



QUANTUM CONFINEMENT EFFECT LINKED DYNAMICAL ANALYSIS OF QUANTUM NANO-MATERIALS APPLICABLE IN ELECTRONIC DEVICE STRUCTURES

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Abstract: Various research papers have discussed quantum mechanical study of many homo/hetero Nano-structured (NS) materials. In this paper, we wish to propose some efficient nanostructured semiconductor materials on the basis of quantum mechanical analysis (model) of Quantum Confinement Effect (QCE) in terms of its electronic properties for electronic devices.

Quantum confinement effect (QCE) in Nano-Structured (NS) materials (quantum materials) is essentially because of the changes in the energy levels (quantum) and very small length scale on the closely spaced discrete energy levels within a very narrow energy band.

In other words, QCE as a reduction in allowed phase space, i.e. if we decrease material particle's size to Nano scale ($1\text{nm}=10^{-9}\text{m}$), the decrease in confining size creates the energy levels discrete (Quantized) and the band gap (E_g) energy increases and the number of discrete energy levels also increases. Due to this QCE in Nano-structured materials, significant changes occur in electronic and optical properties of materials.

The QC of electrons and holes in Semiconductor Nano-structures (SNS) means limiting their movement (quantized) in the Euclidian 3D space with dimension of their de Broglie wavelength.

The consequence of this confinement in phase space is the quantization of their momentum and energy. In this case, they are subjected to the principles of quantum mechanical motion rather than classical mechanical motion.

Index Terms - Band Structure; Energy levels; Euclidian space; Hilbert Space; Nano-structures; Phase space; Wave function.

I. INTRODUCTION

Using quantum mechanical band structure of semiconductor materials (Block's Theorem) within the regime of band theory of solids, we are interested in dynamics of electrons CB and holes in VB. QCE in the quantum dot with states of energy density, $\rho(E)=g(E)=\frac{\partial N}{\partial E}$ with respect to number of states per unit volume N as shown in Fig (1) and Fig (2). Energy bands are closely spaced allowed quantum energy levels within a narrow energy range. [1]

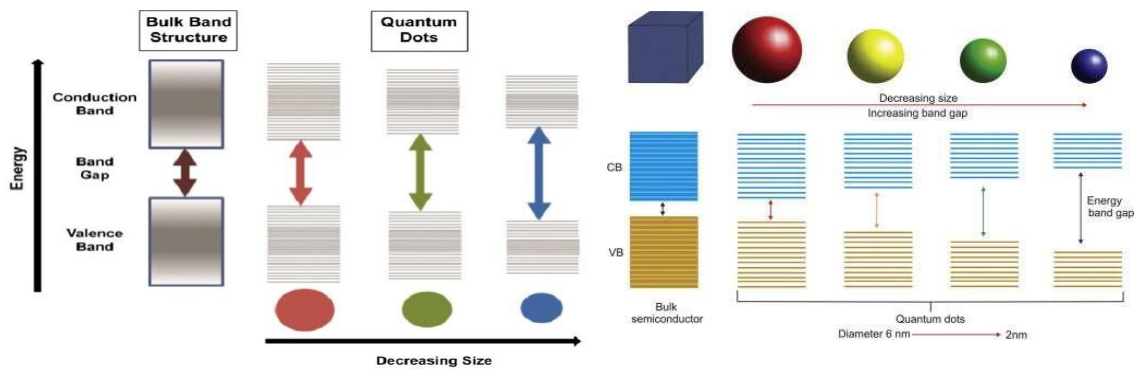


Fig (1) Decreasing in confining size creates quantized energy levels with increased band gap.

