Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2015, 4(3): 637-800

(International Peer Reviewed Journal)

Perspective Review

Computational Quantum Chemistry (CQC)
Part 1: Evolution of a computational tool into an instrumental probe

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Accepted on 13th May2015

(Dedicated to Smt. R. Adi lakshmi, mother of RSR, on her ninetieth birth anniversary)

CONSPECTUS

Background:In conventional experimental science, human senses and/or instrumental probes observe/make direct or indirect measurements on an existential object or its response under perturbed environment. This is to grasp scientific force driving it as well as manifested characteristics. In simulation, a mathematical/statistical model generates data about a process, object with the same goals of experiments. Animation, emulation etc.are add-ons to get a real feel of the realistic scenario through the model. Theoretical models are arrived for a real life task based on fundamental principles of a disciplines and mathematical frame is deemed to reproduce the behavior of system in real time. Computational science brings forth the numerical solution of mathematical equations and software/hardware are only high performance supportive tools pushing away the drudgery of number crunching and ensuring reproducibility of even thousands of man-hours of time in a fraction of second. The quantum mechanics, the core of quantum chemistry now spread its wings in functional form to make a mark itself as probe alike hyphenated instruments.

In basic quantum mechanics, the system considered consists of electrons revolving around nucleus and the physical model relates the energy of the system with a function of electron density in the Eigen frame. Schrodinger wave equation (SWE) is a second order partial differential equation in XYZ co-ordinates connecting energy with ψ. The mathematical solution is exact for hydrogen atom in ground state, the primary output being a tensor of second order (matrix) of orbitals and corresponding electronic energies with dimensions of 2 x number_of_orbitals.

Computational methods:For multi-electron atoms or molecules even in gas phase and in absence of environment, the exchange/correlation phenomenon renders the solution of SWE impracticable. This led to approximation of exact equations starting with complete neglect of differential overlap (CNDO), the pioneering contribution of Pople. The battery of SEMO methods from this school and Dewar is a novel admixture of employing already available experimental data for chemical species to develop parametric methods in QC. The description of electron density profile is through STO, GTO and plane waves etc. The basis sets simplifying the picture of discriminating valence and core electrons, diffusion and polarization contributions improve accuracy of computational quantum chemistry (CQC). For metal ions,

special basis sets are developed. DFT with functionals is an alternate paradigm for the same applications but consuming comparatively lesser CPU time. The interest in first stage to explain electronic spectra, NMR, ESR, photochemistry resulted in considering the effects in Hamiltonian operator. Now, the field is at a mature level and transformed CQC into experimental probe without employing half century aged electronic instruments. The next venture in QC was extending the applications to solutes in solvent, solvent mixtures, solid surfaces, interfaces and inside macro-molecules/ nano-structures. The hybrid paradigms with MM, QC, and
DFT paved way for viable investigation of large systems atdifferent levels of theory based on reactive site/ reaction center and remaining bulk moiety. Thus, wave function is fundamental quantity relating the energy of multi-electron atomic/ molecular system. Statistical experimental design in choosing functionals/basis sets and neural networks for interpolating electron densityare new directions in quantum chemistry computations. The derived parameters from primary output of CQC with varying factors output many chemically significant descriptors.
Software:The research in CQC is with a wide variety of packages and wide used ones are Gaussian 09, GAMESS, SCHRODINGER, Hyperchem, ADF etc. The range of hardware is QUAD core laptops, blade architectures to super computers and the sizes of molecule are 20 to thousands of atoms through hundreds.
Applications:The typical tasks in CQC are optimization of geometry, frequency analysis for stable chemical structure/TS/higher order saddle points, IRC, DRC, spectra, characteristic properties, thermodynamic quantities, solute-solvent optimized geometric structures. The significant characteristics derived from energy, its first and second derivatives are IP, charges, multi-pole moments, polarizabilities, microwave constants and Fuki/ softness/ hardness parameters.The systems studied pervade almost all disciplines of science and engineering. The select chemical systems reviewed here include molecules in aqueous solution/organic solvent/mixture of aquo-organic mixtures, pKas, transition state (TSs) in chemical kinetics, bio-molecules, nano-structures, drugs, reactions including hydrogen atom, hydride transfer and NLO materials. The advanced applications of CQC are using peta scale hardware for proteins, enzymes and reactions at interfaces. Another phase in CQC is in ab initio DFT modeling of plasmas, superconductivity, mixtures of fermions and bosons.

Keywords: Ab initio, DFT, Semi-empirical, Hybrid, Conceptual-QC, Software, Thermo dynam ics, Solvents, Electron density, ESP, Excited states, Exotic molecules, Descriptors, Optimized geometry, Experimentalconcurrence.
