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Edited by

D. R. Bates

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ADVANCES IN ATOMIC AND MOLECULAR PHYSICS

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D. R. Bates

DEPARTMENT OF APPLIED MATHEMATICS AND THEORETICAL PHYSICS
THE QUEEN'S UNIVERSITY OF BELFAST
BELFAST, NORTHERN IRELAND

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ATOMIC AND MOLECULAR POLARIZABILITIES—A REVIEW OF RECENT ADVANCES

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I. Introduction

The electric dipole polarizability of an atom or molecule describes the response in lowest order of the field strength of the electron cloud to an external electric field. This property plays an important role in those collision processes where the relevant electric field is that produced between collision partners, one or both of which is a neutral atom or molecule. Indeed, some

TABLE I
MANIFESTATIONS OF THE ELECTRIC DIPOLE POLARIZABILITY α^a

Long-range electron- or ion-atom interaction energy	$V = -e^2\alpha/2r^4$
Ion mobility in a gas ^b	$K = 13.876/(\alpha\mu)^{1/2} \text{ cm}^2/\text{volt sec}$
Relation between $\alpha(v)$ and oscillator strengths ^c	$\alpha(v) = \frac{3}{4\pi n} \left(\frac{\eta(v)^2 - 1}{\eta(v)^2 + 2} \right)$
van der Waals constant between systems a, b (Slater-Kirkwood approximation) ^d	$C_6 = \frac{3}{2} \left(\frac{\alpha_a \alpha_b}{(\alpha_a/n_a)^{1/2} + (\alpha_b/n_b)^{1/2}} \right)$
"Dipole-quadrupole" constant C_8^e	$C_8 = \frac{15}{2} \alpha_d \alpha_q \left[\frac{1}{\bar{\omega}_d} + \frac{1}{\bar{\omega}_q} \right]^{-1}$
Clausius-Mosotti relation ^f	$\alpha(v) = \frac{3}{4\pi n} \left(\frac{n(v)^2 - 1}{n(v)^2 + 2} \right)$
Dielectric constant ^g	$K(v) = 1 + 4\pi n\alpha(v)$
Index of refraction ^h	$\eta(v) = 1 + 2\pi n\alpha(v)$
Diamagnetic susceptibility ⁱ	$\chi^m \simeq e^2[a_0 n_e \alpha]^{1/2}/4mc^2$
Verdet constant ^j	$V(v) = \frac{vn}{2mc^2} \frac{d\alpha(v)}{dv}$
Rayleigh scattering cross-section ^k	$\sigma(v) = (8\pi/9c^4)(2\pi v)^4 [3\alpha(v)^2 + \frac{2}{3}(v^2)]$
Modified effective range cross-section ^l	$\sigma(k) = 4\pi A^2 + \frac{8\pi^2\mu}{3\hbar^2} Z^2 e^2 \alpha A k + \dots$
Langevin capture cross-section ^m	$\sigma(v_0) = \frac{2\pi}{v_0} \left(\frac{e^2\alpha}{\mu} \right)^{1/2}$
Casimir-Polder effect ⁿ	$V(r) = -g \left(\frac{3\alpha^2 E_i}{4r^6} \right)$

^a α is the static polarizability; frequency-dependent polarizabilities are indicated by $\alpha(v)$, which reduce to α for $v = 0$. Anisotropic effects are not included, except where specifically noted; cgs units are used except where noted.

^b α in units of \AA^3 , μ is the ion-atom reduced mass in units of the proton mass. Assumes pure polarization interaction $-e^2\alpha/2r^4$; classical limit.

^c f_{0k} is the average oscillator strength over magnetic substates, and refers to a transition between the state whose polarizability is $\alpha(v_0)$ and all other states connected to this state by dipole matrix elements.

^d $n_{a,b}$ are number of electrons in outer shells of a, b .

^e α_d, α_q are the dipole and quadrupole polarizabilities; $\bar{\omega}_d, \bar{\omega}_q$ are the average transition frequencies for dipole and quadrupole transitions (see Stwalley, 1970; Kramer and Herschbach, 1970).

^f For a gas of atoms or of molecules that do not possess permanent electric dipole moments. $\eta(v)$ is the frequency-dependent index of refraction. n is number density.

