

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 $\alpha(\nu)$ and oscillator strengths ^c	$\alpha(\nu) = \frac{3}{4\pi n} \left(\frac{\eta(\nu)^2 - 1}{\eta(\nu)^2 + 2} \right)$
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	$\alpha(\nu) = \frac{3}{4\pi n} \left(\frac{n(\nu)^2 - 1}{n(\nu)^2 + 2} \right)$
Dielectric constant ^g	$K(\nu) = 1 + 4\pi n \alpha(\nu)$
Index of refraction ^h	$\eta(\nu) = 1 + 2\pi n \alpha(\nu)$
Diamagnetic susceptibility ⁱ	$\chi^m \approx e^2 [a_0 n_e \alpha]^{1/2} / 4mc^2$
Verdet constant ^j	$V(\nu) = \frac{\nu n}{2mc^2} \frac{d\chi(\nu)}{d\nu}$
Rayleigh scattering cross-section ^k	$\sigma(\nu) = (8\pi/9c^4)(2\pi\nu)^4 [3\alpha(\nu)^2 + \frac{2}{3}\gamma(\nu^2)]$
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 $\alpha(\nu)$, which reduce to α for $\nu = 0$. 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 $\alpha(\nu_0)$ 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. $\eta(\nu)$ is the frequency-dependent index of refraction. n is number density.

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

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

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

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

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_i 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

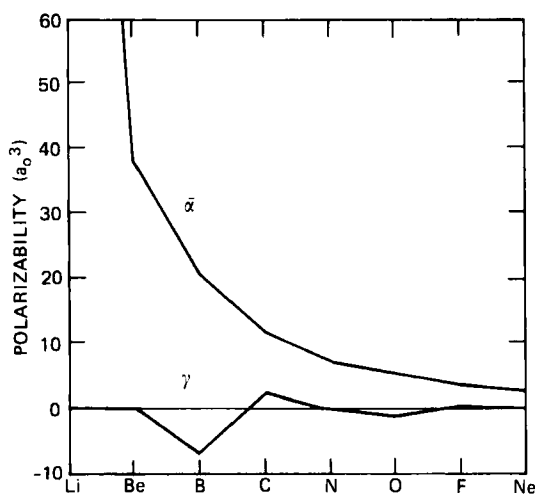


FIG. 1. Atomic polarizabilities and polarizability anisotropies across the first row of the periodic table. (Results of Werner and Meyer, 1976.)

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

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

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 $\boldsymbol{\beta}$ is zero. One is generally concerned only with the *polarizability* $\boldsymbol{\alpha}$, a second-rank tensor; however, the *hyperpolarizability* $\boldsymbol{\gamma}$ (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 $\boldsymbol{\alpha}$. If intense laser radiation fields are also present, then both the polarizability $\boldsymbol{\alpha}$ and the hyperpolarizability $\boldsymbol{\gamma}$ are needed to determine the induced electric dipole moment, although of course for this situation one is referring to $\boldsymbol{\alpha}(\nu)$, $\boldsymbol{\gamma}(\nu)$, 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),

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

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)

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

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 \mathbf{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

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

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, $\alpha_{zz}(m_J = J)$.

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

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

and

$$\begin{aligned} \eta(J, J + 1) &= (J + 1)(2J + 3), \\ \eta(J, J) &= J(J + 1), \quad \eta(J, J - 1) = J(2J - 1) \end{aligned}$$

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 $n_0 \text{S} - n_0 \text{P}$, 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^L -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.

C. PERTURBATION THEORY

In relation to the early work on the summation of oscillator strengths, it may be said that the goal of perturbation theory is to avoid a summation over states. The average polarizability can be written

$$\bar{\alpha} = \frac{2e}{3} \langle \psi_0 | \sum_{i=1} (x_i + y_i + z_i) | \psi_1 \rangle \quad (24)$$

where ψ_0 is the unperturbed wavefunction and ψ_1 the first-order correction. The electronic coordinates are (x_i, y_i, z_i) . The first-order correction to the wavefunction satisfies

$$(H_0 - W_0) | \psi_1 \rangle = e \sum_{i=1} (x_i + y_i + z_i) | \psi_0 \rangle \quad (25)$$

where H_0 is the unperturbed hamiltonian and W_0 the zeroth-order energy. In the case of spherically symmetric atoms, the average polarizability is simply

$$\bar{\alpha} = 2e \langle \psi_0 | \sum_{i=1} z_i | \psi_1 \rangle \quad (26)$$

Various approaches have been used to determine ψ_0 and ψ_1 . There is the intuitive idea that a Hartree-Fock procedure should give accurate polarizabilities (Musher, 1967; Kreiger and Kaufman, 1976). The most straightforward approach is the so-called coupled Hartree-Fock method of Dalgarno (1959), Allen (1960), and Kaneko (1959). This is a fully self-consistent procedure, which leads to perturbed orbitals that are coupled both by direct and exchange interactions. The solution involves laborious computation (Dalgarno, 1962). However, the results are the best obtainable within the Hartree-Fock approximation, in which the wavefunctions are written as an antisymmetrized product of one-electron spin-orbitals. The perturbed Hartree-Fock wavefunction is variationally determined. The coupled Hartree-Fock method has only been applied to six elements, in the first two rows of the periodic table (also to some ions).

There have been efforts to find approximations that uncouple the first-order Hartree-Fock equations. Comparisons of the various methods have been given by Langhoff *et al.* (1966), Chang *et al.* (1968), and Tuan and Davidz (1971). Langhoff and Hurst (1965) have shown that Dalgarno's original uncoupled Hartree-Fock theory (1962) is equivalent to the application of first-order perturbation theory to the unperturbed Hartree-Fock problem. Other uncoupled approximations retain some additional terms present in the coupled equations but prove easier computationally (Langhoff *et al.*, 1966; Yoshimine and Hurst, 1964; Langhoff and Hurst, 1965). Dalgarno (1962) has shown that his coupled Hartree-Fock method yields polarizabilities correct through first order. The uncoupled schemes all contain error terms of first order. Langhoff *et al.* (1966) have estimated that the uncoupled

Hartree-Fock approximations represent a computational savings between a factor of 4 to 300 over the fully coupled approximation, depending on which uncoupled scheme is used.

Tuan *et al.* (1966), Musher (1967), and Tuan and Davidz (1971) have investigated the possibility of applying double perturbation theory to obtain corrections to the uncoupled Hartree-Fock results, hopefully without a severe increase in computational effort. Musher (1967) has shown that the uncoupled Hartree-Fock approximation corresponds to the leading term in a perturbation expansion, while the coupled Hartree-Fock is correct to one higher order. He shows that an attempt to improve upon the coupled theory with a perturbation correction is fruitless since the self-consistency terms in the coupled theory are caused to vanish, and one ends up with the uncoupled Hartree-Fock approximation. Musher (1967) also shows that the different uncoupled schemes are related as leading terms in a Taylor series expansion of the uncoupled results. He argues that the uncoupling process does not eliminate "unwanted" nonlocal potentials from the problem, but simply creates a series expansion in which the leading term does not contain nonlocal potentials and in which it is hoped that the remaining terms are negligible.

Schulman and Musher (1968) performed a perturbation calculation of higher-order terms in the polarizability of the hydrogen molecule. Their results indicated that the corrections followed a geometric progression, and they suggested a "geometric approximation" for the polarizability,

$$\alpha_{\text{geom}} = \alpha_0(1 - \alpha_1/\alpha_0)^{-1} \quad (27)$$

where α_0 and α_1 are the polarizability and first-order correction to it, obtained with an uncoupled Hartree-Fock approximation with first-order perturbation correction. Amos (1970) showed that the geometric approximation was applicable to all of the uncoupled Hartree-Fock schemes. Tuan (1970) has shown that the geometric approximation is an approximation to the coupled Hartree-Fock result. Tuan and Davidz (1971) have evaluated a number of the polarizability approximations described here, for the helium and beryllium isoelectronic sequences. They find that α_{geom} , evaluated using one particular uncoupled scheme, leads to the closest agreement with the fully coupled result. Tuan and Davidz (1971) allowed for different amounts of self-consistency in their potential, via a parameter τ that could be chosen between 0 and 1. They used $\tau = 0, \frac{1}{2}$, and 1 in their computations for the helium and beryllium isoelectronic sequences, and found that $\tau = \frac{1}{2}$ gave the best agreement with the fully coupled results, when the perturbation correction was applied to the uncoupled approximation. The implication is that there is an optimum τ near $\frac{1}{2}$ for a given isoelectronic sequence.

Stevens and Billingsley (1973) have reported highly refined calculations of

the polarizabilities of the first-row atoms, including some excited-state polarizabilities. They used an extension of the coupled Hartree-Fock method due to Cohen and Roothaan (1965), which they apply to multiconfigurational self-consistent-field wavefunctions. By including higher configurations in their calculations, Stevens and Billingsley were able to investigate the importance of electron correlation on the polarizability. Beryllium showed the greatest lowering of the polarizability below that of the base configuration, as higher configurations were considered. The base configuration yielded a polarizability of 6.75 \AA^3 , in agreement with the coupled Hartree-Fock result of Cohen (1965). Mixing of nearby configurations resulted in a polarizability of 5.41 \AA^3 .

A further interesting result of Stevens and Billingsley is the large anisotropy in the polarizability of boron, which has a ^2P ground state. For $m_L = 0$ (external electric field parallel to the atomic symmetry axis), the correlated polarizability is 3.44 \AA^3 . For $m_L = \pm 1$ (perpendicular case), the correlated polarizability is 2.56 \AA^3 , 26% lower. The work of Werner and Meyer (1976), to be discussed below, shows an even larger anisotropy for boron.

The work of Stevens and Billingsley is an important contribution to polarizability theory because their method has a wider applicability than do the coupled and uncoupled Hartree-Fock methods, and because an estimate of the accuracy of the calculations can be obtained from the magnitude of the electron correlation effects. Their method can be applied to degenerate as easily as to nondegenerate atoms; excited states may be considered without difficulty, and electron correlation effects may be included. In the work referred to above (Stevens and Billingsley, 1973) the accuracy was estimated to be within 5% for the first-row atoms. However, their result for neon is 10% below the most accurate experimental result.

