COMPUTER DETERMINATION OF MOLECULAR PROPERTIES FOR DIATOMICS

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1 INTRODUCTION

To understand and characterise matter, we determine as completely as possible the different properties of atoms and molecules to gain insight into their behavior; how they interact and react. The determination of molecular properties can be accomplished experimentally, by performing the appropriate measurement in the laboratory, or theoretically by using the laws of quantum mechanics to compute the desired property. In principle, the experiment will obviously yield the correct result, while the theoretical determination rests on our belief that quantum mechanics correctly describes atomic and molecular structure. In practice, both procedures are fraught with difficulties, which are, however, quite different for the two methods. While many properties of a wide variety of molecules can be determined with ease by experiment, some are more readily and reliably obtained by computer. To be sure, the experimental approach is way ahead; experimentalists have determined molecular properties for more than a century, contributing greatly to our understanding of molecular structure and to the development of the laws of quantum mechanics. Nevertheless, there are cases, where the experimental approach breaks down or is severely hampered by difficulties, especially when the molecules in question are unstable or difficult to make. These present no limitations to the theoretical approach, since any molecule can be made and kept stable inside a computer. Here the problems and difficulties are of a different nature. The equations to be solved, and the quantities to be computed for a reliable theoretical determination of molecular properties are so complex that availability of high speed electronic computers was required before it became feasible to travel the theoretical avenue. Computers are young and the availability of machines with large
enough capacity and high enough speed still more recent and limited. It is therefore not surprising that theoretical determination of molecular properties lags well behind experimental measurement.

In addition, computers alone are not enough, we need to learn to use them, to use them effectively and efficiently. To this end, it is first of all important to develop the quantum theory, which was in a form appropriate for the interpretation of experimental data and cast it into a form, which is appropriate for computation of molecular properties. This development started with the advent of computers and was focused by and large on the computation of electronic wavefunctions and energies as solutions of the non relativistic, clamped nuclei Schrödinger equation; a development, which has been highly successful, making the computation of accurate electronic wavefunction of small molecules (up to 30 electrons) almost routine. To be sure, although routine, the accurate determination of a correlated electronic wavefunction and energy of a small molecule is a large computational task, this makes it desirable, almost mandatory that we do not stop here, but obtain as much useful information as possible from the wavefunction computed. There remains, aside from the electronic energy, a host of important molecular properties, which can be computed once the electronic wavefunction is known. Examples are the spectroscopic constants, electric and magnetic moments of the molecule as well as a number of fine- and hyperfines-structure coupling constants. The computational effort to determine these from the known electronic wavefunction is frequently small compared to the initial task of solving the electronic Schrödinger equation. Unfortunately, the theory, written in a form for the interpretation of spectra, is frequently not suitable for the calculation of the several spectral constants. It is this deficiency, which we hope to remedy with the present article, by pointing to the various molecular properties obtainable once the electronic wavefunction is known, casting the theory in a form amenable to the computation of these properties and giving examples and suggestions for such calculations, in the hope of encouraging theorists to obtain as much information as possible from their electronic wavefunction calculations, which are laborious and expensive.

Certainly it will not be possible in the present article to deal exhaustively with all possible properties of molecules in general. We therefore restrict ourselves to diatomic molecules and the properties observed spectroscopically, ignoring by and large phenomena associated with ionization, atomic and molecular collisions, reactivity and the like. In the first part of the present article we present the adiabatic approximation in a form appropriate to the later development and give a brief review of the standard methods for obtaining highly accurate correlated electronic energies and wavefunctions. This will be followed by a survey of the diverse spectroscopic properties and constants frequently determined in experimental investigations of diatomics. Associated with this