MOLECULAR BEAMS

ADVANCES IN CHEMICAL PHYSICS

VOLUME X

ADVANCES IN CHEMICAL PHYSICS

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MOLECULAR BEAMS

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PREFACE

Studies of molecules in nearly collision-free and unidirectional motion, that is, in molecular beams, have been made for over fifty years. The technique has long been recognized as particularly suitable for the determination of the interaction of a single molecule with another molecule, with a photon, with external fields, or with surfaces. (See the Appendix for some general references.) In principle, at least, molecular beam experiments provide the means for direct measurements of molecular properties. Of course, the properties of macroscopic systems are related to those of their molecular constituents by the theories of statistical mechanics. These relations are always some statistical average of molecular properties, an average which obscures the dependence of the macroscopic measurement on the molecular properties. In practice the removal of all statistical averages even in molecular beam experiments presents extreme problems.

The articles in this volume are reviews of some of the current molecular beam research in the general area of chemical physics. Interest in such experiments has increased sharply in the last ten years, especially among chemical kineticists. The predominant, common theme throughout the volume is molecular interactions.

Elastic scattering is discussed in two articles, one reviewing high-energy scattering and repulsive forces, the other low-energy scattering and a number of quantum-mechanical effects for which both attractive and repulsive forms are of importance. Reactive scattering is the topic of four articles, two on neutral reactions and two on ionic reactions. Information on chemical reactions may be obtained by molecular beam measurements on the scattered chemical product or from the study of elastic scattering in reactive systems. Both methods are reviewed. Ion–molecule and charge-transfer reactions are also discussed in separate articles. The remaining sections of the volume are devoted to inelastic scattering of metastable atoms, the determination of atomic polarizabilities, and the technique of hypersonic beams.

The articles are representative of current molecular beam research in chemical physics, but the selection is by no means complete. For

instance, reviews on nonreactive inelastic scattering, on the use of beams as a technique for molecular resonance spectroscopy, and on the interactions of molecules with surfaces are among the omissions.

I wish to thank my colleague Professor E. F. Greene for much help and advice in editing this volume and Dr. G. P. Flynn for compiling the subject index.

JOHN ROSS

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OF ATOMIC POLARIZABILITIES*

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I. INTRODUCTION

Polarizability is a seemingly ubiquitous atomic property which appears as a parameter in the description of many important atomic processes. The calculation of the van der Waals interaction, the description of charge transfer and other ion–atom and electron–atom collision processes, of optical lifetimes, and of optical dispersion all directly involve or are related to the static polarizabilities of ground and excited states of neutral atoms and molecules. In a general sense one can expect that the atomic polarizability will be a useful parameter when dealing with any atomic process in which the outer part of the electronic wave function plays an important role. Direct experimental determinations of atomic polarizabilities provide a very sensitive check on the accuracy of electronic wave functions, where these are

available. In addition, since the approximation methods used in calculating quadrupole shielding factors can also be used to calculate polarizabilities,[1] comparison of such calculations with experiment provides an independent check on these methods, and is therefore helpful in providing more reliable values of nuclear quadrupole moments.

Atomic beam methods would appear to be eminently suited to measuring polarizabilities, because of the absence of particle–particle interactions. Yet, there have been only a few such experiments in recent years, notably the deflection experiments of Chamberlain and Zorn[1] at Yale, and the balance experiments[2-4] by the N.Y.U. group. (The earlier work of Scheffers and Stark[5] is primarily of historic interest.) Our purpose in this article is to discuss these experiments in some detail, and also to briefly describe some of the principal methods by which atomic polarizabilities have been calculated in recent years.