Werner and Meyer (1976) and Reinsch and Meyer (1976) have also applied the method of finite perturbation of Cohen and Roothaan (1965) to determine atomic and molecular polarizabilities. They used two types of wavefunctions, obtained from the pseudo-natural-orbital configuration interaction (PNO-CI) and the coupled-electron-pair approximation (PNO-CEPA) of Meyer (1973). Although the PNO-CEPA wavefunctions are not variationally obtained, they had been found to yield better results in molecular structure calculations. Werner, Reinsch, and Meyer noted two competing electron correlation effects in their calculations:

(a) Unoccupied low-lying p orbitals make possible a very effective angular correlation. If one wants to describe a state where two s electrons tend to keep apart from each other by preferring a geometrical configuration on different sides of the nucleus, one has to admix configurations to the ground state with the two s electrons excited into two p orbitals. In case there exist

low-lying unoccupied p orbitals in the atom, this means that this type of correlation is favored, in contrast to the case where such orbitals are energetically more expensive. This preference of opposite configurations will lead to a reduction of the shielding of the nuclear potential and thus a contraction of the valence shell and a reduction of the polarizability. This effect dominates in the left-hand side of rows of the periodic table because there are empty p orbitals available.

(b) Electrons tend to avoid each other by one keeping nearer to the nucleus and the other farther away (in/out correlation). This is achieved by configurations using orbitals with additional radial nodes and is more effective for a more diffuse distribution since in this case the excitation energies are lower. This effect dominates to the right-hand side of rows of the periodic table.

Intershell correlation is mostly of type (a) and is called core polarization. Core polarization is larger in the second row of the periodic table than in the first because the cores are increasing in size. However, core polarization decreases across a row as the valence p orbitals fill up and tend to neutralize each other. Figure 2 shows the relative contributions of electron correlation to the polarizabilities of the first- and second-row atoms, as calculated by Werner and Meyer (1976) and Reinsch and Meyer (1976). Also shown are the corresponding relative changes in $\langle r^2 \rangle^{1/2}$ due to electron correlation, where $\langle r^2 \rangle^{1/2}$ is the mean value of the radial distribution of charge in the valence shell.

The calculations of Werner and Meyer (1976) cover the atoms lithium through neon, and their results were displayed in Fig. 1. Reinsch and Meyer (1976) extended the calculations through calcium. These polarizabilities compare very well with experiment, where available, and the accuracy is estimated at $\pm 2\%$ by the authors.

Reinsch and Meyer are extending their calculations to the third row of the periodic table, which will include atoms through krypton. These results will be important since there are presently no reliable theoretical, and no experimental values, across a long row of the periodic table. Some of their preliminary results have been included in a tabulation of average polarizabilities in the Appendix. An interesting result of Reinsch and Meyer's latest calculations is the finding for gallium that the anisotropy is 70% of the average polarizability. This is the largest atomic polarizability anisotropy yet reported, in the ground state.

Werner and Meyer (1976) also point out that ordinary perturbative treatments would have difficulty in including coupling elements between substituted configurations of different pairs, because these effects correspond to three- and four-body interactions, which appear only beyond second-order

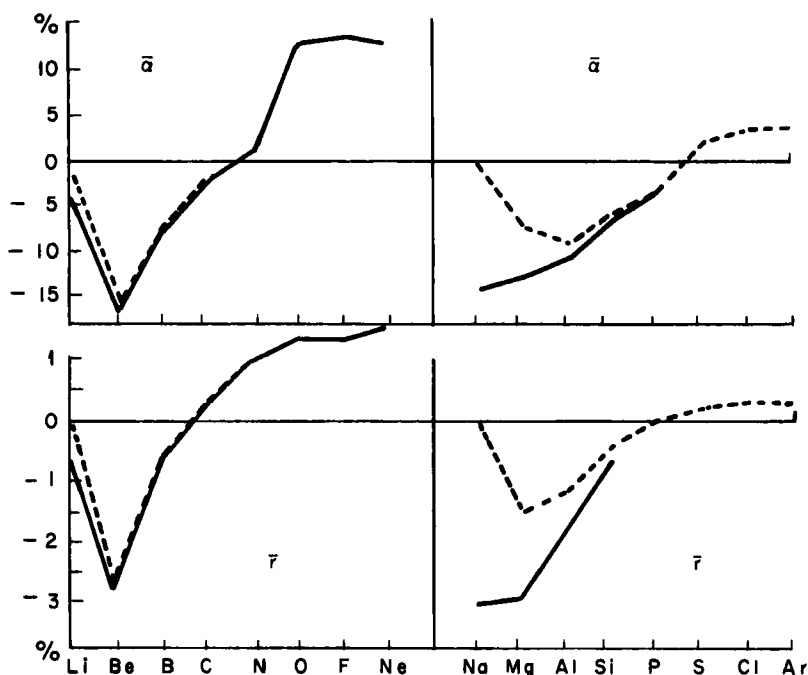


FIG. 2. Relative electron correlation contribution to the polarizabilities (upper part) and to the size of the valence shell $\bar{r} = \langle r^2 \rangle_{val}^{1/2}$ (lower part) for atoms in the first two rows of the periodic table. Dashed lines, valence shell correlation only; solid lines, total including intershell correlation. (From Reinsch and Meyer, 1976.)

perturbation theory. An interesting example is the oxygen atom polarizability where there is a disagreement even in the *sign* of the polarizability anisotropy, between the results of Werner and Meyer and those of Kelly (1964), who used many-body perturbation theory.

Dehmer *et al.* (1975) and Cummings (1975) have calculated dipole oscillator strength distributions for the first- and second-row atoms, using Hartree-Slater wavefunctions. Their moment $S(-2)$ is related to the polarizability by $\alpha = 4S(-2)a_0^3$ and comparisons with more exact treatments of the polarizability were given by these authors.

Sternheimer (1962, 1969) has performed extensive atomic structure calculations, numerically computing accurate solutions to the simpler Hartree perturbation equations. In his latest work on the alkali metal atoms, Sternheimer (1969) gave an approximate correction to his earlier polarizabilities, due to shielding of the valence electron by the core from the external electric field. The corrected values are in good agreement with the best experimental results. Sternheimer (1969) remarks that his method is not as accurate, in

principle, as the coupled Hartree-Fock method or the Brueckner-Goldstone many-body theory. However, the later two methods are considerably more complicated.

Kelley (1963, 1964, 1966), Caves and Karplus (1969), Chang *et al.* (1968), Matsubara *et al.* (1970), Miller and Kelly (1972), and Doran (1974), have applied the many-body perturbation theory of Brueckner and Goldstone (Goldstone, 1957) to the calculation of atomic polarizabilities. Caves and Karplus (1969) and Chang *et al.* (1968) have used the diagrammatic method to shed light on the various Hartree-Fock methods of calculating polarizabilities, i.e., which diagrams are excluded from the various approximations.

Chang *et al.* have categorized the contributions of various diagrams in the following way. The *intrinsic* polarizability is due to the direct perturbation of the individual orbitals by the external electric field. *Self-consistency* accounts for the further distortion of each electronic orbital through the averaged coulomb and exchange potentials produced by the orbitals. Self-consistency is divided into intra- and intershell consistency, depending on whether the interacting orbitals are in the same electronic shell. *Correlation* is interpreted as the dynamic dependence of one electron on another. In many-body theory, self-consistency is represented by single-particle excitations, and correlation by two- or more-particle excitations. Conventional Hartree-Fock theory (the coupled theory) includes self-consistency as well as some two-body excitations.

The Brueckner-Goldstone many-body calculation is, in principle, exact. If the interelectron potential is chosen to be the Hartree-Fock potential, a number of diagrams vanish. Then, the remaining diagrams may be regarded as improvements over the coupled Hartree-Fock theory. In the case of lithium, treated by Chang *et al.* (1968), electron correlation proved to be negligible so that their result for the polarizability was close to that of the corresponding coupled Hartree-Fock value. It is useful to display the contributions of the intrinsic, intershell, and intrashell consistency, and correlation diagrams, as Chang *et al.* have done for lithium. However, in this particular case, the nonintrinsic contributions are on the order of 0.1%. A similar analysis for atoms such as oxygen or boron would be interesting.

We conclude our discussion of perturbation techniques with a remark on the importance of the wavefunctions used in various calculations. Most of the calculations we have referenced utilized analytic functions to represent the single-electron unperturbed Hartree-Fock wavefunctions and the first-order corrections. Chang *et al.* (1968) noted that different authors frequently obtain different results using the same method depending primarily on whether their wavefunctions were determined variationally or numerically. If variationally obtained, the properties of the trial functions must be scrutinized. The numerical procedure is more accurate but tedious to set up.

Because the polarizability is mostly dependent on the valence electrons, the outer part of the radial wavefunctions is most crucial in determining the polarizability. Wavefunctions that differ only slightly can yield greatly different polarizability values. Yoshimine and Hurst (1964) found that careful attention must be paid not only to the selection of the basis functions, but also to the precise determination of the variational parameters. They gave an example in which the solutions to the Hartree-Fock equations were determined precisely enough to give a wavefunction that gave the correct free-atom energy to within 0.0005 hartrees, but the polarizability obtained with this wavefunction was incorrect by a factor of two! Further, it should be noted that the Hartree-Fock wavefunction is not necessarily the best choice for the unperturbed wavefunction, particularly when using an approximate theoretical method. An interesting example is that of Norcross' (1973) calculation of the polarizability of cesium. He used a semiempirical model potential involving two adjustable parameters, based on the lowest few spectroscopic term values. Norcross' calculation included the core dipole and quadrupole contributions to the valence-electron hamiltonian (even dynamical effects), a spin-orbit potential with an additional relativistic correction.

Norcross' result is close to that found by Sternheimer, but he shows that individual contributions to the total polarizability are not the same in the two calculations. In Table II are given the direct valence-electron polarizability (neglecting the effect of the external electric field on the core) α_v ; the effect of the dipole moment induced in the core by the valence electron α_{vc} ; the polarizability of the ionic core α_c ; and the total polarizability α_t , for both the Norcross (1973) and Sternheimer (1969) calculations on cesium. Particularly striking is the difference in the two values for the valence-electron polarizability α_v . Both values for α_t are close to the latest experimental results, $(59.6 \pm 1.2) \times 10^{-24} \text{ cm}^3$ (Molof *et al.*, 1974a) and $(63.3 \pm 4.6) \times 10^{-24} \text{ cm}^3$ (Hall *et al.*, 1974).

