Quest for Computation-Solving Quantum Mechanical Calculation on Molecules

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ABSTRACT- A lot of computational facilities is required to solve quantum mechanical problems even for a smaller molecule. Advancement or the innovation in computational field increases the knowledge about molecular properties exactly by going deep into the quantum mechanical calculations. As a Case study, Conformational analysis on small molecules involving hydrogen bonded 1:1 dimeric complexes of hydrogen cyanide (HCN) with hydrogen chloride (HCl) molecules and smaller cluster molecules namely Fullerene-Carbon60 is calculated and reported by ab initio quantum mechanical methods with the same computer configuration.

Key Words: Quantum mechanical Software Firefly- Conformational study- HCN- HCl- Fullerene Carbon60 Ab initio-Hydrogen bonded dimers-Avogadro2.

I. INTRODUCTION

Ab initio quantum mechanical methods can be computed in two directions to solve the Schroedinger equation for any molecular problems. One way is by increasing the methods from HatreeFock(HF), MollerPlesset(MP) perturbation theories like MP2, MP3, MP4., full configuration interaction (CI) in the form of increasing electron correlation and Post-SCF methods. The other way is by increasing the basis sets from STO-3G (minimal basis set), split valency, polarised, diffused, high angular momentum basis sets which extends to infinity within HF limits. In the case study first, hydrogen bonded 1:1 dimers involving HCN with HCl is studied. Because of the advent of computational field in both directions by increasing the correlation methods and by increasing the basis sets within HF limits were tried and reported. Secondly small molecular cluster of carbon60 were tried with the same computer configuration.

Electronic Structure Theory
- The Schrodinger Equation

$$H(R,r)\psi(R,r) = E\psi(R,r)$$

$$H(R,r) = -\frac{1}{2}\sum_A \frac{1}{M_A}\nabla_A^2 + \sum_{A,B} Z_A Z_B \frac{1}{R_{AB}} \ \}H_{nuc}(R)$$

$$-\frac{1}{2}\sum_i \nabla_i^2 + \sum_{i,j}\frac{1}{r_{ij}} - \sum_{A,j} Z_A\frac{1}{R_{Ai}} \ \}H_{elec}(R,r)$$

GLIMPSE OF THEORY [1]
Independent particle Models
Hartree -Fock, Density Functional
and
Semi empirical Methods

Electronic Structure Theory
The born-oppenheimer approximation

$$H(R,r) = H_{el}(R,r) + H_{nuc}(R)$$

$$H_{el}(R,r)\psi_{el}(R,r) = E_{el}(R)\psi_{el}(R,r)$$

Electronic wave function solved at each (fixed) nuclear configuration R

$$[H_{nuc}(R) + E_{el}(R)]\psi_{nuc}(R) = E_{BO}\psi_{nuc}(R)$$

$E_{el}(R)$ from the electronic wave function

gives rise to the potential energy surface, $V(R)$

$$V(R) = E_{elec}(R) + \sum_{A,B} Z_A Z_B \frac{1}{R_{AB}}$$

Common Features of IPM
- Effective one – electron models based on orbitals

$$H^{\mathit{eff}} \phi_i = \varepsilon_i \phi_i$$

- Different approximations for Hamiltonian in

  - Hartree-Fock (HF)
  - Density Functional theory (DFT)
  - Semi-Empirical (SE)

- Solved self consistently
- Equations are solved iteratively
- Electrons are treated quantum mechanically

(Coulomb + Exchange interaction)

Contributions to IPM

$$H\phi_i = \varepsilon_i \phi_i$$

$$H = T + V_{ne} + J + K + V_C$$

1- electron: Kinetic energy (T)
            Electron-nuclear attraction (V_{ne})

2-electron: Coulomb (J)
            Exchange (K)
            Correlation (V_C)

Hartree-Fock: exact T, V_{ne}, J and K; no V_C

DFT: exact T, V_{ne}, J ;approximate K and V_C

SE: all terms parameterized

II. METHODS OF CALCULATIONS

All the calculations have been performed using ab initio quantum mechanical program package [2, 3]. Two isomers of HCN with HCl complex involving 1:1 hydrogen bond was tried, Which is carried out at RHF/6-31G**, MP2/6-31G** and DFT/6-31G**B3LYP5 using Firefly 8.11 version. The Interaction energy or the hydrogen bonding energy is calculated by the procedure [4].

$$\Delta E = \Delta T \ \Delta M$$

where ΔT is total energy of the ΔM is the sum of the total energy of the monomers and ΔE is the interaction or HB energy expressed in kcal mol-1. Small cluster molecules of carbon60 which is called as Bucky ball or Fullerene were tried with same levels of 1:1 hydrogen bonded dimer. Calculations were carried out at the R&D. center of the department of Physics, RRCE, Bangalore.