II. THEORY

The energy of an atom in an external field is readily calculable from perturbation theory, provided one has means of estimating the relevant matrix elements. Let an unperturbed atom have a Hamiltonian $\mathscr{H}_0$ with energy $\mathscr{E}_0$. In the presence of an electric field E, the Hamiltonian becomes $\mathscr{H}_0 + \mathscr{H}'$. The perturbation $\mathscr{H}' = -\mu_e \cdot E$, where the electric dipole operator

$$\mu_e = -\sum_i e r_i$$

with r_i the position vector of the ith electron. The first-order perturbation energy is

$$\mathscr{E}_1 = \langle 0|\mathscr{H}'|0\rangle = \langle 0|\mu_e \cdot E|0\rangle \tag{1}$$

where $|0\rangle$ is the unperturbed state vector. Since $\mathscr{H}'$ is an operator of odd parity, the matrix element in Eq. (1) will vanish if $|0\rangle$ has a definite parity. That is, states of definite parity have zero permanent dipole moments.

The second-order perturbation energy $\mathscr{E}_2$ is given by a summation containing matrix elements of μ_e between $|0\rangle$ and other states $|k\rangle$ of the form

$$\mathscr{E}_2 = -\sum_{k \neq 0} \frac{\langle 0|\mu_e \cdot E|k\rangle \langle k|\mu_e \cdot E|0\rangle}{\mathscr{E}_k - \mathscr{E}_0} \tag{2}$$

The denominator $\mathscr{E}_k - \mathscr{E}_0$ is the energy difference between $|k\rangle$ and $|0\rangle$. Alternatively, if $\hat{n}$ is a unit vector in the direction of $\mathbf{E}$,

$$\mathscr{E}_2 = -E^2 \sum_{k \neq 0} \frac{\langle 0|\boldsymbol{\mu}_e\cdot\hat{n}|k\rangle\langle k|\boldsymbol{\mu}_e\cdot\hat{n}|0\rangle}{\mathscr{E}_k - \mathscr{E}_0} \qquad (3)$$

The summation in Eq. (3) may be written explicitly in terms of the rectangular components μ_x, μ_y, μ_z, of $\boldsymbol{\mu}_e$ and a, b, c of $\hat{n}$ as follows,

$$\mathscr{E}_2 = -E^2 \sum_{k \neq 0} \left[\frac{a^2|\langle 0|\boldsymbol{\mu}_x|k\rangle|^2}{\mathscr{E}_k - \mathscr{E}_0} + \frac{b^2|\langle 0|\boldsymbol{\mu}_y|k\rangle|^2}{\mathscr{E}_k - \mathscr{E}_0} + \frac{c^2|\langle 0|\boldsymbol{\mu}_z|k\rangle|^2}{\mathscr{E}_k - \mathscr{E}_0} \right.$$
$$\left. + \frac{ab\langle 0|\boldsymbol{\mu}_x|k\rangle\langle k|\boldsymbol{\mu}_y|0\rangle}{\mathscr{E}_k - \mathscr{E}_0} + \cdots \right] \qquad (4)$$

The polarizability tensor is defined by the relation

$$\mathscr{E}_2 = -\tfrac{1}{2}\mathbf{E}\cdot\alpha\mathbf{E} \qquad (5)$$

By comparing Eqs. (4) and (5) it is seen that the (symmetric) tensor components α_{xy}, etc. are given by the relation

$$\alpha_{xy} = 2 \sum_{k \neq 0} \mathscr{R} \frac{\{\langle 0|\boldsymbol{\mu}_x|k\rangle\langle k|\boldsymbol{\mu}_y|0\rangle\}}{\mathscr{E}_k - \mathscr{E}_0} \qquad (6)$$

etc., where $\mathscr{R}$ signifies "real part."

If the electric field direction coincides with the axis of symmetry of the atom, then M_J is a good quantum number, the off-diagonal components of α vanish, and the tensor components α_{xx} and α_{yy} (hereafter designated α_x and α_y) are equal. The discussion will be restricted to this case. (It is further assumed that the permanent dipole moment vanishes.) There are then at most two different components of α in each magnetic substate M_J. If use is made of the fact that $\boldsymbol{\mu}_e$ is a so-called T operator,[6] one whose components satisfy the same commutation rules with the components J_x, J_y, and J_z of the total angular momentum $\mathbf{J}$ as do J_x, J_y, and J_z themselves, the tensor components in the various magnetic substates, $\alpha_x(M_J)$ and $\alpha_z(M_J)$ become

