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Unitary Model for atomic structure-

CRITIQUE OF QUANTUM MECHANICS IN CHEMISTRY

(Justification for this critique: The major failures of Quantum Mechanics are in chemistry. These had been overlooked because of the notion, attributed to P.A.M.Dirac, that QM solves ALL the problems of Chemistry and major parts of those in Physics. The difficulties in application to Chemistry are not simply a matter of complicated mathematics involved in the process. There are severe problems of elementary logic. The problem may be indicative of a deeper malaise. It may be the basic premise of QM itself that is questionable. We leave it open and limit ourselves to the deficiencies in the application of QM to Chemistry.

The citations below are mostly to books. The concepts under criticism are part of the School curriculum the world over. They are not abstractions found in fringe literature; hence the importance of the Critique.)

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Part II S. K. Balasubramanian, Science submission no. 116288

ABSTRACT: (Word count 63) The difficulties are dealt with under the following heads:

1. Chirality of molecules and molecular systems: Molecular chirality is incompatible with QM.

2. Aufbau model and its application to chemical systems

3. Molecular systems: ad hoc approaches

4. Electric Current and magnetism

5. Inert Gases, superconductivity and Meissner effect

6. Cold fusion

7. Proton sites and nuclear structure

8. Central dogma

Critique of Quantum Mechanics in Chemistry¹

1. Chirality of molecules and molecular systems.

Chirality is the phenomenon in which molecules having an asymmetric center are known to exist in non-superimposable mirror image forms. Thus glyceraldehyde is known to exist as left-handed and right-handed molecules.

These molecules are separable and are capable of independent existence. They are identical in all respects except the direction in which they rotate the plane of

polarization of plane polarized light. The property is known as optical activity. Chiral systems are fundamental in biology. In entirety life molecules are based on a single chiral sense.

A 1978 paper published in the Journal of the American Chemical Society said that QM does not permit chirality ^{2a}. In a conference held five years later it was concluded that QM applies only to a single molecule and not to a collection of molecules ^{2b}. A single Chiral molecule, if isolated, would lose its chirality. This is strange, to say the least. For all practical purposes we have to take it that chirality is not compatible with QM. The most fundamental phenomenon of Chemistry is not accountable on the QM.

2. Aufbau model and its application to chemical systems.

The aufbau model ³ is central to Quantum Chemistry. It postulates that a certain number of electrons determined by the atomic number occupy extra-nuclear space governed by the exclusion principle. The support for this comes from the interpretation of atomic spectra as transitions from one set of atomic energy levels to another. Problems arise in chemistry in the detailed examination of the energy levels known as orbitals and their shapes.

2.1. Carbon and tetrahedral carbon atom

Carbon is known to be quadrivalent and has a tetrahedral structure. The aufbau model would lead to an atom with a configuration $1s^2, 2s^2, 2p^2$. Ideally this atom is divalent against the observed tetravalency of carbon. To account for the higher observed valence, it is assumed that the orbitals undergo either hybridization or form molecular orbitals at the time of formation of molecules ⁴. The change looks innocuous but is highly irrational. It means equating inequalities. The 2s and 2p orbitals differ in energy and orientation. They cannot be equated whatever the acceptability of the Mathematical procedure. It violates the essence of logic. Bond formation is a primary phenomenon. There cannot be compromise or equivocation at this fundamental level.

In another case we would be postulating a valence of five for one compound of carbon. This would entail the use of one of the 'inner' electrons for bonding which is not allowed in the aufbau model. Such pentavalency is allowed on our unitary model. The division of the extra-nuclear electrons into groups of 'inner' and 'valence' electrons is not rational and exceptions are found throughout chemistry.

The aufbau model with the distribution of electrons around the nucleus is clearly in error. Since the exclusion principle is inviolable we have to suspect that either the assumption of the presence of electrons in extra-nuclear space or the number of electrons around the nucleus may be the source of error.

2.2 Beryllium-Argon

Beryllium poses a different problem. It has the electronic configuration $1s^2, 2s^2$. (Mingos 1998) With closed shells it should be inert. But the element forms simple and complex compounds, because, as is commonly explained, it has a vacant 2p shell. The reverse of this problem is found in Argon. It has a configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$. The 3d shell is vacant. By analogy with Beryllium, Argon should be reactive. It is not.

2.3. Argon-Potassium

Argon has a vacant 3d orbital ³. We know by analogy with Lithium and Sodium that the next element Potassium in the group should have one s electron. So here the convenient assumption is introduced that the 4s shell is of lower energy than the vacant 3d shell. The assumption leads to a circular argument, namely, an assumption treated as an explanation. The situation is worse in the successive period breaks after the higher inert gases.

