the effects of the electron–electron interactions in the Bohr model by simply considering changes in the effective mass as expressed by \mathbf{n} . In models for FQHE, these electron–electron interactions are introduced through changes in the charge, e , of the electron. We may do so equivalently in terms of e/m , by changing the mass m , retaining thereby the hydrogen-atom-like character to which the Bohr model may be accurately applied. This would result in fractional changes in the Bohr radius when electron–electron interactions similar to that in the fractional quantum Hall effect are taken into account. Assuming a fractional charge e/q_e where q_e is an integer (or $1/q = p/q'$ where p and q' are mutually prime integers, $p > 1$ and q' odd) with mass, m^q , orbiting a central charge, $-q_n e$, the total energy, E_{tot}^q , is given by

$$E_{\text{tot}}^q = \hbar^2/2m^q r^2 - q_n e^2/q_e r. \quad (4)$$

The corresponding Bohr radius, a_H^q , is given by

$$a_H^q = (q_n/q_e)(m_o/m_q)a_H = a_H/m^*, \quad m^* = (q_e m_q/q_n m_o), \quad (5)$$

assuming that q_n , q_e and m_q are effectively unchanged as functions of r . The relation between m^* and ν has not been established although it has been conjectured upon by Halperin *et al*¹³ who state that “the value of m^* will of course increase $\propto B^{1/2}$ for larger values of B ”.

As mentioned in the introduction, evidence for the influence of the “1/3” effect of the fractional charge in the chemical bond may be seen in the systematics of the changes in

interatomic distances. In a recent empirical development¹¹, the inter-nuclear distance of the hydrogen molecule, d_{H-H} , was found to be a sum of universal atom-independent length components, D^+ ($\approx -0.37 \text{ \AA}$) and D^- ($\approx 1.11 \text{ \AA}$) associated respectively with positive and negative charges such that

$$d_{H-H} = (D^+ + D^-) = 0.74 \text{ \AA}, \quad (6a)$$

and, of direct relevance to this communication,

$$D^-/D^+ = -3. \quad (6b)$$

Equation 6b suggests (from the preceding discussions) that fractional charges (or their equivalents) such as $e^* = -e/3$ and integral charge, e , may have an important role in determining electron–electron interaction in the chemical bond.

The ground state of the chemical bond could contain some important aspects common to that in the 2DEG FQHE. In particular, we extrapolate from the tunneling results in shot-noise experiments that establish the fractional charge. In these experiments^{9,14}, the negatively charged particles tunneling through the positive background are electron-like, while the tunneling through the 2DEG showing FQHE is that of quasiholes with fractional charge $-e/3$. We examine the possibility that the charge transfer in the chemical bond is similar to the tunneling event of electron-like negative charges, e , and hole-like positive fractional charge, $e^* = -e/3$ in the shot-noise experiments. Instead of considering the electron charge, e^* , we consider the e/m^\pm ratio, which is e/m_o for the electron-like negative charge, (e^-) and $-e/3m_o$ for the hole, (h^+). The hole, (h^+), is treated as particle with charge of $-e$ and a mass, m^+ of $3m_o$, instead of a fractional charge of $-e/3$ and mass, m_o .

It is now proposed that instead of having these tunneling particles (e^-) and (h^+) interact with the pair of neutron electrons^{6a}, $e^o - e^o$ in the neutral hydrogen atoms $H_A e^o - H_B e^o$ (H_A and H_B being the positively charged nuclei) participating in the bond in hydrogen molecule. This leads to the formation of opposite and singly charged, spinless composite particles^{11a} ($e^o e^-$) and ($e^o h^+$) with mass m^{ee} and m^{eh} , respectively. These charge transfer states exist together in the ground state of the chemical bond and contribute to the bonding. They have no existence by themselves in isolation. On attaching an electron-hole pair we signify the “the crossing of a phase boundary” *à la* Laughlin^{8c}, in the “emergent phenomenon” of the atom-bond transition due to the charge-transfer electron–electron interaction. Interactions within the composite particles may be simply represented by their reduced masses. In this approximation we obtain

$$1/m^{ee} = 1/m_o + 1/m_o = 2/m_o, \quad (7)$$

and

$$1/m^{eh} = 1/m_o - 1/3m_o = 2/3m_o, \quad (8)$$

where m_o is the mass of the free electron. By treating the composite quasiparticles ($e^o e^-$) and ($e^o h^+$) to be in hydrogen-atom-like Bohr orbits around the positively charged nucleus (H_A or H_B), the masses m^{ee} and m^{eh} yield Bohr radii, $a_H^{ee} = 2a_H$ and $a_H^{eh} = -2a_H/3$ at the minimum of the energy.