D. R-MATRIX CALCULATIONS

Allison *et al.* (1972a,b) have described the use of the R-matrix (reaction-matrix) theory of Burke *et al.* (1971) in the calculation of atomic polarizabilities. The method is especially suitable for the calculation of dynamic polarizabilities since the logarithmic R-matrix boundary conditions are well specified, and loss of flux through the boundary surface is easily calculated (photoionization). The perturbed atomic wavefunction is expanded in terms of R-matrix states, which form a complete and rapidly converging basis set in the region of space where the perturbed atomic wavefunction has nonvanishing probability amplitude. Computer programs to generate the R-matrix

TABLE II

CALCULATED VALUES OF THE VALENCE ELECTRON POLARIZABILITY α_v , THE CORE POLARIZABILITY INDUCED BY THE VALENCE ELECTRON α_{vc} , THE CORE POLARIZABILITY INDUCED BY THE EXTERNAL ELECTRIC FIELD α_c , AND THE TOTAL ATOMIC POLARIZABILITY α_t OBTAINED BY NORCROSS (1973) AND STERNHEIMER (1969) FOR CESIUM^a

Research	α_v	α_{vc}	α_c	α_t
Norcross	65.72	9.24	2.82	59.30
Sternheimer	71.31	13.26	3.14	61.19

^a The total polarizability is $\alpha_t = \alpha_v + \alpha_c - \alpha_{vc}$. The value of the ionic core polarizability α_c used in obtaining these results in both cases was taken from another source. The units are 10^{-24} cm^3 for the polarizabilities.

states for any atom had been written earlier (Burke *et al.*, 1971) in connection with low-energy electron scattering calculations.

The R-matrix method has been used by Robb (1973, 1974, 1975) to calculate dynamic atomic polarizabilities of a number of the first-row atoms and to obtain van der Waals coefficients (as did Allison *et al.*, 1972b). Robb and Reinhardt (1974) have calculated photoionization cross sections.

E. VARIATIONAL CALCULATIONS

In a uniform external electric field, the total energy of an atomic system will be decreased. A variational procedure can be used to determine a wavefunction Ψ that minimizes the total energy in the electric field E . The polarizability can be obtained from the calculated energy change $\Delta\epsilon$, namely,

$$\alpha = \lim_{E \rightarrow 0} (-2 \Delta\epsilon / E^2) \quad (28)$$

Chung and Hurst (1966) have applied the variational procedure to ground and excited states of the helium isoelectronic system using a 72-term wavefunction. In the case of $\text{He}(2^1S_0)$ 96 terms were included in the variational wavefunction to obtain convergence. [As an aside, we remark that the accurate calculation of the polarizability of $\text{He}(2^3S_1)$ is important as it is used as a standard in many of the experimental determinations of atomic polarizabilities.] Chung (1977) has recently calculated dynamic polarizabilities for $\text{He}(2^1S_0)$ and $\text{He}(2^3S_1)$ using a variation-perturbation scheme due to Glover and Weinhold (1976).

Schwartz (1961) has pioneered the variational approach in calculating atomic polarizabilities, applying it to H^- and He.

Sims and Rumble (1973) have used the variational procedure described by Weinhold (1972) to determine rigorous lower bounds to the polarizabilities of the beryllium isoelectronic series. The variational formulation is such that systematic improvement of the bound is possible, to any desired extent. Sims and Rumble (1973) presented both the lower bounds and "recommended" values for the beryllium isoelectronic series, obtained with a 105-term unperturbed wavefunction and a 53-term perturbed wavefunction for beryllium. For C^{2+} and O^{4+} an 89-term unperturbed wavefunction was used. They estimate the accuracy of their "recommended" results to be better than 2%. Sims *et al.* (1976) have also made calculations for atomic lithium and their result is in close accord with experiment and other accurate calculations. Because lithium has been used as a standard in some recent polarizability measurements (Molof *et al.*, 1974b; Schwartz *et al.*, 1974; Miller and Bederson, 1976) we present in Table III a comparison of these results.

TABLE III
A COMPARISON OF RECENT POLARIZABILITY VALUES FOR
ATOMIC LITHIUM

Source	α (\AA^3)
Sims <i>et al.</i> (1976) (rigorous lower bound)	23.47
Sims <i>et al.</i> (1976) (variation-perturbation)	24.27
Molof <i>et al.</i> (1974a)	24.3 ± 0.5
(<i>E-H</i> gradient balance experiment)	
Werner and Meyer (1976)	24.38
(multiconfigurational perturbation)	
Adelman and Szabo (1973)	24.3
(effective quantum numbers)	

F. STATISTICAL CALCULATIONS

Dalgarno reviewed various theoretical approaches to polarizabilities in 1962 and noted that calculations based on the Thomas-Fermi (TF) model considerably overestimated the polarizability for neutral atoms. Improvement was seen for increasing atomic mass and increasing excess charge. Bruch and Lehnen (1976) have recently calculated the polarizabilities of neutral inert gas atoms using the TF and Thomas-Fermi-Dirac (TFD) statistical models. They found, as did Roberts and DelleDonne (1975), that the TF atom has *infinite polarizability* on the basis of a variational calculation. An interpretation of this result is that the TF atom completely screens a

static electric field from its interior. Bruch and Lehnen found the TFD polarizabilities for the inert gas atoms to be many times larger than experimental values although there was considerable improvement for larger atomic number. On the other hand, TFD polarizabilities for the alkaline earth atoms beryllium and calcium turn out to be smaller than accepted values.

III. Experimental Measurements of Polarizabilities

In 1971, Teachout and Pack published an extensive compilation of experimental and theoretical values of atomic polarizabilities. It is immediately clear from their tabulation that most of the periodic table has not been touched upon by direct experimental work, although there are several theoretical values available for most elements. Very accurate polarizability values for the noble gas atoms are known from experiments in which the dielectric constant is measured with low-frequency fields. The other elements are more difficult to handle experimentally and beam techniques have been applied in some cases, notably with the alkali metal atoms. Optical techniques in vapor cells, or shock tubes, have been applied in a few other cases. For a number of atoms these methods have been used to determine excited-state polarizabilities, even for Rydberg states.

A. BULK EXPERIMENTS

The polarizability of atoms or molecules that are in the gaseous state at normal laboratory temperatures, say 77–400°K, can be measured accurately by determining the dielectric constant K of the gas. The polarizability is then $(K - 1)/4\pi N$, where N is the number density of the gas. The dielectric constant is best measured with an ac capacitance bridge in which the change in the capacitance of a parallel-plate condenser is determined, with and without the gas present.

With this method one obtains the average polarizability. For molecules, the polarizability is further an average over the thermal distribution of rotational and vibrational states. Experiments performed with hydrogen molecules at low temperatures, however, have yielded very accurate results for the polarizability for the ground rotational and vibrational states of H_2 (see Kolos and Wolniewicz, 1967). Dielectric-constant experiments with atoms are possible only with the noble gases, and the accuracy is superb, $\sim 0.1\%$ (Orcutt and Cole, 1967). The other elements are atomic gases only at high temperatures where one runs into a number of experimental difficulties, among them pressure gradients, pressure measurements, excitation, and ionization.

Microwave interferometry has been used to determine the index of refraction of molecular gases and noble gases, and hence polarizabilities at low frequencies (Newell and Baird, 1965). Optical measurements of the index of refraction $\eta(\omega)$ of gases are useful in determining the static polarizability in cases where the photon energy of the probe beam is small compared to the lowest excitation energy of the gas under study. The (frequency-dependent) polarizability is given by $[\eta(\omega) - 1]/2\pi N$, where N is the gas number density. Optical experiments in vapor cells possess the same limitations as do the capacitance measurements, with one important exception: by measuring the depolarization of the probe beam in passing through a cell, one can determine the relative value of the polarizability anisotropy. Such measurements for H_2 have been important in comparisons between experiments and theory for this "simple" molecule.

For atomic systems, only the noble gases would seem viable as candidates for optical refractivity work, insofar as static polarizabilities are concerned. However, Alpher and White (1959) were able to use a shock tube to dissociate N_2 and O_2 in order to determine the index of refraction of nitrogen and oxygen gases. They performed the experiments for different Mach numbers to obtain different degrees of dissociation (33–53% for N_2 , 36–91% for O_2) and used three different wavelengths of light (412.2, 451.5, and 544.6 nm). Alpher and White found $(1.13 \pm 0.06) \times 10^{-24} \text{ cm}^3$ for the average polarizability of nitrogen, and $(0.77 \pm 0.06) \times 10^{-24} \text{ cm}^3$ for oxygen. It is interesting that the ratio of $\bar{\alpha}(N_2)/\bar{\alpha}(N)$ is 1.55, while $\bar{\alpha}(O_2)/\bar{\alpha}(O) = 2.11$. That is, the polarizability of N_2 is less than that of two separated nitrogen atoms, but the polarizability of O_2 is greater than that of two separated oxygen atoms. Alpher and White did not see any variation of the polarizability with photon wavelength, within the scatter in their data; the values they report are probably close to the static polarizabilities.

In the shock tube method, the major part of the tube is filled with the gas under study. The tail end of the tube is filled with a driving gas, perhaps helium, behind a metal diaphragm that has been scratched along desired rupture lines. When the pressure of the driving gas reaches a high value that can be fairly accurately estimated, say 50 atm, the diaphragm ruptures and compression of the sample gas begins. The sample gas and the driving gas remain well separated by a shock front. Moving ahead of this shock front is the sample gas in thermodynamic equilibrium at a high temperature (say, 5000°K). The temperature, pressure, and percent dissociation in the gas can be calculated accurately. Downstream in the shock tube the gas passes between optical viewing ports and one has typically 0.2 msec for interferometric observation.

Marlow and Bershader (1964) have used this technique to measure the polarizability of atomic hydrogen, at 587 nm. In their case, the H_2 was

70–85% dissociated (4000–5000°K). In the interferometer a fringe shift of about one fringe was observed, with a precision of 6%, due to the introduction of the atomic hydrogen gas. With 27 measurements at different initial pressures, the precision of the experiment was improved to 1.5%. Marlow and Bershader found $0.683 \times 10^{-24} \text{ cm}^3$ for the polarizability of atomic hydrogen at 587 nm. They compared this to the polarizability calculated in perturbation theory for 587 nm, $0.691 \times 10^{-24} \text{ cm}^3$ (Podolsky, 1928; Dalgarno and Kingston, 1960), a value that is 3.6% greater than the static polarizability. Marlow (1965) later investigated the temperature dependence of the polarizability of H_2 , motivated by the possible need for such a correction to the data of Marlow and Bershader (1964). He found that a correction of $-0.004 \times 10^{-24} \text{ cm}^3$ should be applied to the atomic hydrogen result. The correction is very small because the fractional dissociation of H_2 in the shock tube was large.