III. RESULTS AND DISCUSSION

Structure of hydrogen cyanide, hydrogen chloride and the hydrogen bonded 1:1 complexes involving HCN with HCl is shown in Figure1. Calculated total energies, interaction energy or HB energy, dipole moment, bond lengths including HB length and the frequency analysis are favoring linear bonded structure as a stable one.
Total energy of the dimers favors the nitrogen atom bound HB structure as a stable one than the Chlorine atom bound

HB 1:1 dimer. The interaction energy or the HB energy also favors the same trend. Calculated dipole moment of monomers were compared with the experimental values [5] and is found to be in good agreement. For the 1:1 dimers it needs the experimental support from the gas phase spectroscopy experts. The HB length of the conformer with nitrogen atom is 3.4919 A0 at RHF/6-31G**,3.3757 A0 at MP2/6-31G** and 3.3388 Aoat DFT/6-31G** B3LYP5, which is in very good agreement with the experimental value[6] of 3.405 A0. For the second conformer involving Chlorine atom the HB length is reported in the table, which needs the experimental proof. So far no experimental work is reported for this conformer.

Calculated frequencies were analyzed. Absence of negative frequencies indicates the validity of the stable 1:1 binary complexes of HCN with HCl involving HB bonds. The experimentally observed [7,8] stretching frequency of 2888 cm-1 for the ClH stretching mode is in good agreement with 3130.9 cm-1 at   RHF/6-31G**,   3024.5cm-1at MP2/6-31G** and 2794.3cm-1 at DFT/6-31G**B3LYP5.

From the above results it is clear that if we go for higher method of quantum mechanical calculations the accuracy between theory and experiment seems to be closer for monomers and dimers of smaller molecules.

Structure of Fullerene-Carbon60 is shown in the Figure.2. It shows the electrostatic potential surface of the Bucky ball which is drawn and optimized with Avogadro [9]. We can calculate the properties of this cluster only at the level of HF. Experimental values of Double bond length is 134.1pm [10] and single bond length is 145.5pm. [10]. HF calculated value of double bond length is 137.6pm at STO-3G, 136.7pm at 3-21G,137.5pm at 6-31G and 137.3pm at 6-31G(d) basis sets. Single bond length is 146.3pm at STO-3G, 145.3pm at 3-21G, 145.2pm at 6-31G(d) basis sets. Single bond length is 146.3pm at STO-3G, 145.3pm at 3-21G, 145.2pm at 6-31G and 144.9pm at 6-31G(d) basis sets. Double bond lenths and single bond lengths agrees with experimental values reasonably. But which needs the advent of more powerful computation al configuration to solve at the higher quantum level of calculations.

This shows computer in biological systems especially on bio molecules exploding. We receive the profit of million dollar prizes.
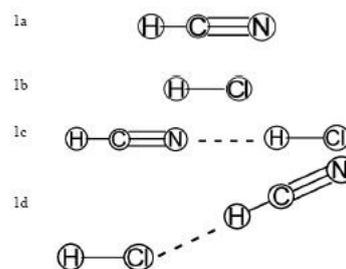

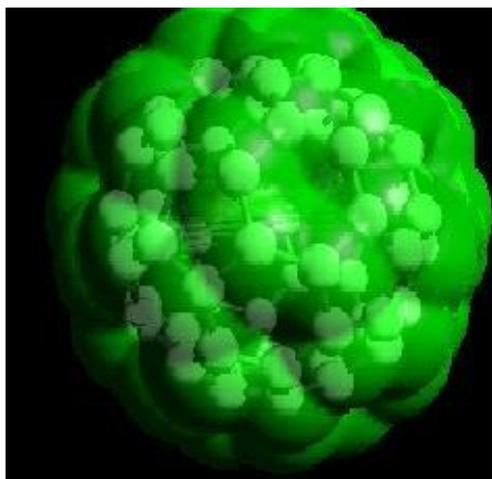Figure 1.a)stucture of HCN, b) structure of HCl, c) structure of HCN...HCl dimer and d) structure of HCl...HCN dimer.

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Figure 2. Structure of Carbon-60 with EPS

IV.CONCLUTIONS

With the same computer configuration, case studies of abinitio Calculations at the levels of increasing electron correlations and basis sets with RHF/6-31G**, MP2/6-31G** and DFT/6-31G**B3LYP5 were carried out for the smaller molecules with minimum time and for the smallest cluster carbon60, RHF/6-31G(d) was possible with two days. This study emphasizes the need for gas phase spectroscopy at its best to support the theoretical calculations for the dimers. Thus it clearly indicates the need for more computation facilities to solve quantum mechanical problems. Bigger molecular cluster calculations are waiting for a big leap in computation in the coming decades.

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