2.4 Atomic number and periodicity.

The interpretation of atomic number or the position of an element in the periodic table as the number of extra-nuclear electrons depends upon Moseley's excellent work ⁵ on the characteristic frequency of X-ray emissions by elements. Bohr model predicted proportionality between Z^2 and the frequency of the emission, Z being the number of extra-nuclear electrons. The plot of Z against frequency should be a straight line. It was not found to be so. $(Z-1)^2$ gave

straight-line plot. The explanation before 1980 was that an electron dropped into the nucleus to give an effective atomic number of $Z-1$. After 1980 Z is plotted against the square root of frequency ⁶. A straight line is got and is presented as proof of the validity of the concept of atomic number.

This is obfuscation of an excellent experimental result. The change from Z^2 to Z is in effect a compression of the ordinate. Any set of results may be made to give a straight-line graph by suitable compression of the ordinates. So I would say that the Moseley results show a correlation of the frequency of x-rays with the arrangement of the elements in the order of increasing mass numbers. The Correlation of atomic number and nuclear charge should be considered open to question. Besides the generation of x-rays is a high-energy process that is not clearly understood. It should not be made the basis for such a far-reaching conclusion.

2.41- Inorganic fluorides and number of electrons in an atom.

The inorganic fluorides ³ present an interesting picture. Many fluorides are gases. In a gas the intermolecular interactions are minimal. This should be so even in multi-electron systems like Uranium hexafluoride with 86 non-bonded electrons in the inner shells and 6 bonded electrons. Even the formation of the covalent fluoride should be a matter of surprise as the outer shell electron orbitals ($Rn, 6s^2, 5d^1, 4f^3$) have to hybridize themselves to form 6 equivalent orbitals. UF_6 is the heaviest binary molecule and its property of being a gas above $55^\circ C$ shows that it may not have all the required 86 non-bonded electrons on the central atom. The presence of non-bonded electrons on the central atom is not compatible with its gaseous nature.

BF_3 , CF_4 , SiF_4 and GeF_4 are all gases though they have two or more non-bonded electrons. The fluorides of 5th group elements, Phosphorous and Arsenic, show more bizarre behavior. Besides being gases the trifluorides are acceptor ligands and the pentafluorides are Lewis acids. The two elements are normally electron donors. This property is best brought out in Gallium Arsenide where the Arsenic atom donates a pair of electrons to the acceptor Gallium. If such an atom with a

surplus of electrons turns to be an electron acceptor we have to look for a far-reaching change in the electron count consequent on formation of fluorides.

The hexafluorides of Sulfur, Selenium and tellurium confirm the trend. These are gases besides being dielectrics. The last property shows that electron effects are totally and measurably absent in these molecules. Selenium and Tellurium have 10 non-bonded electrons in the outer shells.

The property is not restricted to fluorides. Nickel tetracarbonyl is a gas above 30deg.C though Nickel has six non-bonded electrons in the carbonyl. These examples show that the electron count on an atom may be variable and support our contention that Moseley result should be interpreted with caution and circumspection.

In other words electrons or charges may 'come and go' or, as we prefer to say, 'rise and subside' in an atom. We use the vague expression electrons or charges purposely because we do not know for certain if electrons are involved in chemical bonding. The phenomenon of 'rise and subsidence' of electrons or charges is different from beta decay that involves a rearrangement in the nucleus. Soddy's law of radioactive decay does not apply here. We are dealing with an atomic and not a nuclear phenomenon. In all probability the rise and subsidence of charges is mediated by the weak force. At present we cannot say more.

2.5 Orbital shapes:

There are only three dimensions in Space. These are exhausted with the p orbitals for any atom. With higher orbitals the shapes become bizarre ⁴. They are mathematical constructs and there is no way to realize their reality in physical shapes. The difficulty arises from having to account for the atomic number and exclusion principle together. The two together form a rigid cage from which there is no escape for the theory. The doubtful factor in these cases is the number of electrons on an atom in the context of molecule formation.

The problem may be due to the realities of Chemistry where everything fits into a structure. An unstructured or an abstract mathematical formula has no relevance in Chemistry.