B. INDIRECT METHODS

In Table I we listed a number of formulas involving the polarizability, any of which could be turned around and used to determine polarizability values, with varying degrees of reliability. The use of the dielectric constant of a gas to deduce the atomic or molecular polarizability has proven to be accurate, for example, and even higher-order corrections can be made if warranted. Other techniques that carry no guarantee as to accuracy we will class as "indirect methods." Ion mobilities have been used to determine polarizabilities (Hackam, 1966), for example. The problem here is that such a result depends on the induced dipole force between colliding ions and atoms being the only important force (McDaniel, 1964). Sometimes this is true; but sometimes it is far from being true, most notably when resonant charge transfer takes place. Indirect results are generally of value only when no direct measurements have been made. The tabulation of Teachout and Pack (1971) does not show any indirect measurements for elements for which no other measurements exist, except for radon. Here, the adsorption rate of radon from a surface has been used to deduce the polarizability of radon (Tuck, 1960).

C. BEAM TECHNIQUES

1. General Remarks

An atomic beam technique was used by Scheffers and Stark in 1934 to measure the polarizabilities of the alkali metal atoms, not too long after the introduction of atomic beam magnetic deflection methods by Gerlach and

Stern in 1924. It was not until the late 1950s that further atomic beam work on polarizabilities was carried out, inspired by development of the atomic beam resonance method in the 1940s.

The beam experiments can be separated into two groups: (a) those in which a transverse inhomogeneous electrostatic field is used to induce a dipole moment in the beam atoms and to exert a deflecting force on them; and (b) those in which a homogeneous electrostatic field is used, and a radiation field (optical, rf, or microwave) serves to induce a transition between two Stark-shifted levels of the atoms. In the first type of experiment the full polarizability for a given atomic level is obtained, while in the second only the polarizability difference for the two relevant levels is found. In the deflection experiment, the tensor components of the polarizability may be determined if the beam is somehow state-selected, since the selection of different m_j states permits measurements to be made with the atom oriented in different directions with respect to the applied electric field. In the nondeflecting experiments, the difference polarizability may be essentially equal to the full polarizability of the higher-lying level in many cases, since polarizability values increase rapidly as the principal quantum number n increases (n^7 if there is no core penetration). By exciting to different m_j states then, the tensor components of the higher-lying level may be specified. Thus, both types of experiments have considerable potential. In the sparse amount of data available, we find complementary results rather than redundancy.

2. Electric Deflection Experiments

Conceptually, the simplest polarizability measurement is made in the manner of Scheffers and Stark (1934). A collimated atomic beam is passed through a region where a transverse inhomogeneous electric field has been established. The electric field \mathbf{E} at the beam position induces a time-averaged dipole moment

$$p_z = \alpha \cdot \mathbf{E} = \alpha_{zz} E \quad (29)$$

in the atoms, where the z direction is chosen to be the direction of \mathbf{E} , about which the polarizability tensor is assumed to be diagonal. The electric field gradient interacts with the induced moment to exert a force

$$F_z = p_z dE/dz \quad (30)$$

on the atoms, and the beam undergoes a deflection from its original course. If the beam is well collimated, the deflection can be detected downstream from the electric field region of the apparatus. The deflected beam is dispersed by the velocity distribution. (There is also broadening caused by the variation of the electric field gradient across the finite beam width.) It is thus

necessary to know the beam velocity distribution in order to infer the polarizability from the deflected beam profile. Scheffers and Stark (1934) used an effusive beam source and hence assumed a Maxwellian velocity distribution.

Scheffers and Stark (1936) also measured the polarizability of atomic hydrogen (one of the very few such measurements in the literature, even to this day). They used a water-cooled discharge tube to dissociate H_2 , and a MoO_3 -coated surface as a detector. Reduction of the MoO_3 by hydrogen produced a visible image of the beam profile. Their result was less than half that calculated quantum mechanically. But Scheffers (1940) later altered their value of the polarizability of atomic hydrogen to $(0.6 \pm 0.2) \times 10^{-24} \text{ cm}^3$ after finding that the temperature of the hydrogen discharge was closer to 600°K than room temperature. The calculated static polarizability is $0.67 \times 10^{-24} \text{ cm}^3$.

Scheffer and Stark's apparatus was miniscule by modern standards—the field electrodes and flight path totaled 14 cm. Their alkali atom polarizability results are of historical interest only (30–50% low), but their contribution to beam technology was considerable.

No other deflection experiments are recorded until 1952, when Drechsler and Müller reported measurements on barium and lithium. Their work was followed by Liepack and Drechsler (1956) on the metals nickel, copper, molybdenum, and tantalum. This group used a field electron microscope apparatus. They found that if an atomic beam was passed close to the field-emitting tip, the beam was deflected. They detected the undeflected and deflected beams by letting the metal beam deposit on a glass plate. The greatest uncertainty in the experiment involved the calculation of the electric field strength and the field gradient at the beam position. Their result for lithium has been shown to be at least 28% too small, while the barium figure is 90% too large. Their other results are yet to be tested.

Zorn and co-workers at Yale, and later Michigan, have also used an electric deflection technique over many years to measure the polarizabilities of the alkali metal atoms (Zorn and Fontana, 1960; Chamberlain and Zorn, 1960, 1963; Hall and Zorn, 1974), strontium (Hall *et al.*, 1968), and metastable-state argon (Johnson, 1970) and helium (Crosby and Zorn, 1977). This group has improved the electric deflection experiments by (1) using an electrode configuration in which the electric field strength and field gradient can better be determined, (2) using an improved measurement technique (called the “small-shift” method), and (3) using a velocity selector in their latest work.

As presently set up (Fig. 3) the experiment consists of a beam source, a rotating-disk velocity-selector, a beam collimating slit, deflection electrodes, and a beam detector at the end of a flight path of about 93 cm. A typical deflection pattern is shown in Fig. 4. The electrodes are of the “two-wire”

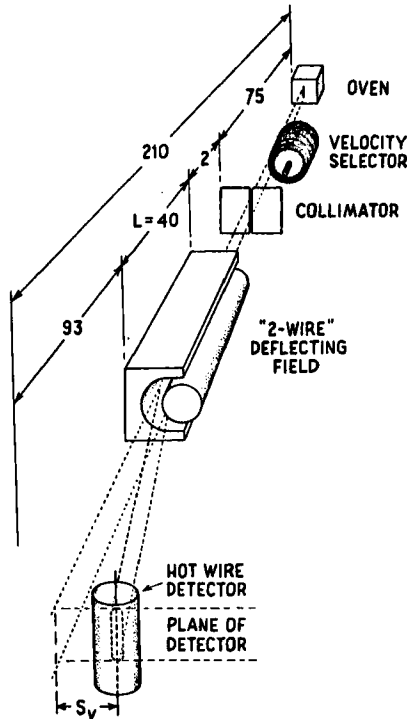


FIG. 3. Schematic diagram of the electric-deflection apparatus used at Michigan. The dimensions are in centimeters. (From Hall and Zorn, 1974.)

configuration (Ramsey, 1956). The field and the field gradient can be calculated analytically and it can be shown that the value of $E \, dE/dz$ does not vary significantly over the beam height. The Michigan group has made electrolytic-tank tests and found that fringing fields effectively add $\sim 3\%$ to the length of their electrodes.

The beam atoms with an average polarizability $\bar{\alpha}$ are deflected by an amount

$$Z = \frac{1}{2}(\bar{\alpha}E \, dE/dz)L^2/mv^2 \quad (31)$$

as they pass through the electric field electrodes a distance L . The atom mass is m and the velocity is v . The net deflection s at the detector plane is directly proportional to Z . In the small-shift method, the beam detector is located off-center at a point where the undeflected beam profile has a large slope, near the half-intensity point. As the deflecting field is turned on, the detected intensity changes rapidly by an amount

$$\Delta(Z, E) = (dI/dZ)s \quad (32)$$

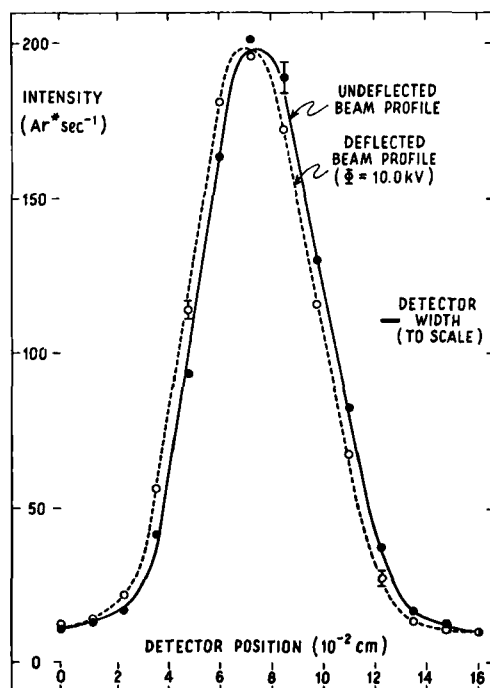


FIG. 4. Deflected and undeflected beam profiles for velocity-selected (547 m/sec) metastable argon, obtained with the Michigan electric-deflection apparatus. (From Johnson, 1970.)

where $I(Z)$ is the detected intensity, dI/dZ the slope of the beam profile at the detector position Z , and s the net beam deflection. Thus, the measurement of Δ and $I(Z)$ enables one to obtain s , then $\bar{\alpha}$, provided that the electric field strength and field gradient at the beam position are known. These quantities are calculated from the electrode geometry and the applied electric potential.

In the older "large-shift" method, the beam deflection is on the order of the beam width, and a more complicated analysis of the experiment is required (see Zorn *et al.*, 1963; and Bederson and Robinson, 1966), because the beam profile is broadened due to the velocity dispersion. (No large-shift measurements have been made with the velocity-selected beam.)

