PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

# Introductory Remarks

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# Introductory remarks

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It is for me a great pleasure to be here and to have the privilege of opening this first international meeting of workers in the flourishing new field of photoelectron spectroscopy. It is a special pleasure to be able to meet here with the pioneers of the field, in particular Dr Turner, Professor Price, and Professor McDowell, who have worked with ultraviolet photons, and Professor Siegbahn who has worked mainly with X-rays.

Photoelectron spectroscopy has already shown, and will continue to show, unique ability to see down into the depths of molecules. It has given a new reality to the idea of molecular orbitals, by determining quantitative values for their binding energies, and also by giving information about their bonding characteristics.

Strictly speaking, molecular orbitals are no more than convenient theoretical building blocks for *approximate* descriptions of the electronic structures of molecules. When we speak of the binding energy, or the orbital energy, of a molecular orbital, the actual physical reality is an *ionization energy*, that is to say, the energy required to create a stationary state of the positive ion of a molecule by removing one electron from that molecule. In general, these are excited states of the molecular ion. However, the molecular ion states which are disclosed by photoelectron spectroscopy correspond, for the most part at least, to the removal of an electron from a particular molecular orbital.

It has been quite usual up to now to speak of *the* ionization potential of an atom or molecule. What is really meant is the *minimum* ionization potential, corresponding to production of the molecular ion in its ground state. Because there was relatively little possibility of determining deeper, i.e. inner-shell, ionization potentials, they were largely ignored. To be sure, in a few cases, especially for diatomic and a few triatomic molecules, two or three inner-shell ionization energies have been determined before the advent of photoelectron spectroscopy. This method now makes possible for the first time the wholesale exploration of inner-shell orbital energies.

We are interested here, I believe, primarily in individual molecules in the gaseous or vapour state. As simple examples, consider the nitrogen and carbon monoxide molecules, whose electron configurations in terms of molecular orbitals can be written as

$$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2 \quad \text{and} \quad 1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ 5\sigma^2.$$

The minimum ionization potential corresponds to removal of an electron from the $3\sigma_g$ m.o. (molecular orbital) in $N_2$, or the $5\sigma$ in CO. The resulting ground state of the $N_2^+$ molecular ion can be called $(3\sigma_g)^{-1}$. But there are other states $(1\pi_u)^{-1}$, $(2\sigma_u)^{-1}$, and so on. One way in which we can learn about these is through a study of the band spectrum of $N_2^+$, where emission spectra $(1\pi_u)^{-1} \rightarrow (3\sigma_g)^{-1}$ and $(2\sigma_u)^{-1} \rightarrow (3\sigma_g)^{-1}$ are known. From data on these, if the minimum ionization potential, that for $3\sigma_g$, is accurately known, those for $1\pi_u$ and $2\sigma_u$ can be determined accurately. Analogous statements apply to CO. X-ray spectroscopy, both in absorption and emission, has been used in a similar way to optical spectroscopy, but not very much for gaseous molecules; it is difficult to obtain accurate results.

To determine the *minimum* ionization potentials of molecules, electron impact methods have been widely used. However, these usually result in values that are of limited accuracy. More accurate is the photoionization method, in which the molecule is allowed to absorb almost monochromatic light of varying frequency until a frequency is reached at which ionization begins and ions can be collected; this (with rare exceptions) gives the minimum ionization potential, usually determined to within 0.01 or 0.02 V.

A direct method of determining accurately not only the minimum but also some of the inner-shell ionization potentials of molecules is the observation of the limits, i.e. the convergence points, of Rydberg series absorption spectra. Professor Price was one of the pioneers in using this method for many molecules. The method has been employed successfully for the $3\sigma_g$, $1\pi_u$ and $2\sigma_u$ m.o. of the nitrogen molecule. However, because of the complexity of their spectra or sometimes for other reasons, the use of this method has largely been limited to the simplest molecules, and has not always been successful even for these. Photoelectron spectroscopy is in theory a related procedure but by-passes all the complexity of the Rydberg series, going directly, for each inner shell excitation, to what would be the limit of the Rydberg series, namely the ionization potential.

Paralleling the development of experimental methods for determining molecular ionization potentials there has been an outburst of activity in theoretical computations on molecular electronic structure, using large digital computers. In particular, the forms and the orbital energies of m.o. in the s.c.f. (self consistent field) approximate descriptions of larger and larger molecules are now being computed with considerable accuracy. On the basis of Koopmans's theorem, the s.c.f. orbital energy of a m.o. is approximately, but not exactly, equal to the ionization energy for removal of an electron from that m.o. Thus s.c.f. theory gives values of inner-shell ionization energies which, while rather rough, are usually good enough to corroborate or to serve as a guide if needed, to the identity of the m.o. whose energies are being determined accurately by photoelectron spectroscopy. The theory tells us not only the energy but also the symmetry type (e.g. $\pi_u$ or $\sigma_g$ in the example of $N_2$), and beyond this, the detailed form of each m.o. with, as a corollary, an *approximate* indication as to whether it should be bonding, non-bonding, or anti-bonding. In favourable cases photoelectron spectroscopy gives amazingly *accurate* evidence about the bonding characteristics of m.o. and at the same time gives detailed information on the vibrational levels of the molecular ion states.

S.c.f. theory predicts the approximate characteristics not only of outer-shell m.o. but also of inner-shell m.o. down to the K shell orbitals. It makes interesting approximate predictions about how the K shell energies corresponding to various atoms differ in different molecules. For example, in $N_2$, the m.o. $1\sigma_g$ and $1\sigma_u$ are approximately N atom's a.o. (atomic orbitals), or rather, linear combinations of these, $1\sigma_g \approx 1s_a + 1s_b$, $1\sigma_u \sim 1s_a - 1s_b$, where a and b refer to the two nuclei. In CO, $1\sigma$ is, very nearly, 1s of oxygen and $2\sigma$ is, very nearly, 1s of carbon. In $N_2$, the orbital energy is predicted to be slightly less for $1\sigma_u$ than for $1\sigma_g$. In CO, the predicted K shell orbital energies for C and O differ from those for $CO_2$, and for C from those for $CH_4$, $C_2H_4$, $C_2H_2$, and other carbon compounds. However, the theoretical predictions, even with the most accurate s.c.f. wave functions, cannot give accurate ionization potentials, while X-ray photoelectron spectroscopy as developed by Professor Siegbahn, does give accurate values.

In the course of time, accurate theoretical calculation of outer- and inner-shell ionization potentials will become possible, first for various small molecules, then for larger and larger ones. This course of events will proceed in two steps; the first of these will be the making of

more accurate s.c.f. calculations for larger molecules; at present, really accurate s.c.f. approximation calculations are available only for diatomic and perhaps some triatomic molecules. Later will come the introduction of configuration mixing, going beyond the s.c.f. approximation, to get really accurate molecular wave functions. But the second step will take a very long time, and I think we shall have to rely on experimental information from photoelectron spectroscopy for accurate ionization energies and, clearly, for an amazing variety of other interesting and important information about molecules and their ions.



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