3.Molecular systems: ad hoc approaches

3.1 Zeisse salt

Zeisse's Salt is a platinum complex with ethylene⁷. It represents the worst case of ad hoc assumption in the application of QM to Chemistry. It is our criticism that every time a new bonding phenomenon comes into view a fresh ad hoc assumption is necessary to account for it. Such assumptions are without any basis in theory or experiment. They are anathema to our concept of a theory and are what may be called Procrustean methods after the Greek mythological character Procrustes who would fit his guests to a cot of fixed size and chop off protruding portions or pull parts that fall short. In more popular language one would call it a shifting of goal posts. Such usage is permissible only in Alice in Wonderland. Theoretical inconveniences should be confronted and not plastered over or ignored.

For Zeisse's salt a new bonding mode known as the " σ (sigma) donation - π (pi) back donation bond" is introduced. The carbon atoms of ethylene do not have any more electrons for bonding without opening up the double bond. With the double bond intact in Zeisse's salt, the carbon atoms have to participate in a new bond of the above type. This bond violates all sense of logic. It postulates free energy release where none should be possible. When one goes from A to B and returns to A, it is common sense that there should be no energy change irrespective of the path/s followed. This σ -donation- π -back-donation bond demands that such transit, A-B-A, should lead to an energy gain. It justified the conclusion with mathematics. It should make perpetual motion close to realization.

3.2 Propellane

Propellane (C_3H_6) is a small molecule of great importance⁸. It has the shape of a propellor with an axis. The axis must be a chemical bond since the compound has proven existence and stability below $100^\circ C$. But theory does not allow the bond to exist. The problem arises because in propellane the axis bond cannot be a tetrahedral bond. In the latter the bonds radiate from the central atom to the corners of a tetrahedron. In propellane axis the bond is like the handle of a triangular umbrella with all the bonds facing the same direction. The propellane axis bond is called an "inverted bond".

In this case there is no room even for ad hoc assumption. The theory breaks down totally.

The breakdown of theory in propellane has implication for another fully documented property of the carbon atom, bimolecular nucleophilic substitution. This property is ubiquitous in and exclusive to carbon chemistry and had been exhaustively studied for over 100 years. If there cannot be electron density in the direction of the inverted bond, substitution reaction should not occur. Indeed it is known not to occur with other elements.

3.3 Boron

Boron chemistry is another case of total breakdown of theory. Boron should have 5 electrons or the configuration $1s^2, 2s^2, 2p^1$.⁴ It should be trivalent after ad hoc hybridization. It shows variable covalency. In the trifluoride BF_3 it is trivalent. Boron hydrides show strange structures. The simplest is diborane B_2H_6 . It has the two hydrogen atoms located in the space between boron atoms. One hydrogen atom is above the plane of the rest of the molecule and the other is below the plane. A new bond type is introduced here - "two electron three center bond" A normal chemical bond is a two-electron two-center bond. Crystalline Boron is worse. It is one of the hardest materials known. It contains Boron icosahedra that cannot be visualized on the aufbau atom.

We may sum up the ad hoc assumptions in the application of QM to Chemistry: hybridization, σ -donation- π -back-donation bond, and two-electron-three-center bond.

3.4 Oxygen paramagnetism

Molecular oxygen shows paramagnetism⁹. This was described as a prediction of the Molecular Orbital method and was considered to validate the procedure. Oxygen molecule would have a plane of symmetry across which all moments should cancel out. This plane has to be a chiral plane in molecular oxygen for moments do not cancel out across a chiral plane. They retain their opposite sense like the poles of a magnet. A chiral plane means structure at the atomic level in oxygen. Such a structure is not allowed in QM. This 'structure' is responsible for antiferromagnetism displayed by FeO and MnO. The moments acquire opposite sense across a chiral plane mediated by oxygen.

Magnetism is also a chiral phenomenon. The model for the iron $^{26}\text{Fe}_{56}$, based on the assumptions of the Unitary Model atom is made up of two chiral halves that account for the two poles of the ferromagnet.

3.5 Anthracene linear dichroism

Crystalline anthracene shows linear dichroism¹⁰, an indication of dissymmetry in a molecule that looks perfectly symmetrical. Linear dichroism is correctly described as anisotropy in the absorption of polarized light. We had drawn attention to the possibility of q-surface fixation in our comments on anthracene electron density diagram. Q-Surface fixation is responsible for the linear dichroism of anthracene that cannot be accounted for by the QM.

4. Electric Current and magnetism^{5, 11}

(23 February 09)

Magnetism and electricity are related phenomena. Magnetism is capable of transmission through space whereas electricity would need a medium for transmission.

We shall consider electricity first.

The characteristics of electricity are as follows:

It needs the medium of a conductor for transmission. It does not pass through space.

