HIGHLY EXCITED MOLECULAR STATES: QUANTUM DEFECT THEORY AND AB INITIO THEORY

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Full first principles calculations of highly excited complex structures and many-channel decay processes have been carried out in the past for atoms, usually by a combination of *ab initio* methods (e.g. R- matrix theory) with multichannel quantum defect theory (MQDT). A beautiful example is afforded by the work of Johnson et al.[1] on several rare gas atoms, where the first principles relativistic multichannel calculations were of such quality that they could be confronted directly with highly resolved experimental cross sections. Predictions of comparable completeness and accuracy are much rarer in the domain of molecular physics, because *ab initio* computations must be carried out and optimized for many nuclear geometries, and the nuclear (non-Born-Oppenheimer) dynamics greatly complicates the issue.

In the present contribution molecular examples will be described where highly excited bound states have been calculated *ab initio* correctly on the scale of $1cm^{-1}$ (CaF, $n^* \sim 15$) and of $1MHz$ (H_2, $n^* \sim 55$). The first of these examples[2] corresponds to a highly excited electron with principal quantum number $n^* \sim 15$ which interacts with a rotating strongly dipolar ion core. In the second example ultra-high Rydberg states with $n^* \sim 55$, situated $30cm^{-1}$ below the ionization limit, have been excited and their hyperfine structure fully resolved.[3] In the calculations account must be taken of the couplings between the excited electron inluding its spin, with the electronic and nuclear spins of the H_2^+ ion core. The various steps and developments will be described which have been necessary to achieve such accuracy.

Some recent developments in the field of molecular R- matrix theory and the *ab initio* prediction of molecular wave packet motion will also be mentioned.

(1) W. R. Johnson, K. T. Cheng. K.-N. Huang, and M. LeDourneuf, Phys. Rev. **A 22**, 989 (1980).

(2) C. M. Gittins, N. A. Harris, M. Hui, and R. W. Field, Can. J. Phys. **79**, 247 (2001).

(3) A. Osterwalder, R. Seiler, and F. Merkt, J. Chem. Phys. **113**, 7939 (2000).