Chemiluminescence in the gas phase has been observed in systems spanning a wide range of complexity, and theoretical approaches to chemiluminescence are equally varied (Carrington & Garvin 1969, Carrington & Polanyi 1972). The simplest process is the radiative recombination of two atoms on a single potential curve. This can be treated with near-ultimate rigour, though these processes have not attracted wide interest. At the other extreme in the range of complexity, are processes involving polyatomic reactants. Here only qualitative treatments are possible at present, and it seems unlikely that anything quantitative will be possible, or even interesting, in the foreseeable future.

I will discuss a sequence of four types of chemiluminescent systems, of increasing complexity. For each type, the theoretical approach that is most appropriate and practical will be outlined, but the main interest is in the relationship among these approaches. As one moves toward increasing complexity, certain basic concepts or good quantum numbers lose their validity, and the number of well-defined observables decreases. Apart from this loss of detail which must occur in principle, there is of course an additional loss due to practical difficulties in carrying out calculations or experiments on polyatomic systems. The main purpose of the paper is to trace out certain "lines of descent" showing the loss of rigour and detail, and the rise of qualitative concepts, in treatments of successively more complex systems. Any common elements which survive during this descent should be truly fundamental to chemiluminescence. A study of a variety of approaches to chemiluminescence should make it possible to examine a process at several different levels of rigour. A comparison of treatments from
different points of view is nearly always more fruitful than a treatment locked to a single approximation.

The discussion of each type of process takes the following form. First the valid concepts and good quantum numbers are presented, as illustrated by a representative reaction. Then the theoretical methods are outlined, followed by a brief discussion of the kinds of results which are obtainable theoretically and observable experimentally.

I. Radiative Recombination of Atoms on a Single Potential Curve

In this simplest system, a great many concepts and quantities are well-defined. The electronic state of the emitter is well-defined over a large range of internuclear separation, since there are no nearby states of the same parity with which it can interact. This means that the Born-Oppenheimer separation will be an excellent approximation, and the system can be described accurately using continuum radial wave functions and an r-dependent transition moment. As well as being well-defined in principle, parts of the potential curves involved are often known experimentally from analysis of band spectra. Orbital angular momentum is a good quantum number throughout the collision, since we have two-body central forces. The angular momentum, the initial relative kinetic energy, and the potential function determine the collision completely. To get an observable result, one simply averages over a distribution of initial conditions.

Fig. 1. Potential curves illustrating radiative recombination on a single repulsive curve.