As pointed out earlier^{11a}, a negative size is real in the context of an “electron cloud puncture” of the accompanying ($e^o e^-$) bonding quasiparticle. The virial theorem is satisfied separately for the composite particles ($e^o e^-$) and ($e^o h^+$). The more important

result is the conservation of the total energy of the composite particles $(e^o e)^-$ and $(e^o h)^+$ relative to the pair of hydrogen atoms

$$E_{\text{tot}}^{ee} + E_{\text{tot}}^{eh} = -m_o e^4 / 4\hbar^2 - 3m_o e^4 / 4\hbar^2 = -m_o e^4 / \hbar^2 = 2E_{\text{tot}}^H \quad (9)$$

In the model given earlier^{11a}, the negative of a_{H}^{eh} is obtained from energy minimization of the total energy, $E_{\text{tot}}^{eh} = \hbar^2 / 2m^{eh} r^2 + e^2 / r$ when we start with a repulsive interaction between the orbiting charge $(e^o h)^+$ and the positively charged nucleus. It then may be surprising to find, for example, that the energy, E_{H}^{eh} , for the quasiparticle $(e^o h)^+$ is actually negative even when we treat the hole as a positively charged particle. It is important to re-emphasize that we are considering the energies of the quasiparticles taken simultaneously.

4. Universal chemical potential

The changes in energy on the formation of the composite particles $(e^o e)^-$ and $(e^o h)^+$ gives rise to a zero chemical potential. Identifying the chemical potential as $\mathbf{m} = E(N_e + 1) - E(N_e) = \Delta E$ and $\mathbf{m} = 0$ for the isolated Thomas–Fermi-like atom, we may write the sum of the chemical potentials \mathbf{m} and \mathbf{m} respectively, for the $(e^o e)^-$ and $(e^o h)^+$ electron and the hole as

$$\begin{aligned} \mathbf{m} - \mathbf{m} &= \Delta E^+ - \Delta E^- = (E_{\text{tot}}^H - E_{\text{tot}}^{eh}) - (E_{\text{tot}}^{ee} - E_{\text{tot}}^H) \\ &= 2E_{\text{tot}}^H - (E_{\text{tot}}^{ee} + E_{\text{tot}}^{eh}) = 0, \end{aligned} \quad (10)$$

without change in the chemical potential from that of the isolated atom in the ground state. This aspect is consistent with the requirement that at equilibrium the chemical potential of reactant and the product is the same. As discussed by Ganguly^{11a,24}, such a constraint on the equilibrium chemical potential will require that there exists not only an universal equilibrium chemical potential \mathbf{m}_{univ} , but also that $\mathbf{m}_{\text{univ}} = 0$. It also justifies the transferability of the size components a_{H}^{ee} and a_{H}^{eh} in the ground state. It has to be emphasized that in the present case, the chemical potential comes out to be zero because of the “1/3” effect, instead of being imposed upon it (as in the previous communication^{11a}).

The interatomic distance^{11a} of the hydrogen molecule is close to the sum²⁵

$$\begin{aligned} d_{H-H}(\text{calcd}) &= a_{H}^{ee} + a_{H}^{eh} = 4a_H/3 = 0.071 \text{ nm} \\ &\approx d_{H-H}(\text{exptl}) = 0.074 \text{ nm}, \end{aligned} \quad (11a)$$

and, more importantly

$$a_{H}^{ee} / a_{H}^{eh} = -3 = D^- / D^+. \quad (11b)$$

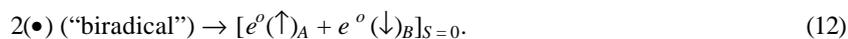
The interesting point is that starting with masses of m_o and $-3m_o$ particles we have generated the masses $3m_o/2$ and $m_o/2$ corresponding to equivalent charges (in the e/m_o sense) of magnitude 1, 1/3, 2/3 and 2 respectively. The early measurements⁶ of the Hall plateaus showing evidence for FQHE had filling factors corresponding to these charges.