The use of a velocity selector makes the experiment straightforward. In the older work, knowledge of the beam velocity distribution was crucial. Hall and Zorn (1974) performed deflection experiments both with and without the velocity selector to study uncertainties associated with the beam velocity distribution. They deliberately introduced background gas into their electrode chamber in order to distort the velocity distribution, and

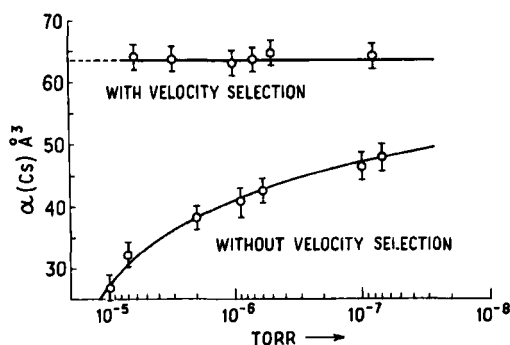


FIG. 5. The apparent polarizability of cesium determined with an electric-deflection apparatus, with and without beam velocity selection, as the background gas pressure was varied. The results show that significant error can occur if the data obtained without velocity selection are analyzed under the usual assumption that the velocity distribution is undistorted Maxwellian. (From Hall and Zorn, 1974.)

found results that were consistent with suspicions that the older measurements were erroneously low due to inadequate vacuum. Their results for cesium are shown in Fig. 5. Note that the velocity-selected beam gave a polarizability value that was independent of the background gas pressure. These data place quite stringent restrictions on deflection experiments performed without velocity selection. Greene and Milne (1968) have reanalyzed the data in Hall's Ph.D. thesis (1968) and find less stringent requirements. In their analysis they include scattering due to the background gas in the entire apparatus—not just the electrode chamber—and they find a curve for the non-velocity-selected data that rises more steeply than shown in Fig. 5. While Hall's analysis leaves the impression that the apparent cesium polarizability would be considerably in error even for apparatus background pressures of 10^{-9} torr, Greene and Milne find that 10^{-8} torr is an adequate vacuum, for non-velocity-selected experiments in a typical 2 m long apparatus. Nevertheless, velocity selection removes the uncertainty and permits measurements to be made in cases where the velocity distribution in the beam is known to be non-Maxwellian, such as with metastable-state atomic beams.

Zorn's group has studied sodium, potassium, rubidium, and cesium with the velocity-selected beam (Hall and Zorn, 1974). They have done unpublished work with a non-velocity-selected strontium beam (Hall *et al.*, 1968) and have unpublished results for the average polarizability of metastable-state argon, (Johnson, 1970). The metastable beam was a combination of $^3\text{P}_0$ and $^3\text{P}_2$ argon, but the polarizabilities probably differ by less than 1%. The atom beam was excited by electron impact. More recently, they have studied metastable-state helium, and are able to separate 2^1S_0 and 2^3S_1

effects using a helium resonance lamp to quench the singlet state via $2^1S_0-2^1P_1$ excitation followed by $2^1P_1-1^1S_0$ radiative decay (Crosby and Zorn, 1977).

The results of the Michigan group are in good agreement with theory and other experiments. There are no other measurements available for 2^1S_0 and 2^3S_1 helium, but the variational calculations (Chung and Hurst, 1966; Chung, 1977) for helium are expected to be more accurate than is possible to achieve with present experiments. The experimental test is important, however, because 2^3S_1 helium is used as a "standard" in other polarizability experiments. Crosby and Zorn (1977) found (108 ± 13) and $(44.6 \pm 3) \text{ \AA}^3$ for the $\text{He}(2^1S_0)$ and $\text{He}(2^3S_1)$ polarizabilities, respectively. These can be compared to the theoretical values of 118.711 and 46.772 \AA^3 , respectively (Chung, 1977).

Greene and Milne (1968) operated an electric deflection apparatus at Midwest Research Institute, Kansas City, but their results are unpublished. Their apparatus was similar in principle to the Michigan apparatus except that it did not contain a velocity selector and they incorporated a mass spectrometer detector. Greene and Milne had a tuning fork beam chopper that was used to modulate the atomic and molecular beams and to pulse them for time-of-flight checks on the velocity distributions.

Greene and Milne were primarily interested in molecular polarizabilities and dipole moments, but measured the polarizabilities of sodium ($25.7 \times 10^{-24} \text{ cm}^3$) and potassium ($44.5 \times 10^{-24} \text{ cm}^3$) as a check on their apparatus. These values are within a few percent of accepted values. We will mention their molecular results in Section III,E.

3. NYU Experiments and the *E-H* Balance Method

At New York University, Bederson and co-workers have used both an electric deflection method and a different technique, the "*E-H* gradient balance" method, to measure atomic and molecular polarizabilities. In doing electric deflection work they have not used the small-shift procedure described above, but have deflected the beams distances that are several times the half-width at half-maximum of the forward beam. Deflection spectra are obtained with the beam detector fixed a distance S away from the axis of the undeflected beam. The potential across the deflection electrodes is swept; at some potential V a maximum is observed in the beam intensity. An example is given in Fig. 6 for rubidium atoms (Molof *et al.*, 1974b). If many such spectra are obtained, a plot of V^2 vs S may be made, as shown in Fig. 7 for rubidium atoms and molecules. A linear plot is expected since the induced dipole moment is proportional to E^2 (or V^2). Molof *et al.* (1974b) have shown that some deviation from the ideal occurs since the beam is of

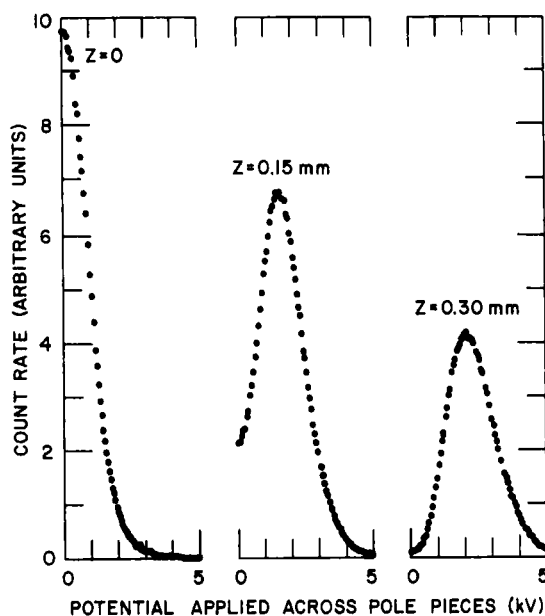


FIG. 6. Electric deflection spectra for rubidium atoms. The detector was positioned off the beam axis by the distance Z and the potential across the deflection electrodes was stepped at 50 V per point. (From Molof *et al.*, 1974b).

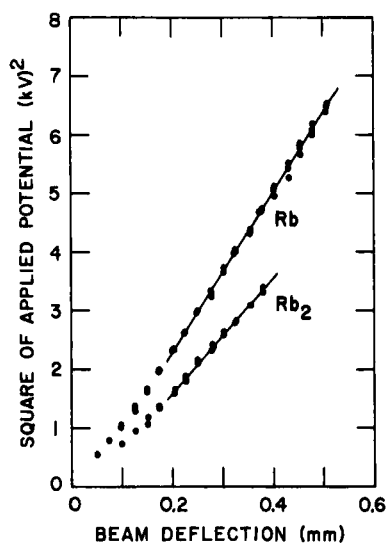


FIG. 7. Typical results obtained from electric deflection spectra for Rb and Rb_2 at 534°K . The applied potential was that corresponding to a maximum in the beam intensity for a particular detector position off axis. The slope of the resulting line is inversely proportional to the average polarizability. (From Molof *et al.*, 1974b.)

finite width, and the data (Fig. 7, for example) show this for small beam deflections. For beam deflections that are larger than the undeflected-beam width, the V^2 vs S lines are linear. The equation for the line for an infinitesimal beam with a Maxwellian velocity distribution is

$$V^2 = (4kT/\kappa\bar{\alpha})S \quad (33)$$

where k is Boltzmann's constant, T the temperature of the beam source, and κ a geometrical constant of the apparatus. The constant κ is the product of the electric field to potential ratio and square of the field gradient to field ratio for the deflection electrodes, and $L_1(L_1 + 2L_2)/2$. The electrodes are L_1 in length and the distance from the end of the electrode set to the detector is L_2 . Because of the difficulty in determining the apparatus constant κ absolutely, the NYU group has chosen to normalize their electric deflection results to known polarizabilities of the alkali metal atoms (Molof *et al.*, 1974b). The normalization was accomplished by making measurements on atoms, then molecules, in the same beam from a single oven source. An inhomogeneous magnetic field was used to remove atoms from the beam, acting on the atomic magnetic moment of one Bohr magneton. The molecules, with magnetic moments on order of nuclear magnetons, comprised only about 1% of the full beam. The ratio of the slopes of the V^2 vs S deflection lines (Fig. 7) for the species under study and for the "standard" is equal to the inverse ratio of the respective polarizabilities. We will discuss the results of experiments on molecular polarizabilities in Section III,E; suffice it to say here that the alkali dimer polarizabilities tend to be $\sim 50\%$ greater than those of the corresponding atoms, at the temperatures studied by Molof *et al.* (typically 600°K). With the normalization procedure, the only uncertainties are in the relative potential measurements, the statistical uncertainty, and the uncertainty in the polarizability of the standard.

Schwartz *et al.* (1974) and Miller and Bederson (1976) have studied the alkaline earth atoms with the electric deflection method. In these experiments the normalization was against the lithium polarizability. Lithium was loaded into the oven source along with the alkaline earth. A mass spectrometer was used to separate the deflections of the two beams. The polarizabilities of the alkaline earth atoms tend to be $\sim 60\%$ of those of the adjacent alkali metal atoms in the periodic table, for the atoms which have been studied thus far (barium, strontium, calcium). The lighter atoms, magnesium and beryllium, are predicted to have polarizabilities further lower than the corresponding alkali atoms in the periodic table ($\sim \frac{1}{3}$ and $\frac{1}{4}$, respectively). A comparison of various results for the alkaline earth atoms is given in Table IV.

Both the NYU and the Michigan groups have noted that the statistical uncertainty in their data is mostly due to the small shifts in the beam position for unpredictable reasons. They are dealing with tightly collimated,

TABLE IV
A COMPARISON OF RECENT ALKALINE EARTH POLARIZABILITY VALUES

Atom	α (\AA^3)	Source
Be	5.297	Sims and Rumble (1973) (rigorous lower bound)
	5.42 ± 0.12	Sims and Rumble (1973) (variation-perturbation)
	5.652	Robb (1973) (R-matrix method)
	5.600	Werner and Meyer (1976) (multiconfigurational perturbation)
		Robb (1975) (R-matrix method)
Mg	11.1 ± 0.75	Stwalley (1971) (experimental oscillator strengths)
	11.11 ± 0.44	Stewart (1975) (Hartree-Fock approximation)
	11.51	Reinsch and Meyer (1976) (multiconfigurational perturbation)
	10.57	Miller and Bederson (1976) (electric deflection experiment)
Ca	25.0 ± 2.5	Stwalley (1976) (experimental oscillator strengths)
	25.0 ± 1.0	Reinsch and Meyer (1976) (multiconfigurational perturbation)
	22.8	Hyman (1974) (experimental oscillator strengths)
	22.8	Adelman and Szabo (1973) (effective quantum numbers)
	24.4	Schwartz <i>et al.</i> (1974) (electric deflection experiment)
Sr	27.6 ± 2.2	Hyman (1974) (experimental oscillator strengths)
	28.4	Adelman and Szabo (1973) (effective quantum numbers)
	30.5	Schwartz <i>et al.</i> (1974) (electric deflection experiment)
Ba	39.7 ± 3.2	Hyman (1974) (experimental oscillator strengths)
	35.8	Adelman and Szabo (1973) (effective quantum numbers)
	43.6	

narrow beams traveling over long distances. In the NYU experiments, the beam-collimating slit on the entrance to the electrode set is 0.005 cm wide; the beam travels over 2 m altogether. The beam deflections must be measured with a precision of about 0.0002 cm, and must remain steady for periods of at least 15 min. In practice, it is found that random shifts of this order can occur, due to temperature changes or vibrations or whatever.