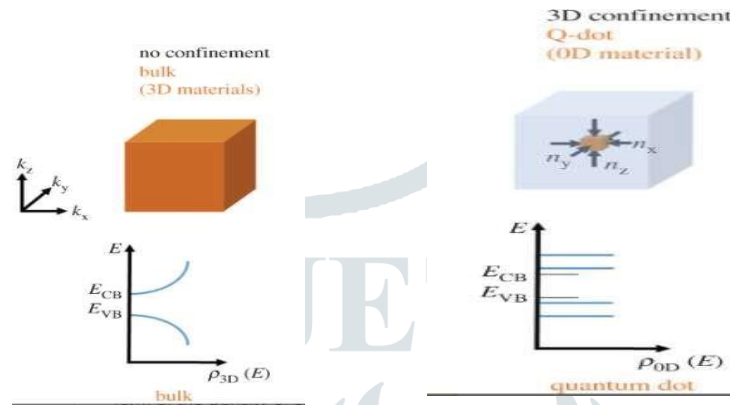


Fig (2) NIL QCE in 3D bulk material and 3D QCE in QD with DOS

Electrons as charge carrier treated as classical particle with total energy, $E = \frac{p^2}{2m}$; linear Momentum, $p = mv$, non-relativistic Fig3 (a) relativistic Fig3(b) and quantum mechanically is shown in Fig3(c) [2]

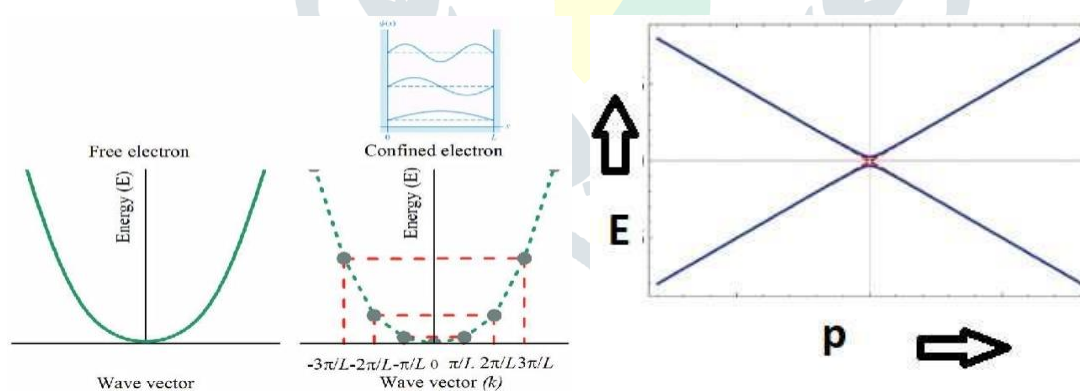


Fig 3(a) Classical non-relativistic

Fig 3(c) Quantum mechanical

Fig 3(b) Classical relativistic

F. Bloch (Bloch Theorem) gave Quantum theory of electrons in solids as a solution of Schrodinger differential wave equation in quantum mechanics for Bloch periodic potential called Bloch wave functions.

$$\psi_{\vec{k}}(\vec{r}) = U_{\vec{k}}(\vec{r}) \cdot \exp(i\vec{k} \cdot \vec{r}) \quad \dots\dots\dots (1)$$

Where $U_{\vec{k}}(\vec{r})$ has the period T of crystal lattice with $U_{\vec{k}}(\vec{r}) = U_{\vec{k}}(\vec{r} + T)$, which is the origin of band theory of solids as shown in Fig3(c).

The energy Eigen state is in Hilbert space, which is a type of vector space, characterized by inner product, norm, orthonormal basis and unitary operators etc. Position vector $\vec{r}$ is in three-dimensional Euclidian space (simpler form of Hilbert space). [4]

Eqn. (1) above indicates that for certain value of momentum $\vec{p}$, no energy states are available there, called forbidden energy states restricted by quantum mechanical selection rule (Band Gap). Later P.A.M-Dirac showed that electron has spin (a purely q.m. property) and the existence of anti-particle (positron) of electron, experimentally proved true. As mentioned earlier, in Fig (2), quantum confined structures is best summarized for DOS with momentum wave vector k , as

$$\vec{k} = \frac{2\pi}{\lambda} = \frac{2\pi\vec{p}}{h}, \lambda = \frac{h}{p} = \text{De Broglie wave length}$$

In 4D (quantum time crystal) nano-material density of states (DOS) is dependent on delta function including spin states. In bulk (3D) materials, DOS is directly proportional to $E^{0.5}$. In QW (quantum well) / super lattices/ ultra-thin films (2D) DOS is directly proportional to E^0 . = constant. In QR (quantum wire)/ nano tube (1D) DOS is inversely proportional to $E^{0.5}$.