^g Obtained from Clausius-Mosotti relation, assuming $K \approx 1$.

^h $\eta^2(v) = K(v)$.

ⁱ In the approximation that the static polarizability is given by the variational formula

$$\alpha = \frac{4}{9a_0} \sum_i (n_i r_i^2)^2$$

low-energy scattering process can be specified accurately by an expression that involves only one parameter—the polarizability.

In some circumstances a part of the atom can also be assigned a well-defined polarizability. Thus, the “core polarizability” refers to the polarizability of the inner shells and is an important parameter in determining quantum defects, nuclear shielding, and polarizabilities of ionized atoms.

Clearly, the polarizability is particularly important in interactions where there is little interpenetration of the wavefunctions of the collision partners. The most loosely bound electrons play the largest role in the redistribution of the electron charge in an electric field; the valence electrons generally account for at least 90% of the polarizability of an atom or molecule.

The manifestations of the atomic polarizability in collision phenomena are manifold. A testimony to its importance is the frequency with which one encounters an expression involving the polarizability. We have gathered a representative collection and give them in Table I, which also includes some references to frequency-dependent polarizabilities. Some of these expressions have been used as a basis for measuring the polarizability, for example, using dielectric constants or ion mobilities. It is sometimes difficult to track down published polarizability calculations for specific atoms and molecules, since these often appear as intermediate steps in other calculations. One of the best calculations of the polarizability of cesium is that of Norcross (1973), in a paper entitled “Photoabsorption by Cesium.” Other examples are the papers of Ice and Olson (1975) entitled “Low-Energy Ar^+ , Kr^+ , Xe^+ + K, Rb, Cs Charge Transfer Total Cross Sections,” and of Garrett (1965), “Polarization and Exchange Effects in Slow-Electron Scattering from Lithium and Sodium,” in which atomic polarizabilities were calculated.

(Table footnotes continued)

(see Hirschfelder *et al.*, 1954, p. 942 ff.). The correct definition of magnetic susceptibility per atom is

$$\chi^m = \frac{e^2}{6mc^2} \sum_i n_i \bar{r}_i^2$$

In the very crude approximation that all the energy denominators in the oscillator strength summation for α are equal to the ionization energy, $\chi^m = (E/4mc^2)\alpha$.

^j Defined from $\theta = V(v)B$, where θ is the angle of rotation of linearly polarized light through a medium of density n , per unit length, for a longitudinal magnetic field strength B (Faraday effect).

$$^k \alpha(v) = \frac{2}{3}\alpha_{\perp} + \frac{1}{3}\alpha_{\parallel}; \gamma(v) = \alpha_{\parallel} - \alpha_{\perp}$$

^l A is the scattering length, μ the reduced mass, k the wavenumber of the scattered particle, $\mu\sigma/h$ (see O'Malley *et al.*, 1962).

^m v_0 is the relative velocity of approach for an ion-neutral pair.

ⁿ $V(r)$ is interaction energy for two nonpolar molecules, at very large distances [$r \gg cE_i/h$], g is a numerical factor, and E , equals an average over the excitation energies (Casimir and Polder, 1938).

This article will review recent advances in the experimental and theoretical determination of the polarizabilities of simple atoms and molecules. We will concentrate primarily on static (as opposed to frequency-dependent) polarizabilities, although some discussion of the latter will be presented. Higher-order polarizabilities, which are becoming increasingly accessible to observation because of the availability of high-intensity lasers, will also be briefly discussed.

The perturbation of atomic levels by electric fields was first reported by Stark (1913) and independently by LoSurdo (1913). The "Stark effect" was treated theoretically by Epstein (1916), who was later to apply the new quantum theory to the same problem (Epstein, 1926). Polarizability values (related to the "quadratic Stark effect") are accurately known for the noble gas atoms and for hydrogen, in theory, but the remainder of the periodic table has proven much more difficult to deal with, both theoretically and experimentally. The static electric dipole polarizability of the ground-state hydrogen atom is almost exactly $4.5a_0^3$, where a_0 is the Bohr radius. Across rows of the periodic table, polarizabilities range from hundreds (of a_0^3 units) for the alkali metal atoms generally monotonically down to a few for noble gas atoms. Excited atoms have much larger polarizabilities; recent polarizability measurements for atoms in Rydberg orbits have yielded values on the order of $10^{10}a_0^3$. In Fig. 1 we have plotted the polarizabilities of the atoms in the first row of the periodic table. On the same graph we show the polarizability anisotropy, which indicates the importance of the orientation

