The purpose of this course is to give an understanding of Density Functional Theory (DFT), as it is presently used in computational chemistry. Let us first understand why there has been a revival of interest in DFT by computational chemists.

As ab initio quantum chemists we now know how to undertake Self Consistent Field (SCF) calculations on large molecules (perhaps 100 atoms), thanks largely due to the introduction of the Direct methodology by Almlof [1]. However if we wish to include the effects of electron correlation, that is to go beyond the SCF approximation, then there are major difficulties, all associated with trying to more accurately represent the electron-electron cusp. We know from the work of Kutzelnigg [2] that the convergence of this problem is very slow, something like $(1 + \frac{1}{2})^{-4}$; this means that very large basis sets are required for correlated calculations. We know that it is more important to include d and f basis functions than to improve the methodology. 6-31G* bases are not appropriate for correlated studies. We also know that the raw cost of correlated methods, MP2, MP3, MP4, CISD, CCSD, CCSD(T) increase with powers of the size of the problem as 5, 6, 7, 6, 6, 7. It is simply not possible to contemplate CCSD(T) calculations with 1000 basis functions, nor will it be sensibly possible to contemplate such calculations this century. Even though there has been
rapid progress by the computer companies in the development of their hardware: more memory, vectorisation compilers, parallel machines, all of which we have taken advantage of, these advances will not cure our outstanding basis set problems.

The physicists have been using Density Functional Theory for many years. Indeed it was one of the pioneer theoretical chemists, J. C. Slater, who pushed them in that direction with his 1951 contribution [3] in which he suggested the replacement of the difficult exchange term in the Hartree-Fock method by the Dirac[4] $\rho^\beta$ potential, which he argued at that time included both exchange and correlation effects. Computational chemists were largely discouraged by the fact that this original DFT made molecules substantially overbound. We ignored the early DFT work of people like Jones[5] who was the first to get the bond length of Be$_2$ correct, although it must be said that the reason the regular quantum chemists got it wrong was that too small basis sets were being used in those days. So although we have all worked hard and made great progress, if we are to study large molecules accurately, we must look for alternatives to regular quantum chemistry. This is why DFT has become an attractive tool. One important point to realise at this stage is that DFT has the same asymptotic cost as SCF as it is dominated by the coulomb interaction, and it probably needs the same size basis sets as SCF. At the same time, in principle it can achieve exact predictions.

2. E. BRIGHT WILSON’S OBSERVATION AND THE KOHN-HOHENBERG THEOREMS

When two of the key theorems of modern Density Functional Theory were introduced in 1965, it is said that the eminent theoretical spectroscopist E. Bright Wilson stood up at the meeting and said that he understood the basic principles of the theory[6]. He said that if one knew the exact electron density $\rho(r)$, then the cusps of $\rho(r)$ would occur at the positions of the nuclei. Furthermore he argued that a knowledge of $|\nabla\rho(r)|$ at the nuclei would give their nuclear charges. Thus he argued that the full Schrodinger Hamiltonian was known because it is completely defined once the position and charge of the nuclei are given. Hence, in principle, the wavefunction and energy are known, and thus everything is known. In conclusion, Wilson said he understood that a knowledge of the density was all that was necessary for a complete determination of all molecular properties. It is this simple argument which is behind most of the aspirations of modern Density Functional Theory.

If $N$ is the number of electrons then $\rho(r)$ is defined by

$$\rho(r) = N \int \ldots \int |\Psi|^2 \, d\mathbf{x}_1 \, d\mathbf{x}_2 \ldots d\mathbf{x}_N$$  \hspace{1cm} (1)$$

where $\Psi(\mathbf{x}_1 \mathbf{x}_2 \ldots \mathbf{x}_N)$ is the electronic wavefunction for the molecule. Wilson’s