Bederson and his co-workers at NYU devised a new method of measuring polarizabilities, which they call the E - H gradient balance technique (Salop *et al.*, 1961). In this method the electrodes of the deflecting field are also the pole pieces of a magnetic circuit. The result is that both an inhomogeneous electric *and* an inhomogeneous magnetic field may be applied in the interaction region of the apparatus. The object is to balance the electric deflecting force against a magnetic force acting on the magnetic moment of the atom. Since magnetic moments are well known, the balance condition permits one to determine the polarizability. One principal advantage of this method is that the balance condition is velocity independent. Thus, one does not need to know the velocity distribution in the atomic beam, the balanced beam intensity is much greater than that of a velocity-dispersed beam, and the balanced beam width is approximately as narrow as that of the undisturbed beam—which leads to greater precision in the data acquisition. Furthermore, since the value of the effective magnetic moment depends on the m_F sublevel of the atom, each sublevel can be brought into balance separately and the tensor components of the polarizability may be obtained. That is, magnetic field permits state-selection of the beam. These experiments are performed on the same apparatus as are the pure electric-deflection experiments described above. The apparatus dimensions are given in Fig. 8, and a cross section of the most recent pole pieces they have used is shown in Fig. 9. The pole pieces are soft iron and are insulated from the magnet yoke by a glass vacuum envelope and from each other by quartz spacers. The position

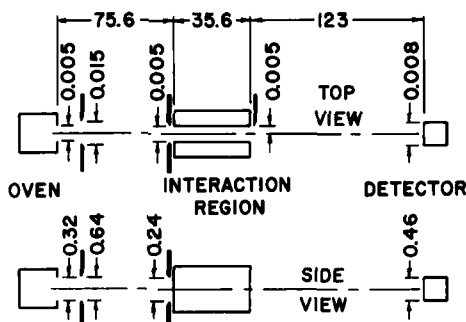


FIG. 8. A diagram of the NYU E - H gradient balance apparatus with dimensions in centimeters. (From Molof *et al.*, 1974a.)

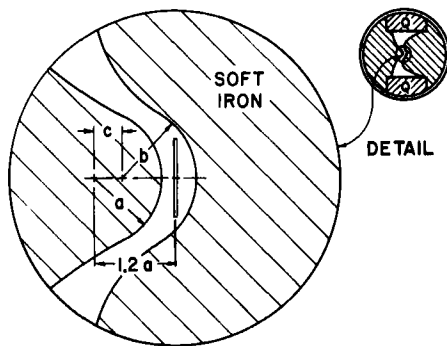


FIG. 9. A cross-sectional view of the iron pole pieces used in the NYU E - H gradient balance apparatus. The pole pieces are 35.6 cm long and the design parameters were $a = 0.159$, $b = 0.172$, and $c = 0.066$ cm. The atomic beam passes between the pole pieces at the position shown (at $1.2a$). Quartz spacers are indicated by Q. (From Molof *et al.*, 1974a.)

of the beam in the pole pieces is indicated in Fig. 9 and is the optimum position for the beam according to calculations of the uniformity of E $\partial E/\partial z$ over the beam height.

In the interaction region of the apparatus an inhomogeneous magnetic field H is applied across the beam, which acts on the effective magnetic moment $\mu(m_F)$ of a beam particle in the magnetic substrate m_F . The magnitude of the transverse magnetic force is $\mu(m_F) \partial H/\partial z$, where $\partial H/\partial z$ is the transverse component of the gradient of the magnitude of the magnetic field. If one also applies an inhomogeneous electric field E across the beam, there is an electric force that for a scalar polarizability α is simply $\alpha E \partial E/\partial z$. The induced electric force is always directed toward the direction of stronger field, while the direction of the magnetic force depends on the sign of $\mu(m_F)$. If $\mu(m_F)$ is negative it is possible to adjust the field strengths so that the electric and magnetic forces are equal and opposite. When the forces are so balanced,

$$\alpha E \partial E/\partial z = \mu(m_F) \partial H/\partial z \quad (34)$$

and since atomic magnetic moments are known, it is possible to obtain α by determining E and H when the balance condition of Eq. (34) prevails. Salop *et al.* (1961) first used this technique to measure the polarizabilities of the alkali metal atoms. If the electric and magnetic fields are congruent, then the balance equation may be written

$$\alpha E^2 = \mu(m_F) H \quad (35)$$

and the result is independent of the ratio of the field gradient to field strength, C , where

$$C = E^{-1} \partial E/\partial z = H^{-1} \partial H/\partial z \quad (36)$$

which has been cancelled on both sides of Eq. (35). It is still necessary to know the magnetic field strength H , and in practice the ratio of the electric field strength to the applied potential,

$$K = E/V \quad (37)$$

Thus, the balance equation is

$$\alpha K^2 V^2 = \mu(m_F)H \quad (38)$$

Salop *et al.* calculated the geometrical constant K and determined the magnetic field strength at the beam position from knowledge of field strengths at which the effective magnetic moments for certain m_F values become zero. Thirteen years later, Molof *et al.* (1974a) studied the alkali metal atoms on an improved apparatus with better data-acquisition equipment. They were able to determine C and K experimentally for their apparatus and concluded that it is difficult to calculate accurate values of these constants. They depend on the precision with which the pole pieces are machined, their spacing, the accuracy with which the beam position is known; and the importance of the fringing fields. In conventional electric deflection experiments, the product CK^2 must be accurately known. In the E - H balance experiment of Salop *et al.* (1961), K^2 was required.

Molof *et al.* (1974a) chose to normalize their measurements to the polarizability of 2^3S_1 metastable helium, a value that has been accurately calculated (Chung and Hurst, 1966). With the normalization, the balance equations for the atom in question and for 2^3S_1 helium provide the unknown polarizability:

$$\alpha = \alpha_{\text{He}} [\mu(m_F)/\mu_{\text{He}}(1)] (V_{\text{He}}/V)^2 \quad (39)$$

where α_{He} and $\mu_{\text{He}}(1)$ refer to metastable helium in the $m_J = 1$ state, and V and V_{He} are the applied electric potentials used to achieve balanced beams without changing the magnetic field strength.

Examples of the E - H balance data of Molof *et al.* (1974a) are shown in Figs. 10 and 11. Figure 10 is a coarse scan of the magnetic sublevels of cesium at an intermediate field strength of 1010 G. As the potential across the pole pieces is increased, the components of the beam corresponding to different magnetic sublevels come into balance. Those with the largest magnetic moment require the largest applied potential for balance. The $(F, m_F) = (4, 4)$ sublevel has a magnetic moment of one Bohr magneton, independent of magnetic field strength. When clearly resolved, Molof *et al.* used this sublevel to obtain their polarizability data since there is no ambiguity in $\mu(m_F)$. In routine data acquisition, Molof *et al.* scanned only over a range of potentials necessary to capture the top part of the balance spectrum for the sublevel of interest in order to achieve greater precision. Typical data

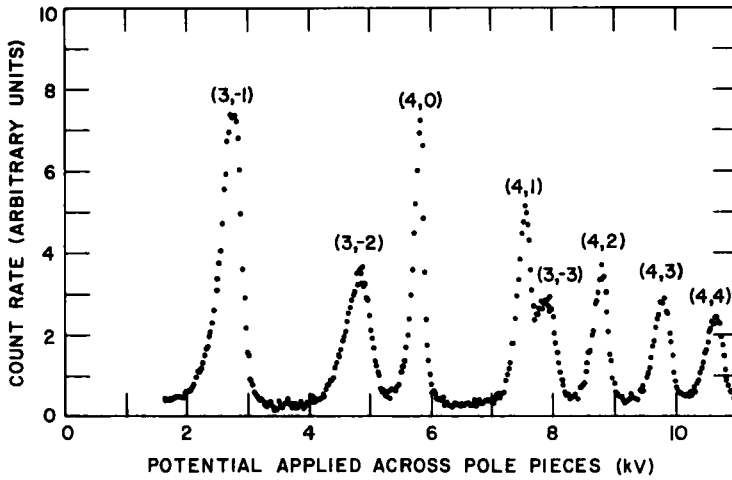


FIG. 10. A coarse scan of the potential applied across the E - H gradient pole pieces of the NYU apparatus at a magnetic field strength of 1010 G. The peaks result from a balancing of electric and magnetic forces acting on cesium atoms in different (F, m_F) sublevels. (From Molof *et al.*, 1974a.)

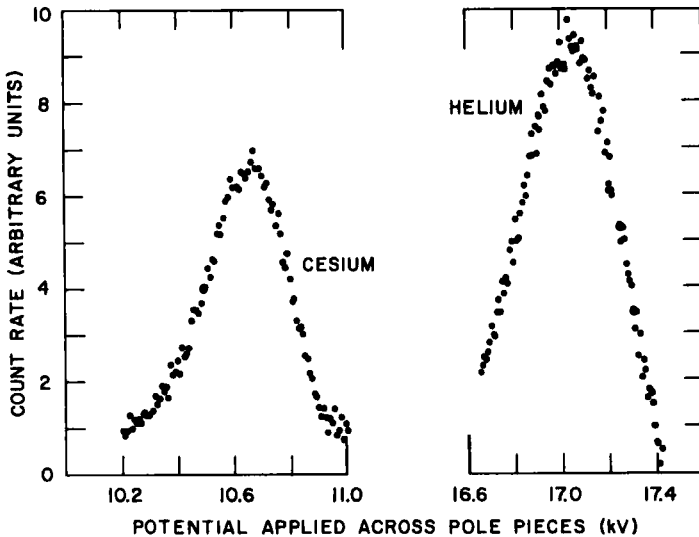


FIG. 11. Fine scans of a cesium $(F, m_F) = (4, 4)$ E - H balance peak and a balance peak for the $m_J = 1$ sublevel of 2^3S_1 metastable helium, at a magnetic field strength of 1010 G. In this manner the cesium polarizability is normalized to that of $\text{He}(2^3S_1)$. (From Molof *et al.*, 1974a.)

for the $(F, m_F) = (4, 4)$ spectrum in cesium are shown in Fig. 11 along with the $2^3S_1(m_J = 1)$ spectrum for helium, obtained at the same magnetic field strength. Each point in Fig. 11 corresponds to an 8.1 V increment in the applied potential, out of many thousands of volts, hence the precision of the experiment.