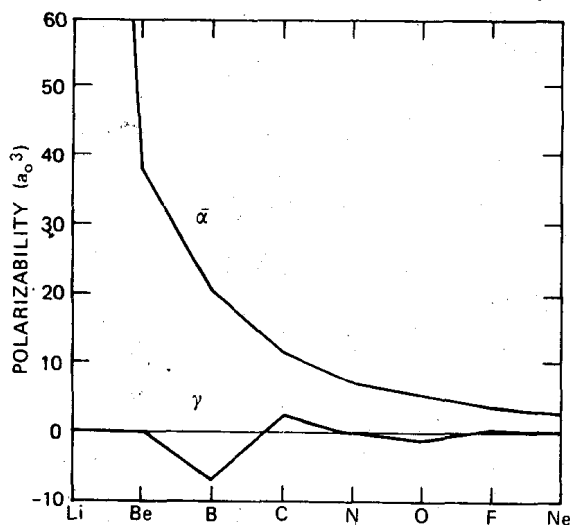


FIG. 1. Atomic polarizabilities and polarizability anisotropies across the first row of the periodic table. (Results of Werner and Meyer, 1976.)

of the atom in an external electric field. The anisotropy is largest when the first p electron is added (boron) and becomes smaller for successive P states as the valence shell fills.

A. MOMENTS

An atom or molecule in a uniform electric field \mathbf{E} has an electric dipole moment

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

We will deal with cases where there is no permanent dipole moment \mathbf{p}_0 , only induced moments. Thus this discussion is restricted to the class of all atoms, and homonuclear molecules. For spherically symmetric states β is zero. One is generally concerned only with the *polarizability* α , a second-rank tensor; however, the *hyperpolarizability* γ (a fourth-rank tensor) is of current interest in relation to laser studies of nonlinear effects in atoms. Higher-order hyperpolarizabilities are not significant in present-day experiments. Practically speaking, for static laboratory fields the induced electric dipole moment is adequately described by the polarizability α . If intense laser radiation fields are also present, then both the polarizability α and the hyperpolarizability γ are needed to determine the induced electric dipole moment, although of course for this situation one is referring to $\alpha(\nu)$, $\gamma(\nu)$, where ν is the frequency of the laser field. For the ground state of the hydrogen atom, the polarizability α , as already mentioned, is $4.5a_0^3$, while the hyperpolarizability γ is exactly $1333.125a_0^6/\text{Hartree}$.

The hyperpolarizability should not be confused with higher-order multipoles of the atomic charge distribution. The full quadrupole moment also contains induced terms, which depend on the electric field strength and on the field gradient. A complete treatment of the dipole and quadrupole expansions and the symmetry properties of the coefficients has been given by Buckingham (1967). All coefficients in these expansions depend upon the frequency of the applied external electric field. We are interested primarily in dc fields and most of our discussion will be for *static* polarizabilities. The polarizability is not significantly different from its static value for frequencies of the external electric field much less than the frequency corresponding to the lowest excitation energy of the atom. For resonant frequencies or very large frequencies the atom may absorb energy from the external field via excitation or ionization of the atom, and loss of flux to these channels will affect the polarizability. Calculation of the polarizability for complex frequencies yields the total photoionization cross section, proportional to $\alpha(i\omega)$, where i denotes the imaginary part of the angular frequency ω .