$$\alpha_x(M_J) = A(J^2 + M_J^2 - J) + B(J^2 + J - M_J^2) + C(J^2 + 3J + 2 + M_J^2)$$
$$(7a)$$

$$\alpha_z(M_J) = 2A(J^2 - M_J^2) + 2BM_J^2 + 2C(J^2 + 2J + 1 - M_J^2) \qquad (7b)$$

where

$$A = \left(\sum_{k \neq 0} \frac{|\langle 0 | \mu_e | k \rangle|^2}{\mathscr{E}_k - \mathscr{E}_0} \right) \delta_{J-1,J'}, \qquad B = \left(\sum_{k \neq 0} \frac{|\langle 0 | \mu_e | k \rangle|^2}{\mathscr{E}_k - \mathscr{E}_0} \right) \delta_{JJ'},$$

$$C = \left(\sum_{k \neq 0} \frac{|\langle 0 | \mu_e | k \rangle|^2}{\mathscr{E}_k - \mathscr{E}_0} \right) \delta_{J+1,J'},$$

where μ_e is the absolute value of μ_e, and where J, J' are the total angular momentum quantum numbers of $|0\rangle$ and $|k\rangle$, respectively. The average polarizability, $\bar{\alpha}$, is defined as the average of either α_x or α_z over the magnetic substates. In terms of A, B, and C, $\bar{\alpha}$ is

$$\bar{\alpha} = \tfrac{2}{3}[AJ(2J - 1) + BJ(J + 1) + C(2J + 3)(J + 1)] \tag{8}$$

We now show that of the $2(2J + 1)$ equations represented by Eq. (7), no more than two are independent. The difference between any two tensor components is a simple multiple of $(A - B + C)$:

$$\alpha_z(M_J) - \alpha_z(M'_J) = 2(M_J'^2 - M_J^2)(A - B + C)$$

$$\alpha_x(M_J) - \alpha_x(M'_J) = (M_J^2 - M_J'^2)(A - B + C) \tag{9}$$

$$\alpha_z(M_J) - \alpha_x(M'_J) = (J^2 + J - 2M_J^2 - M_J'^2)(A - B + C)$$

It follows from Eqs. (9) that once two independent tensor components are known, all components of all the magnetic substates are determined. It is also easily seen that all the components are equal if $J < 1$, i.e., for atoms with $J \leqslant \tfrac{1}{2}$ the polarizability is scalar.

The matrix elements of μ_e are often expressed in terms of the dimensionless oscillator strengths, f_{0k}, which are defined as

$$f_{0k} = \tfrac{2}{3} \frac{m(\mathscr{E}_k - \mathscr{E}_0)}{e^2 \hbar_2} |\langle 0 | \mu_e | k \rangle|^2 \eta(J, J') \tag{10}$$

where

$$\eta(J, J + 1) = (J + 1)(2J + 3), \quad \eta(J, J) = J(J + 1), \quad \eta(J, J - 1) = J(2J - 1),$$

and e and m are the electronic charge and mass, respectively. The average polarizability in terms of the oscillator strengths is

$$\bar{\alpha} = \frac{e^2 \hbar^2}{m} \sum_{k \neq 0} \frac{f_{0k}}{(\mathscr{E}_k - \mathscr{E}_0)^2} \tag{11}$$

The oscillator strengths satisfy a simple sum rule,

$$\sum f_{0k} = N \tag{12}$$

where N is the total number of electrons in the atom. The summation of Eq. (12) includes oscillator strengths to all possible states of all degrees of ionization and excitation of the atom. A situation that frequently occurs is one in which only oscillator strengths associated with the "first spectrum" of the atom make appreciable contributions to the polarizability. In particular, very often only those transitions which can be represented by the motion of a single electron make appreciable contributions to the polarizability. Under those circumstances there is only one "effective" electron and Eq. (12) becomes, approximately,