There is one other aspect that highlights the common feature of the “1/3” effect in the chemical bond and at in FQHE. Just as extended states are required to carry current of fractionally charged quasiparticle or quasihole excitations of localized states, excited states need to be admixed into the ground state for finite charge transfer reactions to be

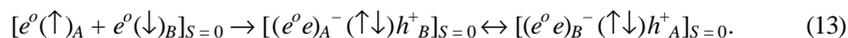
initiated for stabilising the chemical bond. In the case of 2DEG, the extended states render the fractions more “accurately fractional” ($\nu = 1/\text{integer}$, for example) in the thermodynamic limit. In the molecular limit, such an admixture will take the fractions away from ideality always as far as bond lengths and energies are concerned.

5. Atom-bond transition and crossing of phase boundary

The “crossing of a phase boundary”^{8c} in the atom-bond transition occurs because of the violation of conservation laws in the formation of the spinless $(e^o e^-)$ and $(e^o h^+)$ states from two spin $\frac{1}{2}$ electrons. Such a transition requires to be initiated by the pairing of atomic spins in a manner equivalent to the formation of singlet from two radicals (centred, say at nuclei A and B),



Subsequent conversion to charged states²⁶ occurs by a spin-conserving charge transfer written as²⁷



The annihilation of spins is a necessary precondition for the creation of charge. This is reminiscent of Laughlin’s analysis²⁸ of doping with holes a superconducting ground state obeying fractional statistics is to first recognize the neutral particle with a spin, the ‘spinon’ and then remove the electron possessing the spin “*since an electron cannot be removed before its spin state is known*”. Laughlin was addressing himself to the importance of fractional statistics to the $\nu = \frac{1}{2}$ system. The filling factor, $\nu = n_s/n_F$ is the ratio of the electron and quantum flux density. The $\nu = \frac{1}{2}$ state is obtained by the physicist’s artifice of attaching two “magnetic flux tubes”.

We examine spin-pairing in the language of magnetic flux tubes that we used earlier (see end of §2) for obtaining the energy of the hydrogen atom. If B_{Bohr}^{ee} is the magnetic field due to one flux quantum in a first Bohr orbit of radius $2a_H$ and B_{Bohr}^l is the interaction energy of this field with the magnetic dipole of one electron with mass m_o , we find that $B_{\text{Bohr}}^l = -E_H/4$. For a pair of singly charged *independent* electrons, $2e^-$, in a Bohr orbit of radius $2a_H$ we obtain from (2) and (3),

$$E_{\text{tot}}^{ee} = 2B_{\text{Bohr}}^{ee} = -E_{\text{tot}}^H/2.$$

Such an analysis is a consequence of two magnetic flux quanta operating separately on two electrons, e^- without any interaction between the electrons. The charge-flux-tube composite particle model will treat each of the particle as fermions²¹. In the $(e^o e^-)$ composite particle, we may consider the two flux quanta to be attached effectively to one e^- electron, which is a $\nu = 1/2$ state. In this case, the “fictitious” magnetic field arising from the flux tubes exactly cancel each other¹³. This leads to a system of spinless fermions in zero magnetic field. The preferred description of such $\nu = 1/2$ flux tubes is the Cooper pairs of the BCS theory of superconductivity^{13,28}. At the shortest length scales (or highest fields) it perhaps conforms to the chemist’s concept of singlet lone pairs or the bonding pair of electrons in the resonating valence bond description of the metallic state.

