ABSTRACT. Interactions of molecules with intense laser fields produce highly nonlinear effects mediated by the bonding electrons. Recent experiments in nonlinear photoelectron spectroscopy of diatomics such as $\text{H}_2$ have shown the presence of new electronic states and thus new bound states of the molecular ions, which are manifestations of the dressing of the diatomic ion by the large number of photons present at high intensities as predicted by theory. In this chapter we will expose the theory of dressed molecules and present numerical calculations by coupled equations of these new phenomena which occur whenever intense laser fields interact with molecules.

1. INTRODUCTION

Electrons are the "gluons" in molecules which prevent nuclei from exploding apart. Thus electrons provide the necessary bonding to create stable multinuclear species called molecules. Great progress in our understanding of the electronic structure of molecules has come from the introduction of the molecular orbital concept by Mulliken in the 1950's and 60's. Thus as in atoms, electrons in molecules occupy orbitals which envelope the whole nuclear space, creating stable molecular species if the molecular orbitals are bonding and unstable species if these are antibonding [1].

The bonding characteristics of molecular orbitals can be inferred from photoelectron spectroscopy [2]. Recent improvements in this method has even led to determination of the electron momentum distribution in these orbitals [3]. A concomitant structure which appears often in the photo electron spectrum is the vibronic structure of the remaining molecular ion after photoionization. This structure which is created by the coupling of the ionized electron to the core of the ion reveals the vibrational structure of the molecular ion and the
degree of coupling between both electron and ion [4]. We conclude therefore that the electron serves as an essential probe in understanding molecular structure.

The advent of intense lasers has revealed some singular aspects of the nonlinear behaviour of atoms in intense laser fields [5-7]. Recently, similar nonlinear phenomena (e.g., above threshold ionization, ATI), have been observed in molecules [8-11]. In particular, experiments on the nonlinear photoionization of H₂ have revealed that the vibronic structure of the molecular ion is considerably altered with respect to the free ion [9-10]. It is the goal of this chapter to examine a theoretical model, the dressed molecule, which can help us understand nonlinear molecule-laser interactions, which interactions we reiterate are induced by multiphoton transitions (real and virtual) of the electrons in the molecule.

One can classify the regime of coupling between the laser and the molecular system according to the nature of the process they induce. The first regime is that corresponding to low-intensity lasers which couple weakly with the system. As a result, the excitation processes are well described by leading order perturbation theory, such as Fermi's Golden rule. For molecules, this leads to a Franck-Condon picture of electronic (radiative) transitions [12]. At intermediate to high intensities, one encounters a domain in which multiphoton processes begin to take effect. This is signalled by nonlinear behaviour of the transition probabilities as a function of intensity. In particular two or more states may be strongly coupled together as a result of being near resonant. An example of this is the Rabi oscillations of a two level atom [5-6] or an n-level molecule [13]. Another example which this chapter discusses in detail, is the nonlinear interaction between rovibrational manifolds of different electronic molecular states induced by intense laser fields. Judging from atomic experience, [14], one can establish the upper limit of the intensity I of this regime at 10^{12} W/cm² (terawatt/cm²), since for I \approx 10^{13} W/cm², ionization rates exceed dissociation rates for many molecules. Finally one has the very high intensity limit available with current superintense lasers (I > 10^{15} W/cm²), where Rabi frequencies (\omega_R = dE/\hbar, d = transition moment, E = electric field) are comparable to the laser frequency, and highly nonresonant transitions compete with resonant processes. Thus in the case of the nonlinear photoelectron spectroscopy of H₂ mentioned above [8-11], the photoionized electron continues to absorb photons creating ATI peaks with a vibronic structure which has no relation to the vibrational structure of free H₂. We will show in the present chapter, that the H₂⁺ core is dressed by the intense field and that the structure of the ATI peaks reflects the nonlinear interaction of the ion core with the laser while at the same time remaining coupled to the dressed photionized electron.

In particular we will show that intense lasers can create dressed adiabatic states which are degenerate with the excited field-molecule diabatic states, as a result of a laser induced avoided crossing bet-