Its speed had not been measured but it appears to be high comparable to that of light. It would need enormous energy to accelerate the electron, a particle with mass, to such high speeds.

The voltage is the driving force for the flow of electricity. The speed is however independent of the voltage. High voltage current and battery-based current (12v) used in copper cable telephony travel at the same apparent speed. These two facts would preclude any particle with mass like the electron as the carrier of electricity.

Electric current should therefore necessarily be considered a vector field carrying 'charge'. That it is a helical field follows from the fact that the current flowing through a conductor penetrates only a few atoms deep below the surface. Any other configuration for the current like the wave would require deeper penetration. The carbon nano tubes obtained by sparking at graphite electrodes have aromatic rings arranged in a helical fashion. The last important fact is that alternating current has two halves. Their individuality could be explained only in terms of chiral helical fields for the two parts of the AC.

It is known that a positron and an electron annihilate each other. While energy helices may form double helices without annihilating each other the charge vector helices may annihilate each other giving rise to photons. There is therefore no possibility of formation of a double helix with unlike charge vector helices.

Since like charges repel each other there would be no double helix corresponding to dark energy.

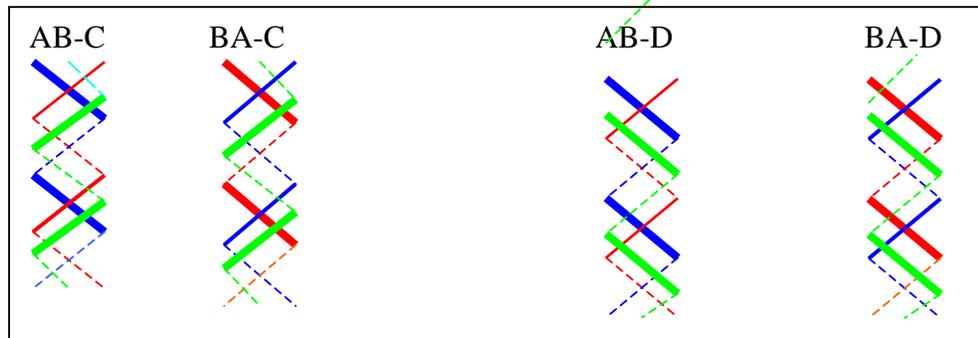
Magnetic fields travel through space. Unlike light they do not travel in straight lines with no specific target. They travel from one magnetic pole to the opposite pole. We have seen such charge vector fields cannot form double helices with both like and unlike helices. Magnetism then is a charge vector field formed by a single helix riding on some medium. Low frequency radiation with a double helical structure would be ideal for this purpose. Radiation provides the 'piggy back' for the charge vector to ride upon. In this view there are four possibilities for the charge vector to form a three-stranded helix with radiation.

If the chiral double helices of radiation are designated AB and BA (red and blue lines) and the chiral helices of opposite electric charges are designated C and D (greenish yellow) there are four possibilities in which the charge helices might form a three-stranded helix with radiation. These are AB-C, AB-D; BA-C and BA-D.

If AB-C and BA-C would designate, say, the North Pole and AB-D and BA-D should designate the South Pole of a magnet. The magnetic field lines between the two poles are represented by these two combinations. These two combinations, {AB-C: BA-C) and {AB-D: BA-D) are also present in the magnetic fields in outer space.

The charge vectors C and D determine the character of the field. The radiation that carries these vectors does not make any contribution. We had pointed out that light would flow in the same direction even in chiral (non super imposable) mirror image universes. This is because the double helix radiation vector (AB-BA) is identical with its mirror image.

(AB-BA || AB-BA)



Radiation helices- Blue and red lines; Charge vector helix yellowish green.

5. Inert Gases, superconductivity and Meissner effect^{5, 12} (Beiser 2004, Scurlock 1992)

Under Beryllium we had argued that Argon should not behave like an inert gas since it has unfilled electron shells. We prefer the alternate assumption that there are no extra-nuclear electrons in inert gases. The spectra are observed under high-energy excitation of the atoms. We examine below the implications of our assumption.

5.1 Liquid Helium^{12, 13}

As we said earlier the inert gases do not have any extra-nuclear electrons. Helium falls in this category. Inter-atomic attraction must be nil in the gas and accounts for its highest atomic volume for any element. Even the so-called 'volume' is due to gravity and not due to weak attractions between atoms. Liquefaction of helium means that the atoms of Helium had lost all their kinetic energy and settled under gravity. This is He-I. Because there is no inter-atomic attraction the liquid has no surface tension or viscosity. It is not a liquid in the conventional sense but only a collection of atoms settled under gravity. It still has atoms vibrating about a mean position. Further cooling arrests even this pseudo motion to give He-II. There is no phase change in going over from He-I to He-II. Gravity would continue to pull these atoms downwards. In response to this force a mono-atomic layer would move upwards along the walls of the vessel and flow

over in a siphoning action. Thus all the properties of Liquid Helium are explained without invoking super-fluid or a special state of matter.