The idea of attaching an even number of flux quanta to each electron is central to the composite fermion model of Jain¹² who used it to construct trial wave functions for fractions of the form,

$$\nu = p/(2np \pm 1),$$

where p is an integer. When $n=0$, the transformed fermions are in an integer quantized Hall state, with p Landau levels occupied. The sequence of states obtained with $n=1$, is¹² the principal sequence of odd-denominator quantized Hall states. We note that the two possible states, corresponding to $p=1-\nu=1$ and $\nu=1/3$ states, are obtained straightaway once the energy conserving constraints are imposed on the quasiparticles (see §§3 and 4). If the $\nu=1$ state corresponds to the “emergent phenomenon” of spin-eliminating electron–electron interaction in the spinless $(e^{\circ}e)^-$ particle, we could now associate the bond-stabilising electron-hole interaction to emerge from the spinless $(e^{\circ}h)^+$ particle.

6. Dimensionality and bond energy

In the context of an universal ground state chemical potential, $\mu_{\text{hiv}}=0$, it has been proposed^{11a} that chemical reactions take place to reach the $\mu_{\text{hiv}}=0$ condition with changes in the corresponding energies that appear as the heat of the reaction or as bond energy. In this model, the bond dissociation energy of the chemical bond in the hydrogen molecule is a measure of the charge excitation energy of an electron–hole pair. The maximum additional contribution from the interaction of an electron and its hole is the maximum excitonic binding energy of -6.8 eV ($=-E_H/2$) when the electron and the hole have the free electron mass, m_o . The bond dissociation energy, D_{H-H} , of the hydrogen molecule ($\sim 4.46\text{ eV}$) is nearly $E_H/3 \sim 4.54\text{ eV}$. We have not been able to devise an approach in which we are able to consistently manipulate the Bohr radius to be $3a_H/2$ so that the total energy of two effectively independent or non-interacting electrons would yield an extra binding energy of $-E_H/3$ in hydrogen molecule.

There is likely to be additional constraints arising from the anisotropies inherent in the chemical bond of the hydrogen molecule as distinct from the isolated hydrogen atoms. Such constraints could, in particular, emphasize effects due to non-conservation of spin angular momentum in the atom-bond transition, (13). Unlike the centrosymmetric hydrogen atom, the axially symmetric hydrogen molecule must render the electron–interaction in the system to be less than three-dimensional. We have invoked the idea that the asymmetry of the hydrogen molecule renders the electron-hole Bohr orbit to be two-dimensional in character in the sense that there is a loss in one spatial degrees of freedom. From the virial theorem, one obtains thereby a loss of $6.8\text{ eV}/3 = E_H/6$ in the excitonic binding energy in two dimensions by the virial theorem. The bond dissociation energy of the hydrogen molecule is thus given by $D_{H-H} = -(E_H/2 - E_H/6) = -E_H/3$. If this indeed proves to be the case, then there will be additional support for the idea that an application of the two-dimensional Bohr orbit to quasiparticles participating in chemical bonds may begin to be treated on the same footing as the treatments for the 2DEG FQHE.

7. Conclusions

We have endeavoured to show that the language and main effects – the “1/3” effect – of FQHE throws new insights into the prototype chemical bond of the hydrogen molecule. In return, the previous understanding of the “1/3” effect, $|CR^+/CR|=1/3$, on the internuclear distance, d_{H-H} , of hydrogen molecule, and the energy conserving $\mu_{\text{hiv}}=0$ constraint on the chemical potential at ground-state equilibrium, seems to impose the

simultaneous appearance of various “integral” as well as “fractional” charge (such as e and $-e/3$ along with $2e$ and $2e/3$) in the many-body QHE effect. Some aspects of our approach make strong (but hopefully new) statements regarding the validity of the “primitive” model of two-dimensional Bohr orbits, especially concerning FQHE approach of charge-particle-flux-tube composite.

There is at least one intriguing possibility. Since rate of charge transport from one site to another is formally equivalent to chemical reaction rate, it is possible that spectroscopies, which probe charge-transfer-kinetics could ultimately find evidence for the equivalence of fractional charge. Of particular interest would be the single molecule spectroscopy of large molecules²⁹.