We have not mentioned dipole and quadrupole shielding factors that

involve different matrix elements than will be emphasized below, but the calculational methods are the same. The dipole shielding factor is the ratio of the change in the electric field at the nucleus due to the redistribution of the atomic charge, to the strength of the external electric field at the nucleus. The dipole shielding factor is determined by the operator $\sum_{i=1}^N P_1(\cos \theta_i)/r_i^2$, where the sum is over the N electrons of the atom, r_i and θ_i are radial and angular coordinates for the i th electron, and $P_K(\cos \theta_i)$ is a Legendre polynomial of order K . The quadrupole shielding factor depends on the operator $\sum_{i=1}^N P_2(\cos \theta_i)/r_i^3$. Dipole and quadrupole shielding factors are required for the determination of nuclear moments from measurements of atomic hyperfine structure. They correct for the distortion by core electrons of the effect of nuclear moments on the energy of the valence electrons. According to the Hellmann-Feynman theorem (Chang *et al.*, 1968), the dipole shielding factor is unity for a neutral atom and N/Z in general. Application of various theoretical techniques to its calculation provides grounds for comparisons between these techniques.

B. MATRIX ELEMENTS

It is customary to treat the external electric field as a perturbation. The perturbation hamiltonian is $-\mathbf{p} \cdot \mathbf{E}$, where \mathbf{p} is the dipole operator $-e \sum_{i=1}^N \mathbf{r}_i$. The summation is of the position coordinates \mathbf{r}_i of the N electrons in the atom. The electronic charge is e . The first-order energy correction $\langle \psi_0 | \mathbf{p} \cdot \mathbf{E} | \psi_0 \rangle$ is zero if the unperturbed state $|\psi_0\rangle$ has definite parity. This is to say that there is no permanent dipole moment. The second-order energy correction W_2 is quadratic in E ,

$$W_2 = -E^2 \sum_{k \neq 0} \frac{|\langle \psi_0 | \mathbf{p} \cdot \hat{\mathbf{n}} | \psi_k \rangle|^2}{\mathcal{E}_k - \mathcal{E}_0} \quad (2)$$

where $\hat{\mathbf{n}}$ is a unit vector defined by $\mathbf{E} = E\hat{\mathbf{n}}$, k denotes a state of the atom of energy \mathcal{E}_k , and the sum is over all states of the atom except for $k = 0$.

We can compare this energy correction to the negative integral of Eq. (1),

$$W = -\frac{1}{2}\alpha : E^2 \quad (3)$$

in which we have taken $\mathbf{p}_0 = \beta = 0$ and have ignored higher-order dipole polarizabilities. We see that the second-order energy correction in perturbation theory may be identified with the polarizability α . The fourth-order energy correction gives γ .

If we consider a cartesian coordinate system (x, y, z) , the components of the polarizability tensor are

$$\alpha_{ij} = 2 \sum_{k \neq 0} \frac{\langle 0 | p_i | k \rangle \langle k | p_j | 0 \rangle}{\mathcal{E}_k - \mathcal{E}_0} \quad i, j = x, y, z \quad (4)$$

The components of the hyperpolarizability tensor are (Buckingham, 1967)

$$\begin{aligned} \gamma_{ijmn} = & S(i, j, m, n) \sum_{k \neq 0} \\ & \times \left\{ \sum_{l \neq 0} \times \left[\sum_{q \neq 0} \frac{\langle 0 | p_i | k \rangle \langle k | p_j | l \rangle \langle l | p_m | q \rangle \langle q | p_n | 0 \rangle}{(\mathcal{E}_k - \mathcal{E}_0)(\mathcal{E}_l - \mathcal{E}_0)(\mathcal{E}_q - \mathcal{E}_0)} \right. \right. \\ & - \frac{\langle 0 | p_i | k \rangle \langle k | p_j | 0 \rangle \langle 0 | p_m | l \rangle \langle l | p_n | 0 \rangle}{(\mathcal{E}_k - \mathcal{E}_0)^2 (\mathcal{E}_l - \mathcal{E}_0)} \\ & \left. \left. - 2 \frac{\langle 0 | p_i | 0 \rangle \langle 0 | p_j | k \rangle \langle k | p_m | l \rangle \langle l | p_n | 0 \rangle}{(\mathcal{E}_k - \mathcal{E}_0)^2 (\mathcal{E}_l - \mathcal{E}_0)} \right] \right. \\ & \left. + \frac{\langle 0 | p_i | 0 \rangle \langle 0 | p_j | 0 \rangle \langle 0 | p_m | k \rangle \langle k | p_n | 0 \rangle}{(\mathcal{E}_k - \mathcal{E}_0)^3} \right\} \quad (5) \end{aligned}$$

where $i, j, m, n = x, y, z$, and $S(i, j, m, n)$ is a symmetrizing operator implying a summation over all the 24 permutations of i, j, m, n in the expression following $S(i, j, m, n)$.