For quantum dot (QD)/Nano crystal (NC), (0D-Zero degrees of freedom), nil field states in k space for discrete number density DOS as

$$g_{0D}(E) = 2 \sum_{n_x, n_y, n_z} \delta(E - E_{n_x, n_y, n_z}) \text{-----} (2)$$

δ – delta function

And with effective mass solution gives

$$E_{n,m,l}(k_x, k_y, k_z) = \frac{\pi^2 \hbar^2}{2m^*} \left(\frac{n^2}{L_x^2} + \frac{m^2}{L_y^2} + \frac{l^2}{L_z^2} \right)$$

$$\psi(r) = \phi(x)\phi(y)\phi(z) \text{-----} (3)$$

Where, $m^* = \frac{\hbar^2}{\frac{\partial^2 E}{\partial k^2}}$ = effective mass of electron.

For example, an estimate of CdS/ZnS QD core radii bulk properties $m^* = 0.13m_e$, where m_e = electron rest mass $= 9.1 \times 10^{-31} \text{ kg}$. Effective mass m^*_{ij} is a tensor for anisotropic (hetero structure) materials as $m^* = \frac{\hbar^2}{\frac{\partial^2 E}{\partial k_i \partial k_j}}$

Particular energy Eigen value E_{ni} of a particular Eigen state, $E_{ni}, i = x, y, z$ is the quantized energy of a particular confinement direction.

$E_{n_x, n_y, n_z} = \text{Sum of } E_{n_x}, E_{n_y}, E_{n_z}$. $\hbar$ is reduced Planck's constant. $n, m, l \rightarrow 1, 2, \dots$ etc.

The quantum confinement numbers, L_x, L_y, L_z , are the confining dimensions: $\exp i(\mathbf{k} \cdot \mathbf{r})$ is the wave function for describing the electronic motion in x and y directions, similar to electronic wave function.

II. TYPE QUANTUM MECHANICAL BASIS FOR MODELING QUANTUM CONFINEMENT EFFECT (QCE)

Effective mass in Density Functional Perturbation Theory (DFPT) framework with Heisenberg's picture of matrix QM gives [3]

$$(m_{nk}^*)_{\alpha\beta} = \frac{1}{\varepsilon_{nk}^{\alpha\beta}}$$

$$= \langle u_{nk} | \hat{H}_k^{\alpha\beta} | u_{nk} \rangle + \left(\sum_{n' \neq n} \frac{\langle u_{nk} | \hat{H}_k^{\beta} | u_{n'k} \rangle \langle u_{n'k} | \hat{H}_k^{\alpha} | u_{nk} \rangle}{(\varepsilon_{nk} - \varepsilon_{n'k})} \right)$$

+ c.c. 4(a)

For non-degenerate Eigen energy states.

$\hat{H} \rightarrow$ Hamiltonian Operator, $|\psi_{nk}\rangle$
 $\rightarrow$ eigen(ket) wave function, $\alpha, \beta \rightarrow (x, y)$
 $\rightarrow$ Cartesian direction for x and y .

c.c.--complex conjugate of previous term.