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10. There is evidence of interactions due to charging effects in the Integer Quantum Hall Effect. See Cobden D H, Barnes C H W and Ford C J B 1999 *Phys. Rev. Lett.* **82** 4695; see also Song A M and Omling P 2000 *Phys. Rev. Lett.* **84** 3145
11. (a) Ganguly P 2000 *J. Phys. Chem.* **A104** 8432; (b) Ganguly P 1995 *J. Am. Chem. Soc.* **117** 2655
12. Jain J K 1989 *Phys. Rev. Lett.* **63** 199; Jain J K 1990 *Phys. Rev.* **B41** 7653; Jain J K 1992 *Adv. Phys.* **41** 105
13. Halperin B I, Lee P A and Read N 1993 *Phys. Rev.* **B47** 7312
14. In terms of Schottky’s shot noise theory (Schottky W 1918 *Ann. Phys. (Leipzig)* **57** 541), the magnitude of the charge of the current carriers (flowing independently with uncorrelated Poissonian distribution) is equal to the ratio of the mean square fluctuation in the current to the average current. Such experiments cannot measure the actual sign of the charge carriers.
15. When the magnetic field B is perpendicular to the plane of the orbit, we may choose (in FQHE language) a vector potential which is independent of y coordinate, $\mathbf{A}=(0, Bx, 0)$, and write the quantum mechanical Hamiltonian as (E is along X-direction) $H = (1/2m)(\mathbf{p} + e\mathbf{A}/c)^2 + eE_x$.

This allows a choice of wavefunction which has a plane-wave dependence on the y coordinate and satisfies the solution of the Schrödinger equation with eigenvalues of (1).

16. Although the Bohr model is considered primitive when applied to chemistry, its main conclusions remains valid in several areas of modern physics, the most persistent area being perhaps the area of Rydberg atoms (see Gallagher T F 1994 *Rydberg atoms* (Cambridge: University Press) chap. I and II). The effect of anisotropy and magnetic fields on the reactivity of high Rydberg states is an emerging area (see for example, Clark W and Greene C H 1999 *Rev. Modern Phys.* **71** 821, Bartsch T, Schippers T, Müller A, Brandau C, Gwinner G, Saghir A A, Beitelspacher M, Greiser M, Schwalm D, Wolf A, Danared H and Dunn G H 1999 *Phys. Rev. Lett.* **82** 3779)
17. Usually the magnetic length, l , is given as the cyclotron radius with $l = \hbar/2peB^{1/2}$. When one quantum of magnetic flux is present in the first Bohr orbit, B_{Bohr}^l , the magnetic field is $m_e^2 e^3 (\hbar/2p)^{-3} \approx 2.4 \times 10^5$ T (see Lieb E H, Solovej J P and Yngvason J 1992 *Phys. Rev. Lett.* **69** 749). For a magnetic field $\approx (137 \times B_{\text{Bohr}}^l)^2 \approx 5 \times 10^9$ T one would expect the magnetic length, $l_{137} = a_H/137$, where the fine structure constant, $\alpha = e^2/\hbar \approx 1/137$. For a first Bohr radius equal to l_{137} the velocity obtained from the momentum \hbar/l_{137} would exceed the relativistic limit c . In this case the atom would be unstable in the same manner as atoms with large nuclear charge are unstable (see Spruch 1991 *Revs. Mod. Phys.* **63** 151, and references therein). It is in this context that it may be interesting to note that neutron stars have surface fields of 10^8 – 10^9 T. The stability of relativistic matter with magnetic fields has been examined in terms of the Schrödinger equation (Lieb E H, Siedentop H and Solovej J P 1997 *Phys. Rev. Lett.* **79** 1785).
18. Since the magnetic force is always perpendicular to the velocity, v , the centripetal force acting on a charge, e , due to the magnetic field, B , will result in a circular path with velocity perpendicular to it. The classical expression for the radius of this circle is given by $r = mv/eB$. For a Bohr orbit the momentum from the uncertainty principle is \hbar/r from which we obtain the magnetic length $r = (\hbar/eB)^{1/2}$.
19. The magnetic field arising from orbital motion is $B^{\text{orb}} = m_e v/4\pi r^2 = m_e eL/4\pi m r^3$ where L is the orbital angular momentum. For a hydrogen electron in the $1s$ state $L = 0$ while for a $2p$ electron ($r = 4a_H$), the corresponding field is expected to be 0.3 T. From the expression for the field of the electron in the Bohr orbit, the angular momentum is in terms of $\hbar a_H$ so that the fields are extremely large when the Bohr orbit contains one magnetic flux.
20. This satisfies the Haldane requirement (Haldane F D M 1983 *Phys. Rev. Lett.* **51** 605, that $2S$ is integral. Haldane placed the 2DEG on the surface of a sphere.
21. Wilczek F 1982 *Phys. Rev. Lett.* **48** 1144; Wilczek F 1982 *Phys. Rev. Lett.* **48** 1146; Wilczek F and Zee A 1983 *Phys. Rev. Lett.* **51** 2250
22. Goldhaber A S 1982 *Phys. Rev. Lett.* **49** 905; Jackiw R and Redlich A N *Phys. Rev. Lett.* **50** 555
23. In the presence of a transverse magnetic field, the electronic wave function, $\psi_{\pm p}$ (the + or – sign corresponds to magnetic field in the – or + z direction) of a 2D electron gas is determined mainly by the fermionicity of the electrons. This is determined by the amount the phase factor changes on the exchange of two composite particles. The phase associated with each path has two contributions, the Aharonov–Bohm phase, which depends on the flux enclosed in the loop and the statistical phase which depends on how many electrons participate in the path. The nature of the statistics provides the long-range rigidity to the system.
24. It has been suggested (ref. 11a) that the quasiparticles $(\ell e)^-$ and $(\ell \hbar)^+$ are the precursor states to bond formation. This implies that the chemical bond is formed after charge transfer and that the hydrogen molecule is stabilized in energy relative to that of the isolated hydrogen atoms by the electrostatic interactions between the charge transfer states. The point that requires emphasis is that by such an interaction *in a non-equilibrium state, the bond is stabilized at equilibrium in the zero-chemical-potential state.*
25. The discrepancy between the experimental value of $d_{H-H} \approx 0.074$ nm and our value may be accounted for by the inclusion of, say, 1% of the principal quantum number, $n=2$ states.
26. When $V(r) = 0 = m$ the exchange and correlation are balanced out by the kinetic energy term. The conversion of spin to charge by pairing of electrons results in the residual interactions being only electrostatic in nature with the cancellation of exchange and correlation terms by the kinetic energy term. This cancellation is reminiscent of the early, and trend-setting,

