

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., $\sim 10^{-23}$ cm³ 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 η as a function of wavelength λ

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

where $N f_k$ is the number of electrons having a resonance at wavelength λ_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

Table 1.1: Important physical quantities that depend on the scalar polarizability.

Electromagnetic Response Properties	
Quantity	Relation to α
1. Dielectric constant ^a	$\epsilon = 1 + 4\pi\alpha$
2. Refractive index ^a	$\eta = 1 + 2\pi\alpha$
3. Energy shift	$U = -\alpha E^2/2$
4. Phase shift of wavefunction ^b	$\Delta\phi = \int_{x_i}^{x_f} U dx/\hbar v$
Collision Properties	
Quantity	Relation to α
1. Long-range electron- or ion-atom interaction potential ^c	$U = -e^2\alpha/2r^4$
2. Ion mobility in gas ^d	$K = 13.876\sqrt{\alpha\mu} \text{ cm}^2/\text{volt sec}$
3. van der Waals constant between systems a, b (Slater-Kirkwood approximation) ^e	$C_6 = \frac{3}{2} \left(\frac{\alpha_a \alpha_b}{\sqrt{\alpha_a/n_a + \sqrt{\alpha_b/n_b}}} \right)$
Relation to Physical Structure ^f	
Particle	Expression for α
1. Classical metal sphere	R^3
2. Classical dielectric sphere	$R^3(\epsilon - 1)/(\epsilon + 2)$
3. Classical dielectric shell ^g	$\frac{(1-\rho)(\epsilon-1)(2\epsilon-1)}{(2\epsilon+1)(\epsilon+2)-2\rho(\epsilon-1)^2} R^3$
4. Small metal cluster ^h	$R^3 f(R)$

^aThis relation holds for a dilute, nonpolar gas ($\epsilon \approx 1$ limit of the Clausius-Mossotti equation).

^bThe quantity $x_f - x_i$ is the length of the electric field region (in quantity 3, previous line).

^cThe quantity r is the separation between the colliding pair of particles; e is the charge on an electron and we have assumed singly-ionized ions.

^dAssumes α in units of \AA^3 ; μ is the reduced mass of the ion-atom pair in atomic mass units.

^eHere $n_{a,b}$ refers to the number of outer shell electrons in species a and b respectively.

^fHere R is the physical radius of the particle.

^gThe quantity $\rho = \delta R/R$, where the thickness of the shell wall is δR . This expression is derived in Ref. [3].

^hFor a discussion of the function $f(R)$ see Sec. 4.10.4.

formula Eq. (1.2). A straightforward technique for measuring polarizabilities is to deflect the atoms in an inhomogeneous electric field and measure the resulting deflection. This technique was first tried by Scheffers and Stark [21] in 1934. They measured the scalar polarizability (α_0) of alkali atoms to accuracies of 20-50%. To this day the alkali and alkaline earth atoms and those elements which are a gas at room temperature account for most of the accurately measured atomic polarizabilities, with the exceptions being Hg, In, Tl, Al and most recently, U [22], Ga and As [23], and Zn [24]. For most elements, theoretical values are the only ones available.

1																	2	
H																	He	
3	4											5	6	7	8	9	10	
Li	Be											B	C	N	O	F	Ne	
11	12											13	14	15	16	17	18	
Na	Mg											Al	Si	P	S	Cl	Ar	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
55	56			72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba			Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88			104	105	106	107	108	109	110								
Fr	Ra			Rf	Db	Sg	Bh	Hs	Mt									
		Lanthanide Series																
		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71		
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Actinide Series																
		89	90	91	92	93	94	95	96	97	98	99	100	101	102	103		
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Figure 1.1: Periodic table of elements indicating which elements have measured polarizabilities.

A number of reviews of polarizability data, including experimental details and calculations have been published [1, 25–30]. The CRC Handbook of Chemistry and Physics contains an annually-updated list of polarizability values for the elements and many molecules. The book by Atkins [31] contains a clear elementary introduction into the properties and manifestations of molecular polarizabilities. The review paper of Miller and Bederson [25] is particularly useful and includes a discussion of techniques and results on excited states which are not discussed here. They also give an extensive review of theoretical calculations up to 1976; here, we will mention some recent techniques used to calculate polarizabilities. This book reviews the frequency dependence of the polarizability, discusses and compares experimental techniques and calculations, and provides a review of work on clusters (both metal and dielectric). The recent experimental techniques that are discussed in detail include

- Dispersive Fourier transform spectroscopy: used to measure the frequency-dependent polarizability over a broad frequency spectrum.
- M-lines method: used to measure the refractive index and polarizability of thin films and molecules in a thin-film matrix.
- Time-of-flight: used to accurately measure the polarizability of aluminum clusters.

- Light force: used to measure the polarizability of a highly refractory element — uranium.
- Atom interferometry: used to make the most accurate measurements of α for an alkali atom (sodium).

A summary of some of the most important experimental techniques is given in Table 1.2.

Table 1.2: Summary of experimental techniques for measuring ground-level polarizabilities.

Technique	Pol. ^a	Error ^b α_0 (%)	Advantages	Disadvantages
<i>Bulk</i>				
Dielectric const.	α_0	0.05	Accurate	Limited to inert gases/simple molecules
Refractive index	α_0	0.02	Accurate	Limited mainly to inert/molecular gases
Rayleigh scatt.	κ^2	—	Accurate for anisotropic pol.	measurement of α_0 difficult
Kerr effect	$\alpha_0\kappa$	—	Can measure hyperpols.	Cannot measure α_0
<i>Beam</i>				
Deflection	α_0	4.4	Can be applied to clusters	Somewhat sensitive to velocity distribution; large field uncertainties
E-H balance	α_0, α_2	2	Independent of velocity distrib.	Limited to species with magnetic moments
Beam-resonance	α_2	—	Sensitive to $\alpha_2 < 10^{-6} \text{ \AA}^3$	Can only measure α_2
Light-force	$\alpha_0, \alpha_1, \alpha_2$	6	Good for ions, refractories	Must extrapolate to obtain $\alpha(\text{dc})$
Atom interferometry	α_0	0.3	Accurate	

^aThe quantities in column two are the scalar polarizability (α_0), the vector polarizability (α_1), the tensor polarizability (α_2), and the anisotropy of the polarizability tensor (κ). See text for details.