1st Bohr excitonic radius a_B^{ex} of a particle defined as [4]

$$a_B^{\text{ex}} = \frac{\epsilon m_0}{\mu} \cdot a_B^H \text{ for } n = 1 \text{-----} 4(b)$$

Where ϵ is Permittivity/dielectric cont. of the homogenous/isotropic semiconductor/other materials, for heterogeneous/anisotropic materials it is a tensor of rank two, m_0 = rest mass of electron, μ reduced mass of exciton ($\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$); m_e^* = electron reduced mass; m_h^* = hole reduced mass and

$$a_B^H = 1^{st} \text{ Bohr radius of hydrogen atom} = \frac{h^2 \epsilon_0}{\pi m_e^2} \approx 0.53 \text{ \AA}$$

Formation of bound state of electron and hole bound together are to be considered as “exciton”, a “Quasi-Particle”. Is due to coulombian attraction is shown in Fig (4) with comparative size of quantum dots (QD). – (5) It is experimentally confirmed that exciton, an electrically neutral “Quasi Particle” exist in semiconductor, Insulator and some quantum liquids [5,6].

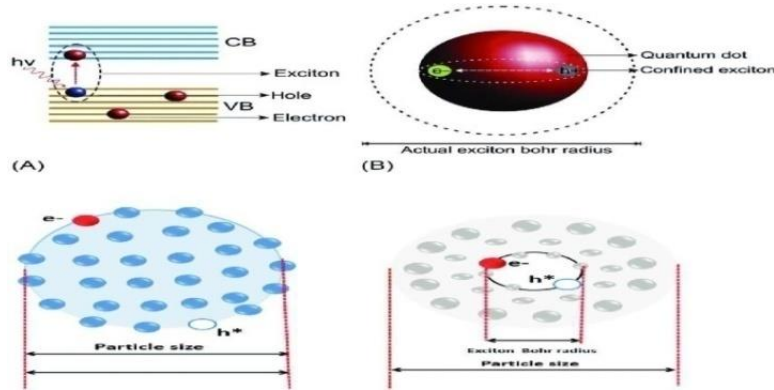


Fig (4) Formation of Exciton (QP) due to Coulombian attraction

“Exciton” follows Bose-Einstein Quantum statistics (Boson) in contrary to its constituent particles *i.e.* electron and hole follow Fermi-Dirac statistics (Fermion).

When a semiconductor/crystal lattice quantum oscillation (phonon) absorbs a photon (quantum e.m. radiation) of energy $E \geq E_g$, an electron is lifted in CB from VB leaving a hole in VB in the context of Band theory (Quantum) of solids as shown in Fig 5(a)& 5(b).

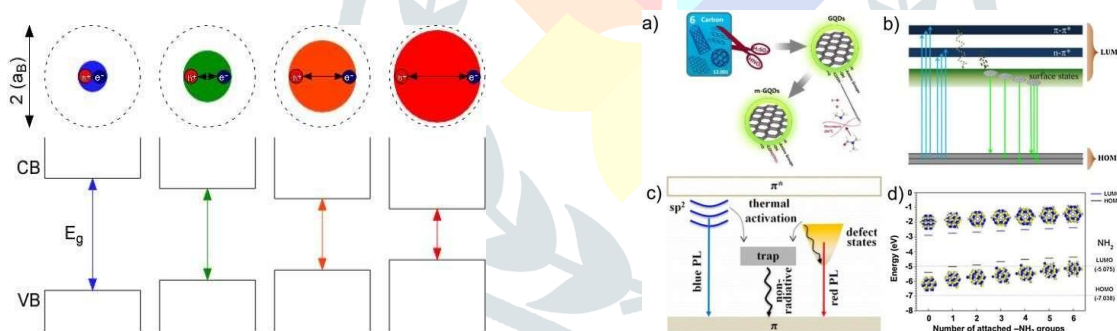


Fig 5 (a) and Fig 5 (b) Electron and hole transition in band theory of solids

$$\text{Three-dimensional Spherical exciton radius is given by } r = \frac{\epsilon h^2}{\pi \mu e^2} \dots \dots \dots (5)$$

ϵ = Permittivity of the given material; e = electronic charge = $1.6 \times 10^{-19} \text{ C}$; h = planck's constant.

The electron – hole separation is about 1nm to 10nm for most of the semiconductor crystals due to its imperial radius and mass calculation.

QC increases the “Oscillator strength” which is understood by studying the dipole matrix element with insight in to electronic transmission selection rules.