$$\sum_k f_{0k} = 1 \tag{13}$$

Eq. (13) is useful in that it sets an approximate upper bound to $\bar{\alpha}$,

$$\bar{\alpha} \leqslant \frac{e^2 \hbar^2}{m} \frac{1}{(\mathscr{E}_1 - \mathscr{E}_0)^2} \tag{14}$$

where $\mathscr{E}_1$ is the energy of the state closest in energy to the unperturbed state whose $f_{0k} \neq 0$. If it is known that almost the entire oscillator strength summation arises from a very small number of transitions, and these f_{0k} are known or can be estimated, then the average polarizability can be determined very simply and with some accuracy. (See, for example, Dalgarno and Kingston's calculation of alkali polarizabilities.[7])

The quantity

$$\alpha_z(M_J) - \alpha_x(M_J) = (J^2 + J - 3M_J^2)(A - B + C)$$

is a measure of the polarizability anisotropy, and is zero if $J \leqslant \frac{1}{2}$. It is indirectly related to the atomic quadrupole moment Q defined as

$$Q = e\langle 3z^2 - r^2 \rangle = 2e\langle z^2 - x^2 \rangle \tag{15}$$

with $|M_J| = J$. Eq. (15) can be rewritten as

$$Q = 2e(\langle 0|z^2|0\rangle - \langle 0|x^2|0\rangle),$$

or

$$eQ = 2[\sum_{k \neq 0} |\langle 0|\mu_z|k\rangle|^2 - \sum_{k \neq 0} |\langle 0|\mu_x|k\rangle|^2]$$

Following the procedure leading to Eq. (7), eQ can be expressed in terms of reduced matrix elements as

$$eQ = (-2J^2 + J)(A' - B' + C') \tag{16}$$

where

$$A' = (\sum_{k \neq 0} |\langle 0|\mu_e|k\rangle|^2) \delta_{J-1, J'}$$

$$B' = (\sum_{k \neq 0} |\langle 0|\mu_e|k\rangle|^2) \delta_{J, J'}$$

$$C' = (\sum_{k \neq 0} |\langle 0|\mu_e|k\rangle|^2) \delta_{J+1, J'}.$$

Thus, the polarizability anisotropy and the atomic quadrupole moment differ only in the energy denominators of the sum over dipole matrix elements.

III. METHODS OF CALCULATING POLARIZABILITIES

The polarizability can be calculated, in principle, without evaluating the summation in Eq. (6). Let $|F\rangle$ be the first-order correction to the unperturbed wave function. The wave equation for $|F\rangle$ is then

$$(\mathcal{H}_0 - \mathcal{E}_0)|F\rangle = -\mathcal{H}'|0\rangle \tag{17}$$

If Eq. (17) can be solved for $|F\rangle$, the second-order energy equivalent to Eq. (2) is

$$\mathcal{E}_2 = \langle F|\mathcal{H}'|0\rangle \tag{18}$$

Eqs. (17) and (18) serve as the starting point for all approximate perturbation calculations of the polarizability.

The simplest procedure is to assume that $|0\rangle$ can be represented by a product of one-electron wave functions, (Hartree approximation) and to apply Eq. (17) separately to each orbital. The total polarizability is then the sum of the polarizabilities of the individual one-electron wave functions. This approach neglects exchange and the mutual effect of the induced dipole moments on each other, (i.e., "screening"), but is applicable to systems of any number of electrons. The amount of labor required is simply proportional to the number of orbitals.

The one-electron wave functions are considered to be derivable from a central potential V_{0i}, with eigenvalues $\mathcal{E}_{0i}$, so that they may be written as products of functions of the radial coordinates of the electrons and spherical harmonics. Following Sternheimer, the equation for the radial part of each unperturbed wave function, $P_i(r)$, has the form (in Rydberg units)

$$-\frac{d^2 P_i}{dr_i^2} + \frac{\lambda_i(\lambda_i + 1) P_i}{r_i^2} + (V_{0i} - \mathcal{E}_{0i}) P_i = 0 \tag{19}$$