We have already indicated that odd-order energy corrections for spherically symmetric atoms are zero. There are also simplifications in the α and γ tensors for isotropic systems. The α and γ tensors themselves must be isotropic; the only second-order isotropic tensors are scalar multiples of the unit tensor δ_{ij} ; therefore,

$$\alpha_{ij} = \alpha \delta_{ij} \quad (6)$$

where α is a scalar and fully represents the polarizability for S-state atoms. Fourth-order isotropic tensors have nonzero components only when i, j, m , and n occur in pairs. The most general isotropic fourth-order tensor can be written

$$\gamma_{ijmn} = \lambda \delta_{ij} \delta_{mn} + \mu (\delta_{im} \delta_{jn} + \delta_{in} \delta_{jm}) + \nu (\delta_{im} \delta_{jn} - \delta_{in} \delta_{jm}) \quad (7)$$

The fourth-order energy correction is

$$W_4 = -\frac{1}{24} \gamma : \ddot{\mathbf{E}}^4 \quad (8)$$

which is

$$W_4 = -\frac{1}{24} \sum_i \sum_j \sum_m \sum_n \gamma_{ijmn} E_i E_j E_m E_n \quad (9)$$

where $i, j, m, n = x, y, z$. Substituting for γ_{ijmn} the general isotropic form given in Eq. (7), we find

$$W_4 = -\frac{1}{24} (\lambda + 2\mu) E^4 \quad (10)$$

where $E^2 = E_x^2 + E_y^2 + E_z^2$. In Eq. (9) we note that $\gamma_{xxxx} = \gamma_{yyyy} = \gamma_{zzzz} =$

$\lambda + 2\mu$, so that if we define a scalar $\gamma = \gamma_{xxxx} = \gamma_{yyyy} = \gamma_{zzzz}$ we can write a purely scalar equation,

$$W_4 = -\frac{1}{24}\gamma E^4 \quad (11)$$

For spherically symmetric atoms then, we have the energy given to fourth order by

$$W = W_0 - \frac{1}{2}\alpha E^2 - \frac{1}{24}\gamma E^4 \quad (12)$$

The geometric arguments above were given by Grasso *et al.* (1968).

In general, the calculation of atomic polarizabilities will involve nonspherical wavefunctions and the polarizability will depend on the orientations of the atom in the electric field. However, the polarizability tensor components are not necessarily independent. If the electric field direction is chosen to be along the axis of symmetry of the atom, the off-diagonal components vanish, and $\alpha_{xx} = \alpha_{yy}$. The dipole operator \mathbf{p} is a so-called T operator (Condon and Shortley, 1951) 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 $\alpha_{xx}(m_J)$ and $\alpha_{zz}(m_J)$ are then (Bederson and Robinson, 1966)

$$\begin{aligned} \alpha_{xx}(m_J) = & A(J^2 + m_J^2 - J) + B(J^2 + J - m_J^2) \\ & + C(J^2 + 3J + 2 + m_J^2) \end{aligned} \quad (13a)$$

$$\alpha_{zz}(m_J) = 2A(J^2 - m_J^2) + 2Bm_J^2 + 2C(J^2 + 2J + 1 - m_J^2) \quad (13b)$$

where

$$A = \sum_{k \neq 0} \left(\frac{|\langle \psi_0 | p | \psi_k \rangle|^2}{\mathcal{E}_k - \mathcal{E}_0} \right) \delta_{J-1, J'}$$

$$B = \sum_{k \neq 0} \left(\frac{|\langle \psi_0 | p | \psi_k \rangle|^2}{\mathcal{E}_k - \mathcal{E}_0} \right) \delta_{J, J'}$$

$$C = \sum_{k \neq 0} \left(\frac{|\langle \psi_0 | p | \psi_k \rangle|^2}{\mathcal{E}_k - \mathcal{E}_0} \right) \delta_{J+1, J'}$$

and $p = |\mathbf{p}|$, and J, J' are the total angular momenta for the ψ_0 and ψ_k states, respectively.

