

# **ELECTRIC-DIPOLE POLARIZABILITIES OF ATOMS, MOLECULES AND CLUSTERS**

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**To our families and parents.**

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# Preface

The seed for this book came from a review article published three years ago [1]. At the time a reviewer suggested that a book on polarizabilities was needed. Since the polarizability is a physical property of particles and materials that is so pervasive and important in describing and understanding the interaction of particles and electric fields, the need for such a book was clear. In this book we have aimed to clearly describe the polarizability as an electronic property, to discuss its importance in the physics and chemistry of atoms, molecules, and clusters, and to review theoretical and experimental techniques for deducing its value in a wide range of particle classes. A rigorous review of the frequency dependence and tensor properties of the polarizability is given. In addition, the last chapter attempts to provide some examples of the relation of the polarizability to important phenomena under recent study such as atom cooling and trapping, optical tweezers, and long-range interactions.

The ubiquitous occurrence of polarizabilities in physical phenomena has spawned a large literature that spans many fields: physics, chemistry, engineering, and biology. It is difficult to manage and maintain a complete command of this vast body of literature. However, we hope that one of the lasting effects of this book is to give an adequate summary of relevant work up to 1996 in the areas covered. We apologize in advance for not citing works that are relevant but that we missed. Also, as with any book, there are invariably mistakes that we inadvertently missed or that were made due to a lack of understanding on our part. In both of these cases, we ask our readers to provide us with a gentle reminder of our errors in exchange for the promise that we will try very hard to avoid the same mistakes in the future.

Many friends and colleagues have helped us in this endeavor, and we gratefully acknowledge their contributions. In particular, KDB thanks Will Happer for encouragement and moral support and especially for introducing him to this important subject in the first place. He is ever grateful to A.R. Marlow for long-term friendship and intellectual support. VVK learned about clusters, polarizabilities, and good science in general from Walter Knight, whose kind support and friendship are deeply appreciated. Joe Louderback was kind enough to read the entire manuscript twice and we thank him for his helpful feedback. We thank Thad Walker for many discussions on all aspects of atomic polarizabilities. We are also grateful to many others for their valuable comments on individual sections or whole chapters, viz., Jörg Becker (semiconductor clusters), Walt de Heer (position-sensitive time-of-flight polarizability technique), George Holzwarth (optical tweezers), Uwe Hohm and Dirk Goebel (refractive index measurements and dispersive Fourier-transform spectroscopy), Mark Pederson

(theory chapter), Dave Pritchard (atom interferometry), Dany Shapiro (biomolecules and organic molecules), and Thad Walker (atom cooling and trapping). Others who gave important comments on the review article that were incorporated into the book include D. Bishop, A.D. Buckingham, and Tom Miller. We owe a debt of gratitude to Michael Kadar-Kallen for his contributions to the experimental techniques chapter (from the original article). His sections formed the core for roughly half of Chapter 5. Judy Swicegood is to be thanked for her help on the bibliography. Many colleagues graciously permitted us to reproduce figures from their papers and provided us with original copies. Work on this book was partially supported by the U.S. National Science Foundation Programs in Chemistry and Atomic, Molecular, Optical, and Plasma Physics (KDB) and Atomic, Molecular, Optical, and Plasma Physics (VVK). KDB thanks Wake Forest University for providing excellent computer facilities and personnel (in particular C.W. Yip). ·

Finally, a special appreciation goes to our families. KDB thanks his children, Alex, Claire, and Caroline, and his wife, Marian, for cheerfully accepting a father and husband whose frequent physical absences, blank looks, and empty stares all indicated a mind present elsewhere. VVK is infinitely grateful to his wife, Susan, for her patience and support.

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# **ELECTRIC-DIPOLE POLARIZABILITIES OF ATOMS, MOLECULES AND CLUSTERS**

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# Chapter 1

## Introduction

The purpose of this book is to review experimental and theoretical techniques for determining electric-dipole polarizabilities of atoms, molecules, and clusters. Interest in polarizabilities of basic particles continues to grow, both to understand the electronic and optical response of new and old materials and to test computational methods for calculating electronic and optical properties. These methods and codes apply to other important material characteristics, such as magnetic response of particles and mechanical properties. Given the growing importance of light forces in atomic and molecular physics and chemistry that rely on the frequency-dependent polarizability, this book considers both static and frequency-dependent polarizabilities. However, for brevity and ease of understanding, in many cases we shall focus on the static polarizability.