5.2 Meissner effect and superconductivity

Meissner effect is the disappearance of magnetic properties under superconducting conditions.⁵ (Beiser, 2004) The two effects are related. As we had seen in Helium, in extreme cold complete electron or charge subsidence takes place. In superconducting systems the electron subsidence is full and complete. We may now define the conditions anticipated for superconductivity. There should be continuous contact at the molecular or atomic level in the superconducting state. The electron or charge subsidence should be complete. The metallic state provides for continuous contact. Even here metals with 'closed shells' like Lead, have an advantage in that they start with a partly electron or charge subsided state. But metallic state is not an imperative condition. Some mixed oxides have been found to serve the purpose.¹³ (Vidali 1993) The electronegativity of oxygen serves to make charge subsidence easier. We had noted the subsidence effect of fluorine atoms in binary compounds. It is not surprising that Boron Nitride has a high super-conducting temperature. The ideal system would be a fluorine-containing metallic polymer like a continuous thread of teflon.

6. Cold fusion¹⁴

Electron or charge subsidence provides a simple explanation for the nuclear fusion at near room temperatures observed by Taleyarkhan and his colleagues under conditions of bubble collapse. The conventional explanation preferred by the authors is that bubble collapse creates immense pressures of the order of a few million atmospheres and similar high temperatures. This assumption violates common sense. A simpler alternative is the assumption of charge subsidence. The first step is the generation of low energy deuterium radicals by the sonar fission of carbon deuterium bond. It would be facilitated by the presence of the adjacent keto group in the deuterated acetone. Alternatively the deuterium atoms may arise from the enol form of the deuterated acetone. Complete fission is not

absolutely necessary for the purpose. Charge subsidence on the D-atom then takes place to give a dineutron.¹⁵ One would expect the subsidence to be more facile at lower temperatures. This is indeed found to be the case. Fusion is observed only close to 0° C. Bubble collapse brings the neutral deuterium atoms or dineutrons within the range of strong nuclear force. Fusion under these conditions is automatic. The probability of the particles being brought within the range of the strong force is of course very low. Consequently the fusion observed is not much. A few million atoms fuse over 12 hours. This would work out to a miniscule 10^{-18} gm. Moles. A corollary is that the Coulomb repulsion is an over-rated obstruction for fusion. Fusion at ordinary temperatures is known even for heavier atoms like lead (atomic number 82) and chromium (atomic number 24)⁴(Greenwood 1997) which fuse to give Seaborgium (atomic number 106).

7. Proton sites and nuclear structure

Nearly 100 years have passed since the discovery of the atomic nucleus. In spite of all efforts we are nowhere near an acceptable view of the structure of the nucleus.^{15, 16, 17}

We have assumed that the nucleus has protons and neutrons but we have no idea about their location. The simple idea that the covalent bonding sites might be proton sites had not been considered. It is also more easily understood that proton or charge sites in the nucleus may all be located on the periphery or the outer surface of the nucleus. In the case of co-valence of Carbon, the tetrahedral carbon survives in all the bonding patterns. Further the swinging olefinic bond, that we find in Zeisse's salt, raised the question of the permanence of electrons in the atom. We have adduced evidence that electron count is variable depending upon the bonding pattern. Additional chemical evidence also indicates that the electrons or charges may rise and subside as the context demands. Because of the survival of the tetrahedral structure in all bonding contexts in carbon, there is no chance for probability about the behavior of electrons. This is the fundamental conflict between our model and QM. A wider debate is called for.

8. Central dogma

The assumption that underlies the quantum model is that the nucleus acts as a point charge holding the electrons within the atom and does not have any influence on the behavior of electrons^{1b} Whatever the validity of the idea in other areas we find that it is not valid for chemical systems. We have indicated that this might be because in chemistry we deal with individuality that cannot be subject to probability considerations. Thus the entire area of quantum mechanics is open to debate. The late J.T. Cushing in his book¹⁸ on the origins of the probability says the idea was accepted due to a 'social contingency' because scientists did not want to leave the field open to doctors of divinity. This is unfortunate. We are facing the consequences of the regressive notion that lacked the objectivity required of scientists.

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