The edge of absorptions spectral lines moved to higher end due to QCE and is proportional to DOS, confirming discrete transition in absorption spectra [7].

In heterostructures NS, Q.M un allowed states becomes allowed due to removed degenerate states [8].

The representation of quantum confined semiconductor systems in effect mass approach is given by the product of Block wave function and envelope function for its initial and final states along quantum confined axes. The product in the inter band transition is given by matrix element as [9, 10],

$$\epsilon_{pl} < u_{vk}(\vec{r}) | \vec{p} | u_{ck}(\vec{r}) > < F_{nk}^h(\vec{r}) | F_{mk}^e(\vec{r}) > \dots \dots \dots (6)$$

Where, ϵ – Polarisation of the light (photon) field.

u_{ck}/u_{vk} – Bloch wave functions either for conduction or valence states,

$F_{nk}^h(\vec{r})/F_{mk}^e(\vec{r})$ —Envelope function for nthband/mthband of charge carriers

Quantum mechanical restrictions for intra band transitions in QD is obtained in terms of spherical harmonics for angular momentum, $\Delta l = \pm 1$, as QC's are in all three directions x, y, z . But for Q-Wire and Q-well (QW), in terms of polarization, becomes more relevant.

The electronic and optical properties of semiconductor cannot be fully understood without discussing “Excitonic state”; be it for bulk materials- [9] or Nano-structure (NS)- [10] and “Multiple–Exciton” generation- [11,12].

As mentioned earlier, “EXCITON”, a bound state of “Electron-Hole” pair due to Coulombian interaction, are typically created in semiconductor NS through optical excitation of carriers (intra band) or by carrier injection and exciton is more positronium like (12), one observes loosely bound excitons or Wannier–Mott” excitons. Excitation Rydberg energy R'_y [13] and exciton energy E_{ex} are given by

$$E_{ex}(n, \vec{k}) = \frac{1}{n^2} + \frac{\hbar^2 k^2}{2\mu}; R'_y = \frac{\mu}{\epsilon^2 m_0} \times 13.6 \text{ eV} \dots\dots\dots(7)$$

Where n =principal quantum number; $\vec{k} = \vec{k}_e + \vec{k}_h$; $\mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*}$ = reduced mass of exciton;

ϵ = Dielectric const. of the materials;

The band gap energy is much more than the magnitude of coulombian energy i.e. more than 10mev to 40mev [14]. Quantum mechanical perturbation can be considered for “strong confinement” as coulombian interaction is much weaker than confinement potential [15]. The Columbian effect can be significant in case of Si, Ge, NS which have larger range of QC with the consideration of thermal energy for excitonic effect [16]. Infinitely thin sheet of graphene (QW), the principal quantum number reduces to $n \rightarrow (n-1/2)$ with system dimensional effect and the general expression in terms of effective dimension; d_{eff} (value from 2 to 3) as

$$n \rightarrow \left(n + \frac{d_{eff}-3}{2}\right); d_{eff} = 3 - \exp\left(-\frac{L}{2a_B^{ex}}\right) \dots\dots\dots(8)$$

Where, L =QW thickness.

Quantum well is utilized in wide field like LED, LASER diode as in Ga As-based VCSEL or AlGaAs. QW solar cells as in p-i-n Diode. QW Inter-sub band-photo-detector (QWID) as in GaAs. For infinitely thin wall shift energy ΔE decreases to half, E_{ex} becomes four times and the oscillator strength becomes eight times. A” BIEXCITON” is defined as bounced state of two excitons observed in a highly excited systems (High excitation density states.) In bulK semiconductor, no possibility of QC, as discussed earlier, for dimension of confining structures, are very large compared to electron de Broglie wavelength or excitonic Bohr radius. This is NIL QC regime, when particle radius, $r \gg a_{ex}$. In weak QC regime, the size (radius) of NSs should be greater than bulk exciton Bohr radius- a_{Bex} . The dominating Coulombian energy term is observed in size quantization of excitonic motion. When particle radius r is slightly greater than a_{Bex} ($r > a_{Bex}$). The shift energy ΔE is inversely proportional to r^2 , the exciton energy states moves to higher end by confinement and excitonic ground state energy is written as (approximately):

$$\Delta E = \frac{\hbar^2 k^2}{2m_{ex} \cdot r^2} \dots\dots\dots(9A)$$

Where m_{ex} =mass of exciton = $m_e^* + m_h^*$; m_e^* & m_h^* are effective mass of electron & hole respectively,