It can be shown that of the $2(2J + 1)$ equations represented by Eq. (13), only two are independent. The difference between any two tensor components is a multiple of $A - B + C$:

$$\alpha_{zz}(m_J) - \alpha_{zz}(m_{J'}) = 2(m_J^2 - m_{J'}^2)(A - B + C) \quad (14a)$$

$$\alpha_{xx}(m_J) - \alpha_{xx}(m_{J'}) = (m_J^2 - m_{J'}^2)(A - B + C) \quad (14b)$$

$$\alpha_{zz}(m_J) - \alpha_{xx}(m_{J'}) = (J^2 + J - 2m_J^2 - m_{J'}^2)(A - B + C) \quad (14c)$$

Therefore, once two independent components are determined, the full polarizability tensor for any m_J can be obtained from Eq. (14). We note from Eq. (13) that the tensor components are independent of the sign of m_J , and that if $J = \frac{1}{2}$ the polarizability is a scalar.

The two independent polarizability quantities are frequently expressed in terms of an isotropic part (the average polarizability) and a nonisotropic part (the anisotropy or the "tensor" polarizability). The average polarizability $\bar{\alpha}$ is defined as the average of either α_{xx} or α_{zz} over m_J . Equivalently, $\bar{\alpha}$ is the average of α_{xx} , α_{yy} , and α_{zz} for a given m_J :

$$\bar{\alpha} = \frac{1}{3}(2\alpha_{xx} + \alpha_{zz}) \quad (15)$$

and $\bar{\alpha}$ is the same for all m_J . The polarizability anisotropy [generally denoted by $\gamma(m_J)$, not to be confused with the hyperpolarizability γ] is defined as $\alpha_{zz}(m_J) - \alpha_{xx}(m_J)$, a quantity that depends on m_J . The "tensor" polarizability α_t is similar to the anisotropy except that the m_J dependence is removed:

$$\alpha_{zz}(m_J) = \bar{\alpha} + \alpha_t(3m_J^2 - J^2 - J)/J(2J - 1) \quad (16)$$

From Eqs. (13) and (15) it follows that

$$\alpha_t = -\frac{2}{3}J(2J - 1)(A - B + C) \quad (17)$$

When the symmetry axis of the atom is exactly parallel to the external electric field, the polarizability is denoted by α_{\parallel} ; in the perpendicular case it is α_{\perp} . In the laboratory the symmetry axis of the atom cannot be oriented exactly along the field direction and instead of α_{\parallel} the projection of α_{\parallel} along the field direction is measured, namely, α_{zz} ($m_J = J$).

The matrix elements for the polarizability are similar to those for the dimensionless oscillator strengths f_{0k} except for the energy factor, where

$$f_{0k} = \frac{2m_e(\mathcal{E}_k - \mathcal{E}_0)}{3e^2\hbar^2} |\langle \psi_0 | \mathbf{p} | \psi_k \rangle|^2 \eta(J, J') \quad (18)$$

and

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

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

and m_e and e are the electronic mass and charge. Comparing Eqs. (13) and (18), the average polarizability may be written

$$\bar{\alpha} = \frac{e^2\hbar^2}{m_e} \sum_{k \neq 0} \frac{f_{0k}}{(\mathcal{E}_k - \mathcal{E}_0)^2} \quad (19)$$

This equation is useful because frequently values of f_{0k} are available from experimental or theoretical work on atomic transitions, and an estimate of the average polarizability may be calculated from knowledge of these.

II. The Calculation of Polarizabilities

Theoretical calculations of polarizabilities have been made by a variety of techniques—semiempirical, perturbation, variational, and statistical—with some intermixing of these concepts. Some calculations are attempts to obtain “exact” results (or rigorous bounds) to an arbitrary degree of accuracy for specific atoms, while others are aimed at finding a rapid technique that can be more easily applied to any atom, sacrificing accuracy. Fortunately, a number of theorists have investigated the relationship between different methods.