The charge redistribution that occurs when a particle is exposed to an electric field is characterized by a set of constants called polarizabilities. The new charge distribution can be written in terms of electric multipole moments. The *lowest-order* moment of a *neutral* particle is a dipole moment  $\mathbf{p}$ . In a uniform electric field  $\mathbf{E}$  the dipole moment of the particle is conveniently written as

$$\mathbf{p} = \mathbf{p}_0 + \boldsymbol{\alpha} \cdot \mathbf{E} + \frac{1}{2}\boldsymbol{\beta}:\mathbf{E}^2 + \frac{1}{6}\boldsymbol{\gamma}:\mathbf{E}^3 + \dots \quad (1.1)$$

The term  $\mathbf{p}_0$  represents the permanent dipole moment. The polarizability  $\boldsymbol{\alpha}$  is a second-rank Cartesian tensor that characterizes the lowest-order *induced* dipole moment in a species. It is this quantity which is the subject of this book. The hyperpolarizabilities  $\boldsymbol{\beta}$  and  $\boldsymbol{\gamma}$  represent third- and fourth-rank Cartesian tensors. For symmetric species, since  $\mathbf{p}(\mathbf{E}) = -\mathbf{p}(-\mathbf{E})$ , the permanent moment  $\mathbf{p}_0 = \mathbf{0}$  and the hyperpolarizability  $\boldsymbol{\beta} = \mathbf{0}$ . Since the advent of lasers, nonlinear optics has blossomed and interest in values of the *frequency-dependent* hyperpolarizability  $\boldsymbol{\gamma}$  for various nonlinear systems has increased.

For neutral species the polarizability is a basic property that characterizes the lowest-order response of the species to an applied electric field. The polarizability has units of volume and is of the same order of magnitude as the volume of the particle (e.g.,  $\sim 10^{-23}$  cm<sup>3</sup> for an atom). Polarizabilities are important in three broad areas of physics and chemistry:

- Electromagnetic field-matter interactions, where polarizabilities determine the response of neutral particles to applied fields, such as those produced by lasers.
- Collision phenomena, where polarizabilities determine the behavior of neutral particles as partners in interactions with other neutrals and/or charged particles.
- As an indication of physical size, structure, and shape.

Polarizabilities are also helpful in determining the electronic structure of atoms, molecules, and clusters. Some important physical properties of atoms and molecules that depend on the polarizability are given in Table 1.1. A more extensive list can be found in the Handbook of Chemistry and Physics [2]. A brief description of different notations and the units used to describe polarizabilities is given in Appendix A.

The earliest observation of an effect that could (subsequently) be directly related to a molecular polarizability was the first notice of anomalous dispersion by Fox Talbot (1840). It was Stokes who first made the crucial proposal that molecules could be treated as having their own natural vibrational frequencies that result in observable effects when interacting with light at a different frequency. This proposition, made in 1852 [4], was an attempt to explain fluorescence, a term coined by Stokes. In 1860 Le Roux [5] reported in the literature his observations on anomalous dispersion of light propagating through iodine vapor. In 1871 Kundt [6–8] first made the general observation that anomalous dispersion occurred whenever an absorption band was present. Almost simultaneously, Maxwell in 1869 [9] and Sellmeier in 1872 [10] suggested a theoretical explanation based on the existence of harmonic oscillators in the material that would become forced when the wavelength (or frequency) of light approached the natural frequency of the harmonic oscillators. Hence, the famous Sellmeier formula for the refractive index of a material  $\eta$  as a function of wavelength  $\lambda$

$$\eta^2 - 1 = \frac{e^2}{\pi m c^2} \sum_k N f_k \lambda_k^2 \left[ 1 + \frac{\lambda_k^2}{\lambda^2 - \lambda_k^2} \right], \quad (1.2)$$

where  $N f_k$  is the number of electrons having a resonance at wavelength  $\lambda_k$ ,  $c$  is the speed of light,  $e$  is the charge on an electron, and  $m$  is the mass of the electron. A modern, microscopic understanding of the response of atoms and molecules to electric fields began with the prediction of Voigt [11] in 1901 that an electric analog to the Zeeman effect should exist. In 1913, Lo Surdo [12] and Stark [13] independently reported the first observations of the splitting of atomic levels by application of electric fields. Although the Stark effect was first treated theoretically by [14–16], it was Kramers [17] who first treated an energy splitting that required an *induced*, field-dependent dipole moment (quadratic Stark effect).

The earliest measurements on free atoms that could be used (later) to deduce polarizabilities were the dielectric constant measurements of Hochheim [18] in 1908 and the refractive index measurements of Cuthbertson and Cuthbertson [19] in 1910. Both sets of measurements involved the inert gases. Koch [20] in 1908 measured the refractive indices of common molecules hydrogen and oxygen as well as air, determining the dispersion constants for these species that are useful in Sellmeier's dispersion