The latest results for the alkali metal atoms are given in Table V, and are accurate to $\pm 2\%$. They are in excellent agreement with the results of Hall and Zorn (1974), who used electric deflection of velocity-selected beams. They also compare well with recent theoretical calculations. It is important to obtain agreement between experiment and theory in the case of these "one-electron" atoms in which the effects of electron correlation are small.

TABLE V
A COMPARISON OF RECENT POLARIZABILITY VALUES FOR THE ALKALI METAL ATOMS,
IN UNITS OF 10^{-24} cm^3

Source	$\alpha(\text{Li})$	$\alpha(\text{Na})$	$\alpha(\text{K})$	$\alpha(\text{Rb})$	$\alpha(\text{Cs})$
Molof <i>et al.</i> (1974a) (<i>E-H</i> balance experiment)	24.3 ± 0.5	23.6 ± 0.5	43.4 ± 0.9	47.3 ± 0.9	59.6 ± 1.2
Hall and Zorn (1974) (electric deflection experiment)	—	24.4 ± 1.7	45.2 ± 3.2	48.7 ± 3.4	63.3 ± 4.6
Sternheimer (1969) (perturbation theory)	24.74	22.33	42.97	45.49	61.19
Adelman and Szabo (1973) (effective quantum numbers)	24.6	23.8	43.2	48.2	61.0
Werner and Meyer (1976) Reinsch and Meyer (1976) (multiconfigurational perturbation)	24.38	24.45	42.62		
Sims <i>et al.</i> (1976) (variation-perturbation)	24.27				
Norcross (1973) (semiempirical model potential)					59.3

Molof *et al.* (1974a) also measured the polarizabilities of the noble gas atoms in the 3P_2 metastable levels, using the *E-H* gradient-balance method. These polarizabilities are interesting because of the similarity of the structure of the metastable-state noble gas atoms to that of the alkali metal atoms. Both possess a single outer electron that dominates the polarizability of the atom. There are differences: the alkali atom has a spherically symmetric core, while the noble gas atom has a p hole in the core; and the outer electron of the alkali atom is more tightly bound than that of the adjacent noble gas atom in the periodic table. The gross one-electron character makes the calculation of these polarizabilities relatively easy on the 10% level of accuracy. The structural differences between the alkali atoms and noble gas

atoms make the calculations fascinating on the 1% level of accuracy. The ground-state alkali metal atom is represented by a scalar polarizability. The 3P_2 noble gas atom is described by a tensor polarizability with two independent components. In Section I,B we remarked that the polarizability in such a case is commonly specified by α_{\parallel} and α_{\perp} , the polarizability with the electric field parallel and perpendicular, respectively, to the symmetry axis of the atom. In the laboratory, the atom is never oriented exactly along the electric field direction; one measures the Z component of the polarizability with the atom in different m_j sublevels in order to determine the orientational dependence of the polarizability.

An example of a coarse scan of the E - H balance spectrum of one of the 3P_2 noble gas atoms is shown in Fig. 12 for krypton. The $m_j = 1, 2$ balance peaks can be seen. The Z component of the polarizability for $m_j = 1, 2$ is determined from fine scans of these peaks in association with a scan of the 2^3S_1 helium balance spectrum. In Table VI, the results for the metastable-state noble gas atoms are given. The experiment of Molof *et al.* was a remeasurement of these polarizabilities, to take advantage of the improvements in the newer apparatus. The earlier measurements of Pollack *et al.* (1964) and of Robinson *et al.* (1966) are listed in Table VI, and it can be seen that the agreement is excellent. They attribute this to the normalization procedure, which tends to overcome errors in alignment, as long as the beam of the standard atom is congruent with the beam of atoms under study.

In Table VII we give the results for the 3P_2 noble gases expressed as $\bar{\alpha}$ and

TABLE VI
A COMPARISON OF MEASURED VALUES OF THE
POLARIZABILITIES $\alpha_{zz}(m_j = 1)$ AND $\alpha_{zz}(m_j = 2)$ OF THE 3P_2
METASTABLE NOBLE GAS ATOMS^a

		MSMB	PRB and RLB
Ne	$\alpha_{zz}(1)$	28.4 ± 0.6	28.0 ± 1.4
	$\alpha_{zz}(2)$	26.7 ± 0.5	26.7 ± 1.3
Ar	$\alpha_{zz}(1)$	49.5 ± 1.0	50.4 ± 3.5
	$\alpha_{zz}(2)$	44.7 ± 0.9	44.5 ± 3.1
Kr	$\alpha_{zz}(1)$	52.7 ± 1.0	53.7 ± 2.7
	$\alpha_{zz}(2)$	46.8 ± 0.9	46.7 ± 2.3
Xe	$\alpha_{zz}(1)$	66.6 ± 1.3	68.2 ± 3.4
	$\alpha_{zz}(2)$	57.4 ± 1.1	56.8 ± 2.8

^a MSMB denotes the results of Molof *et al.* (1974a), PRB denotes Pollack *et al.* (1964), and RLB denotes Robinson *et al.* (1966). The polarizabilities are expressed in units of 10^{-24} cm^3 .

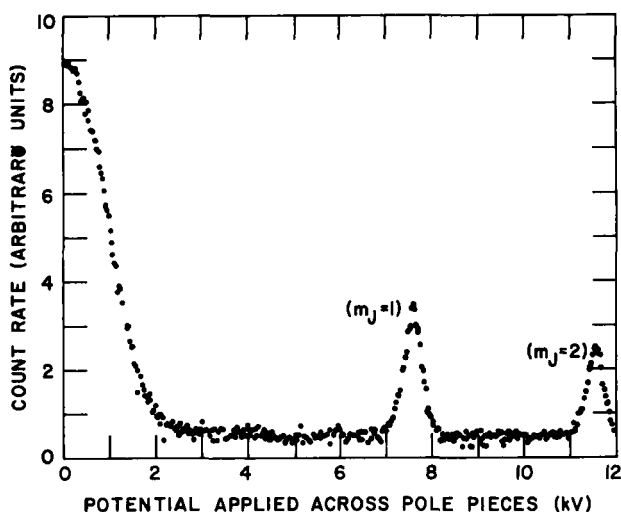


FIG. 12. Coarse scan of the potential applied across the E - H gradient pole pieces of the NYU apparatus at a magnetic field strength of 313 G, for 3P_2 metastable krypton. The tensor components of the polarizability for all m_J are completely determined by a measurement of the potentials corresponding to the maxima of the $m_J = 1$ and $m_J = 2$ balance peaks. (From Molof *et al.*, 1974a.)

TABLE VII

A COMPARISON OF VALUES OF $\bar{\alpha}$ AND THE "TENSOR" POLARIZABILITY α_1 FOR THE 3P_2 METASTABLE NOBLE GAS ATOMS, IN UNITS OF 10^{-24} cm^3 ^a

		RLB			
		MSMB	PS	Theory A	Theory B
Ne	$\bar{\alpha}$	27.8	—	29.6	27.8
	α_1	-1.1	-0.963	—	—
Ar	$\bar{\alpha}$	47.9	—	50.5	48.1
	α_1	-3.2	-2.95	—	—
Kr	$\bar{\alpha}$	50.7	—	59.9	53.5
	α_1	-3.9	-3.90	—	—
Xe	$\bar{\alpha}$	63.6	—	78.2	62.5
	α_1	-6.1	-6.03	—	—

^a MSMB denotes the results of Molof *et al.* (1974a), PS denotes Player and Sandars (1969), and RLB denotes Robinson *et al.* (1966). Theory A is a modification of Sternheimer's method, and theory B uses estimates of oscillator strengths from the Coulomb approximation of Bates and Damgaard (1949).

α_i , the isotropic and anisotropic parts of the polarizability tensor. These values are compared to the calculations for $\bar{\alpha}$ by Robinson (Robinson *et al.*, 1966) and with measurements of α_i by Player and Sandars (1969). The values of $\bar{\alpha}$ of Molof *et al.* compare best with Robinson's results based on the Coulomb approximation of Bates and Damgaard (1949). The values of α_i of Molof *et al.* compare very well with those of Player and Sandars, who used an atomic beam resonance apparatus and quote $\pm 5\%$ accuracy. Because Molof *et al.* obtain α_i as the small difference between two large numbers, the values of α_i are expected to be accurate only to $\pm 100\%$ for neon, to at best $\pm 40\%$ for xenon; but the favorable comparison with Player and Sandars implies that the absolute values of Molof *et al.* may be much better than claimed.

The 3P_2 noble gas results of Molof *et al.* emphasize the capability of the E - H gradient balance technique in determining the tensor components of atomic polarizabilities. The NYU group has also reported results on polarizabilities of metastable states in mercury (Levine *et al.*, 1968). The E - H gradient balance method was used to determine the tensor components of the polarizability of the $6s6p(^3P_2)$ metastable state of mercury. They used an electric deflection method with the same apparatus to measure the average polarizability of $5d^96s^26p(^3D_2)$ mercury. As before, the results of these experiments were normalized against the polarizability of 2^3S_1 helium. The experiment of Levine *et al.* was more difficult than the experiments with the metastable noble gases because the metastable mercury atoms have much less internal energy to release at the detector—hence the detection efficiency is much poorer.

The NYU laboratory has unpublished results on the polarizability of H_2 (Schwartz, 1970) and of In (Stockdale *et al.*, 1976). In both cases the E - H balance method was used.