A. SUMMATION OF OSCILLATOR STRENGTHS

The simplest theoretical technique for the calculation of dipole polarizabilities involves the summation of oscillator strengths, using Eq. (19). The oscillator strengths satisfy a sum rule

$$\sum f_{0k} = N \quad (20)$$

where the summation includes oscillator strengths for all possible electronic transitions including ionization. It would not be feasible actually to obtain *all* f_{0k} , but Eqs. (19) and (20) allow one to place bounds on the polarizability. If f_k is taken to represent known oscillator strengths (whether experimental or theoretical), and F_k are the remaining unknown oscillator strengths, then Eq. (20) becomes

$$\sum f_k + \sum F_k = N$$

and the contribution of the unknown oscillator strengths F_k to the polarizability is

$$\Delta\bar{\alpha} = \frac{e^2\hbar^2}{m_e} \sum_{k \neq 0} \frac{F_k}{(\mathcal{E}_k - \mathcal{E}_0)^2}$$

An upper bound to the unknown contribution $\Delta\bar{\alpha}$ is given by taking the smallest possible energy difference \mathcal{E}_{\min}^2 :

$$\Delta\bar{\alpha} \leq \frac{e^2\hbar^2}{m_e} \frac{1}{\mathcal{E}_{\min}^2} \sum_{k \neq 0} F_k \quad (21)$$

$$\Delta\bar{\alpha} \leq \frac{e^2\hbar^2}{m_e} \frac{1}{\mathcal{E}_{\min}^2} \left(N - \sum_{k \neq 0} f_k \right) \quad (22)$$

Then, we can place bounds on $\bar{\alpha}$:

$$\frac{e^2 \hbar^2}{m_e} \sum_{k \neq 0} \frac{f_k}{(\mathcal{E}_k - \mathcal{E}_0)^2} \leq \bar{\alpha} \leq \frac{e^2 \hbar^2}{m_e} \left[\sum_{k \neq 0} \frac{f_k}{(\mathcal{E}_k - \mathcal{E}_0)^2} + \frac{1}{\mathcal{E}_{\min}^2} \left(N - \sum_{k \neq 0} f_k \right) \right] \quad (23)$$

Dalgarno and Kingston (1959) used the oscillator strength sum rule for the alkali metal atoms. Except for lithium, almost all of the contribution to the sum comes from the resonance transition $n_0 S - n_0 P$, where n_0 is the principal quantum number of the ground state. Since only the valence electron is important, $N \approx 1$. Dalgarno and Kingston used experimental and theoretical estimates of oscillator strengths and estimated the accuracy of the results to be within about 5% except for cesium (10%). Their results are in accord with the latest experimental measurements of the alkali polarizabilities.

Altick (1964) used experimental oscillator strengths to place bounds on the polarizabilities of the alkaline earth atoms, for which there were no other data at the time. Cohen (1967) determined bounds on the polarizabilities of a number of neutral atoms and ions using experimental and theoretical oscillator strengths. Included were the alkali metal atoms, the alkaline earth atoms, and metastable helium states. [Unfortunately, the experimental resonance oscillator strengths used by Altick and Cohen for the alkaline earth atoms were low (Stwalley, 1971).] The alkali atom calculations tend to compare well to experiment, while the alkaline earth results are somewhat low. Hyman (1974) has calculated the polarizabilities of the alkaline earth atoms from experimental oscillator strengths.

B. EFFECTIVE QUANTUM NUMBERS

A semiempirical perturbation method has been developed by Adelman and Szabo (1973), which is an improvement over the coulomb approximation of Dalgarno and Pengelly (1966). They utilize an effective (nonintegral) principal quantum number obtained from the ionization potential, and an effective angular momentum quantum number related to the ionization potential of the closest electric-dipole-allowed state to the state under consideration. Explicit core effects are neglected by Adelman and Szabo, but the use of effective quantum numbers compensates for this neglect to some degree. An analytic expression is given for the 2^1 -pole static electric polarizability for atoms. The expression is evaluated for the dipole and quadrupole polarizabilities of many neutral atoms and ions. The results for S-state monovalent atoms seem remarkably good. The results for divalent atoms and P-state atoms are somewhat less reliable.