- theorem (Phillips J C and Kleinmann L 1958 *Phys. Rev.* **116** 287; Cohen M H and Heine V 1961 *Phys. Rev.* **122** 1821), involving cancellation of the potential energy terms of core states by the kinetic energy terms
27. See Salem L and Rowland C 1972 *Angew. Chem. Int. Edn. Engl.* **11** 92, for example. The distinction between spin-pairing and charge separation is similar to the proposal of covalent and zwitterion formation
 28. Laughlin R B 1988 *Phys. Rev. Lett.* **60** 2677
 29. Hu D, Yu J and Barbara P F 1999 *J. Am. Chem. Soc.* **121** 6936; Single molecule fluorescence studies on MEH-PPV (poly[2-methoxy,5-(2'-ethyl-hexyloxy)-*p*-phenylene-vinylene]) show that the excitations are at random locations. The fluorescence-intensity vs irradiation-time plots exhibit large amplitude discrete intensity fluctuations with many of the transients exhibiting a small number of quasi-discrete intensity levels. The transitions from the higher intensity levels to a lower level is assigned to the photochemical generation of quenched defects and from a lower level to the higher level to the thermal repair of the quantum defect. Among the candidates for the quantum defects include the “dipolaron” described as a separated radical-cation/radical-anion pair. An examination (even if biased) of the noise in the background fluorescence emission as a function of time does seem to indicate a 1:3 ratio in the noise level of the fluorescence background in the ground state after transitions from the excited state (repair of defects) and in the excited state after transitions from the ground state (generation of defects); see also Vanden Bout D A, Yip W-T, Hu D, Fu D-K, Swager T A and Barbara P F 1997 *Science* **277** 1074