In moderate QC regime, radius, $r = a_{Bex}$ as in case of ((II-&-IV) semiconductor materials with condition $ah < r < ae$.

In the strong QC regime, the condition is $r < a_B^{ex}$ or $r \ll a_B^{ex}$ together with $r \ll ah$, size quantization of an electron and a hole are dominating term (as excitations are absent) due to these conditions. Because of electron hole interaction, the Colombian term is small as perturbation and we have to consider individual behavior of electron and hole for above set of situations. Experimentally confirmed change in energy ΔE_s in terms of crystal size on the basics of experimentally confirmed model is given by

$$\Delta E_s = \frac{\hbar^2 k^2}{2\mu \cdot r^2} \dots\dots\dots(9B)$$

Where $\mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*}$ = reduced mass of exciton.

In QD, there is ladder of discrete energy levels (like- molecular system) for excited state and electron, holes are considered to be individual particle in ground state as

$$E_g^{QD} = E_g + \frac{2\hbar^2 \pi^2}{m_e^* r^2} + \frac{2\hbar^2 \pi^2}{m_h^* r^2} \dots\dots\dots(10)$$

Optical transition in QD is usually associated with excitons and approximate formulae called Bruh’s equation gives transition energy in spherical QD as

$$E_g^{QD} = E_g + \frac{2\hbar^2 \pi^2}{\mu \cdot r^2} - \frac{1.8e^2}{4\pi\epsilon_0 \cdot r} \dots\dots\dots(11)$$

Where ϵ = dielectric constant of the material, r -radius of QD, E_g -band gap energy.

Considering electron and hole confinement (QC) as an infinite potential well, Brus equation can be utilized to describe QD emission energy E_{QD} in terms of its radius and bulk properties (QW) [17] as .

$$E_{QD} = E_g + \frac{h^2}{8r^2} \left(\frac{m_e^* + m_h^*}{m_e^* m_h^*} \right) \dots \dots \dots (12)$$

More accurate Burs equation with the mixing of experimental emission maximum energy and CdSe literature bulk material properties give:

$$r = \sqrt{\frac{h^2}{8(E_{QD} - E_g)}} \times \left(\frac{m_e^* + m_h^*}{m_e^* m_h^*} \right) \dots \dots \dots (13)$$

Where the terms have the usual meanings.

Using the tool of QFT for electronic anomalous magnetic moment influenced by external magnetic field, Schwinger predicted a correction to g factor due to its coupling to the e.m field. A new paradigm of electronics called “spinotronics” have emerged by introducing electrons: spin degree of freedom (purely Q.M terms) in place of electronic charge as quantum information carrier. The Langrangian of spin (1/2) field coupled (interaction) to electro-magnetism is written as

$$\alpha_{QED} = -\frac{1}{4} F_{\mu\nu} F^{\mu\nu} + \bar{\Psi} (i\gamma^\mu D_\mu - m) \Psi \dots \dots \dots (14)$$

Where the Q.M terms have the usual meanings.

By plugging in quantized covariant Maxwell field equations into the Langrangian we find that interaction between fermion and photon to be (Quantum Field Theory)

$$\alpha_{QED}^{(int)} = -e A_\mu \bar{\Psi} \gamma^\mu \Psi \dots \dots \dots (15)$$

With current density four vector in Dirac’s theory, $\mu = e \bar{\Psi} \gamma^\mu \Psi$.