^bThis column represents the lowest errors for these techniques, reflecting the accuracy of the best measurements.

The polarizability of bulk matter is a macroscopic quantity whose relationship to the microscopic polarizabilities of the constituent atoms and molecules is quite complex. Bulk matter polarizabilities are only briefly mentioned when needed to discuss an experimental result. A detailed discussion of the dielectric properties of bulk materials can be found elsewhere [32, 33].

Practical use of the polarization properties of particles and bulk materials is quite extensive. Most readers are probably aware of the importance of the polarization

properties of dielectrics used in capacitors and other electronic devices. Fewer are aware of the use of these properties in geophysics. A well-established technique, called Induced Polarization (IP), was discovered by the French scientist, Conrad Schlumberger, in the 1910's. Although he never exploited or developed his discovery, such work began in the mid-1930's and became commercial in the 1950's. Induced Polarization is one of several techniques used in mining and geothermal exploration and in ground-water exploration. Due to its applied nature in a field outside the purview of most scientists, we shall briefly describe the technique of IP. An exhaustive review of IP is given in the two-volume set by Bertin and Loeb [34]. The discussion here is based on a more recent review by Ward [35].

One basic physical setup consists of four electrodes placed in the Earth's surface as shown in Fig. 1.2. The two electrodes on the left are supplied signals which result in constant currents for fixed periods of time [see Fig. 1.3(a)]. The electrodes on the right measure the potential response of the surrounding subsurface region of the Earth [see Fig. 1.3(b)]. The main physical property of the soil that these signals measure is the resistivity. This can be seen by noting that the resistivity ρ is given by the relationship [35]

$$\rho = K \frac{V}{I}, \quad (1.3)$$

where K is a factor dependent on the electrode geometry, V is the potential difference measured between the two right electrodes when a current I flows between the two left electrodes. Information about the soil conductivity is also present in the decay part of the potential curve [Fig. 1.3(b)].

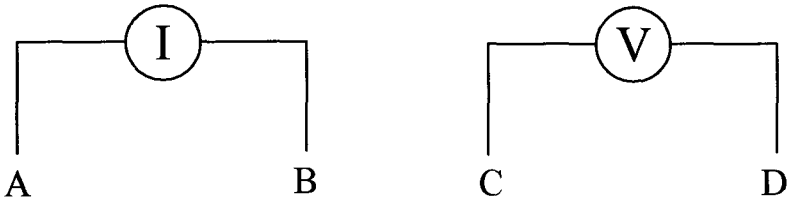


Figure 1.2: A typical dipole-dipole array of electrodes for an Induced Polarization measurement of a region of the Earth's surface to determine subsurface conductivity and other properties. A current is sent through the subsurface of the Earth with a current source connected at points A and B. The resulting electric potential between points C and D is measured.

Two types of polarization play a role in the signals produced with the Induced Polarization method. The first, called electrode polarization, occurs at the boundary of a metal electrode in soil. In the soil layer adjacent to the electrode charge separation occurs that results in a polarization. Here, current conduction occurs in two ways: through the direct flow of ions and through charging and discharging of the charge layers surrounding the electrode. The second type of polarization important in measuring soil resistivity via the IP method is membrane polarization of clay particles in soil. Clay particles are normally negatively charged in soils and so they accumulate a layer of cations near their surface that results in a separation of

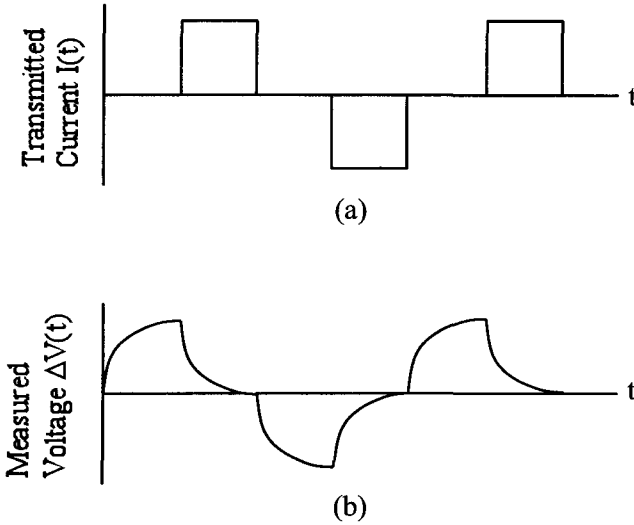


Figure 1.3: The transmitted and received signals for a typical dipole-dipole array of electrodes for an Induced Polarization measurement of a region of the Earth's surface.

charges — the so-called membrane polarization. Clay particles dramatically affect soil conductivity due to their low resistivity. When an electric potential is applied to the soil, i.e. a current flows, the clay particles act as an ion-selective membrane that only allows cationic flow. This produces a region of high concentration of cations and anions at one end of the membrane zone and a deficit at the other end of the zone. This concentration gradient reduces ion mobility and hence results in an increase in resistivity. This fascinating phenomenon is lucidly explained on a microscopic scale, with helpful diagrams, by Ward [35]. Hence, one can view the Induced Polarization technique as a method for measuring soil resistivity which depends on the dielectric constant or 'polarizability' of subsurface soil.