An estimate of CdSe/Zns QD core radii were obtained using bulk material properties of CdSe , $E_g = 1.751 \text{ eV}$, $m_e^* = 0.13m_e$; $m_h^* = 0.45m_e$; m_e = free rest mass of electron = $9.1 \times 10^{-31} \text{ kg}$.

QDs possess increased spatial QCE due to Detailed knowledge of electronic and optical properties of Nano-structures (NS) is significant for explaining the photo-physical/chemical process by incident light photon.[18]. QCE is observed due to optical absorption in experimentally confirmed results with well-set blue shift in absorption spectra by decreasing particle size to nano scale. Another way is to consider decreasing end for observed energy gap between HOMO and LUMO. In QD, quantized energy levels lie within empty and field states also the band gap state are in higher states between “HOMO” and “LUMO” [19,20].

Experimental results are not in good agreement for complex NS semiconductor materials were considered multielectron/holes/assembly are involved. We need to apply “Quantum Field Theory” framework (QFT) with Feynman’s diagram (FD) to model such multi-excitonic complex but real systems more precisely [21,22].

III. PRACTICAL APPLICATION OF QCE WITH EXAMPLES

The ultra-small length scale range corresponding to the quantum confinement (QC) regime ranges from 1nm to approximately 500nm ($1\text{nm} = 10^{-9} \text{ m}$) for periodic table semiconductor element groups of IV (elemental), III-V $\rightarrow$ InP/InAs; & II-VI (Compound), II-IV $\rightarrow$ CdSe/CdS; IV-VI $\rightarrow$ PbSe.

Other important quantum confining material includes MESO (Magneto Electric Spin Orbit) devices, single Nano-crystal of the multi ferric is topological material Bismuth-Iron-Oxide (BiFeO₃) as quantum material for future microprocessor processing many times faster than CMOS (Complementary metal oxide semiconductor) of limiting size and speed according to Moor’s law. Multiferroic magneto electric spin orbit is (MESO) materials harness its magnetic spin up and down configuration to store quantum information and perform quantum logic (QAI) process. Carbon Nano Tubes (CNT), quintessentially one-dimensional quantum object, different types of quanta electronic/electrical and optical properties applicable for various devices and developed on quantum mechanical principles using quantum dots (QD).

A variety of nano scale sensing jobs can be developed using nitrogen vacancy centers in diamond with its unique spin and optical properties, interesting topics in Nano scale magnetics like optical imaging for various applications in solid states and meso-scopic physics, especially in Nano mechanical oscillators.

Emerging commercial applications in nano scale magnetic like optical imaging (HD) in solid state and Mesoscopic physics, especially in nano mechanical oscillator. Also, there is efficient utilization of it in the theory of superconductivity, coulomb blockade effect in QDs, storage devices in quantum computers and Abhearonov- Bohm physics in Mesoscopic systems. Liquids suspended QD for radiation detection like Core/shell QD materials—Cdse/Zns,ZnCuInS. To realize and utilize Majorana zero mode quasi particle (as their own antiparticle) in Advanced Topological Quantum Nano Materials (ATQNMs) which include group (II-V) semi-conductors—Cd3As2, the layered chalcogenides (—Mx2, ZrTeS); and the rare earth pyro-chloreiridates —A2Ir2O7, (where A-rare earth element such as Eu & Pr).

IV. CONCLUSION

Experimental results are not in good agreement for complex NS semiconductor materials where multi-electrons/holes/assembly are involved. We need to apply “Quantum Field Theory” framework (QFT) with Feynman’s diagram (FD) to model such multi-excitonic complexes but real systems more precisely as discussed earlier.

Recently QD based Nano-structured materials are efficiently utilized in many various fields like Q-LEDs, Microprocessors, Solar cells, LASER diode for displays, medical diagnostic devices as in CTMRI, HDCT also in Quantum computers, super conducting quantum interference devices (SQUID) etc.

In July 2021 a case of formation of “quantum time crystal” (sixth state of matter) or 4D Quantum Material in the quantum processor of Google’s “SYCAMORE” 20 Qubits quantum computer was reported, possibility of quantum dynamical analysis using QFT with FD.

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