4. Atomic Beam Resonance Experiments

In atomic beam resonance experiments, one uses an apparatus shown schematically in Fig. 13. The A magnet is used to select a single magnetic sublevel in the beam. The B magnet is generally set to refocus those atoms that have undergone a spin-flip in the main interaction region, between the A and B magnets. In resonance experiments concerned with polarizability work, the interaction region contains parallel plates that establish a homogeneous electric field. In addition, rf energy can be coupled into the interaction region. A typical case, the study of the metastable noble gas atoms, will be described. The A magnet is used to select a particular magnetic sublevel (say, $m_J = 0$) while the B magnet is set to pass only those atoms that have

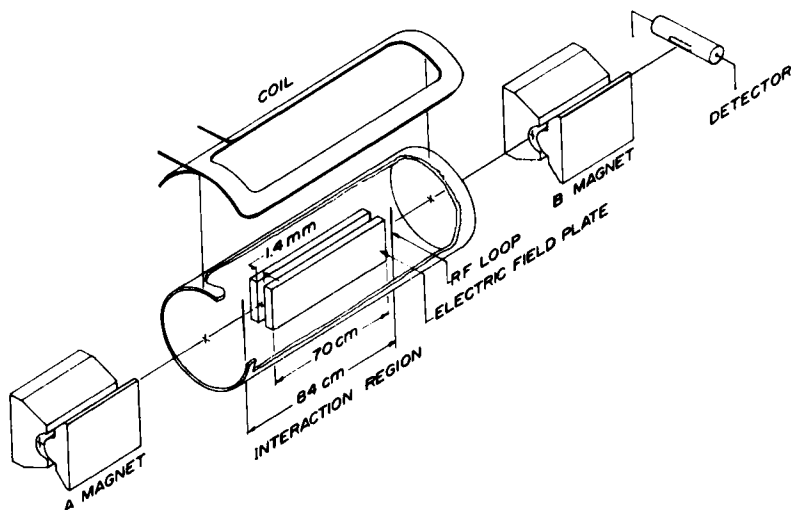


FIG. 13. Schematic diagram of an atomic-beam magnetic-resonance apparatus. Only one of four magnetic field coils around the interaction region is shown. (From Gould, 1976.)

been excited to another m_j sublevel (say, $m_j = 1$) by the ac field in the interaction region. The frequency of the ac field required for the transition depends on the Stark shifts in the energies of the two m_j sublevels involved. Thus, this method yields the difference in the polarizabilities $\alpha_{ZZ}(m_j)$ for the two m_j sublevels involved, and usually the anisotropic polarizability α_i is reported. We have already given the results of Player and Sandars (1969) for the 3P_2 metastable noble gases in Table VII. They also measured the very small anisotropy in the $\text{He}(2^3S_1)$ polarizability, which is due to magnetic spin-spin interactions. Their result, $(5.07 \pm 0.25) \times 10^{-28} \text{ cm}^3$, compares well to the calculation by Angel and Sandars (1968), $(5.23 \pm 0.21) \times 10^{-28} \text{ cm}^3$, and to the experiment of Ramsey and Petrasso (1969) who found $(5.05 \pm 0.16) \times 10^{-28} \text{ cm}^3$.

Gould (1976) has used the atomic beam resonance method to study the $6^2P_{1/2}$ ground state of thallium. He measured $\alpha_i = -2.23 \times 10^{-29} \text{ cm}^3$.

English and Kagann (1974) have used atomic beam resonance to study the polarizability of $c^3\Pi_u$ metastable H_2 . English and Albritton (1975) have reported calculations for this state, which is strongly coupled to the $a^3\Sigma_g^+$ state of H_2 .

A survey of the modern beam work on polarizabilities shows that most of the effort has been with atoms that can be detected by surface ionization, or with metastable-state atoms that have sufficient energy to liberate electrons at surfaces. The need for good detection efficiency is related to the need for narrowly collimated beams.

D. EXCITED STATES

1. Lower-Lying Short-Lived States

In recent years we have seen much experimental work on the polarizabilities of excited states of atoms. We have included metastable states in our general discussion of beam experiments on ground-state atoms, since the techniques have been the same. For short-lived atomic states, however, the deflection methods do not seem practical. Van Raan *et al.* (1976) have used the deflection method with highly excited p states of cesium ($40 \leq n \leq 60$) for which the lifetimes are on the order of milliseconds. The magnitude of the electric fields in this experiment are such that the linear Stark effect dominated the electric moment of the atoms. Homogeneous electric fields have been used by other experimenters to study short-lived states with optical, microwave, or rf transitions indicating the energy shift between two levels in the electric field.

Grotrian and Ramsauer (1927), Yao (1932), and Kopfermann and Paul (1943), measured the quadratic Stark effect spectroscopically for some of the 2P states of the alkali atoms. These data, together with those obtained by Marrus *et al.* (1966, 1969) cover the isotropic and anisotropic parts of the polarizability tensor $\bar{\alpha}$ and α_1 , for the lowest 2P states of sodium, potassium, rubidium, and cesium, and for the second excited 2P states of potassium and rubidium. Marrus *et al.* (1966) and Marrus and Yellin (1969) used an atomic beam resonance apparatus. However, in the electric field region of the apparatus, spin-flips are not induced directly with rf radiation. Instead, a resonance lamp is used to excite some of the beam atoms to the $^2P_{1/2, 3/2}$ states. When these atoms decay, one-half end up spin-flipped in the ground state and give a signal at the beam detector. A strong signal is detected at zero field strength and also at a field strength such that the differential energy shift between the ground and excited states brings the transition into resonance with the other member of the hyperfine doublet of the resonance lamp. At this value of E^2 , the energy separation between the Stark-shifted ground and excited states is then known, and the differential polarizabilities between the ground state and the various m_J sublevels of the $^2P_{1/2, 3/2}$ states are evaluated. Marrus *et al.* used the ground-state data of Salop *et al.* to give the full set of $\alpha_{zz}(m_J)$ for the $^2P_{1/2, 3/2}$ states of potassium, rubidium, and cesium. [Molof *et al.* (1974a) corrected the ground-state results later and applied a small correction to the $^2P_{1/2, 3/2}$ results of Marrus *et al.*] The 2P polarizabilities are typically 2–4 times the ground-state polarizabilities.

Khadjavi *et al.* (1968) used a level-crossing technique in pure electric fields to measure the anisotropic part of the tensor polarizability α_1 , for the second excited $^2P_{3/2}$ state of potassium. Schmieder *et al.* (1971) measured α_1 for the

second excited $^2P_{3/2}$ state of potassium with the same apparatus. They also used the method of Bates and Damgaard (1949) to calculate $\bar{\alpha}$ and α_i for the first, second, and third excited $^2P_{3/2}$ states of the alkali atoms. Their measurements indicate that the calculated values are good to within a few percent. We should point out that $\bar{\alpha}$ or α_i can be positive or negative for the excited states, depending on the location of perturbing states.

In a series of measurements (v. Oppen, 1969, 1970; v. Oppen and Piosczyk, 1969; Kreutztrager and v. Oppen, 1973; Kreutztrager *et al.*, 1974) α_i was measured for the lowest 3P_1 and 1P_1 states of the alkaline earths calcium, strontium, and barium. This group used optical double resonance and level crossing techniques. The polarizabilities were all on the order of $6 \times 10^{-24} \text{ cm}^3$ except for the 3P_1 state of barium, for which they found $0.025 \times 10^{-24} \text{ cm}^3$. The smallness of the latter value was attributed to relative position of the metastable 3D levels in barium as opposed to strontium and calcium.

Bhaskar and Lurio (1974) have measured α_i for the 2^1P_1 state of helium, using an electric-field level-crossing technique. They created a beam of 2^1S_0 metastable helium and in the electric field region they excited some of these atoms to the 2^1P_1 level with $2 \mu\text{m}$ resonance radiation. They detected 58.4 nm emission from 2^1P_1 decay, as a function of electric field strength, in order to determine the Stark shift. They found $\alpha_i = (33.2 \pm 1.0) \times 10^{-24} \text{ cm}^3$, which compares well with a value $33.4 \times 10^{-24} \text{ cm}^3$ obtained by calculating oscillator strengths connecting the 2^1P_1 state to nearby S and D states.

Baravian *et al.* (1976) have studied the quadratic Stark effect in excited neon. They used 16-photon pumping of neon, with a neodymium glass laser. They determined $\bar{\alpha} = 21.8 \times 10^{-24} \text{ cm}^3$ for the $3p'[\frac{1}{2}]_1$ level (Paschen notation).

Sandle *et al.* (1975) have measured differential Stark shifts in the 6^3P_1 levels of ^{198}Hg and ^{199}Hg . They found $-(1.41 \pm 0.02) \times 10^{-24} \text{ cm}^3$ for ^{198}Hg , and $-(0.90 \pm 0.03) \times 10^{-24} \text{ cm}^3$ for ^{199}Hg . (In ^{198}Hg the nuclear spin is zero while in ^{199}Hg it is $\frac{1}{2}$.) They compared their ^{199}Hg results to calculated values and earlier experiments (Khadjavi *et al.*, 1968; Kaul and Latshaw, 1972). The agreement between experiments is excellent, but the theoretical values are $\sim 20\%$ off.

2. Rydberg States

A number of measurements dealing with Rydberg states of atoms have been reported lately: lifetimes, field ionization, collisions, level splittings, and Stark effect measurements (Stebbins, 1976). Hohervorst and Svanberg (1974, 1975) have reported measurements of α_i for $n = 8, 9, 10$ 2D levels in

cesium, using a level-crossing technique.¹ Two-photon pumping of cesium was accomplished with an rf lamp and a tunable dye laser. Hohervorst and Svanberg found values of α_1 ranging from 5×10^{-20} to $5 \times 10^{-19} \text{ cm}^3$. They have also studied potassium and rubidium in the same manner. Fabre and Haroche (1975) used quantum beat spectroscopy to measure α_1 for $n = 10, 11, 12$ ^2D levels in sodium. They also used two-photon pumping but from two dye lasers. Their values of α_1 range from -4×10^{-17} to $-12 \times 10^{-17} \text{ cm}^3$.

Harvey *et al.* (1975) and Hawkins *et al.* (1977) have used Doppler-free two-photon excitation of sodium in order to measure Stark shifts and splittings of the ^2S levels for $n = 5, 6, 7, 8$, and of the ^2D levels for $n = 4, 5, 6$. Absolute frequency shifts and splittings of the levels were determined in static electric fields from interferometric detection of the sodium uv fluorescence. The measurement of both $\bar{\alpha}$ and α_1 allows the contributions to the

TABLE VIII

THE RESULTS OF HARVEY *et al.* (1975) AND HAWKINS *et al.* (1977) FOR THE AVERAGE POLARIZABILITIES $\bar{\alpha}$ AND "TENSOR" POLARIZABILITIES α_1 OF ^2S AND ^2D LEVELS OF SODIUM^a

State	Experiment			Calculated	
	S_0 (GHz)	HIC (GHz)	$\bar{\alpha}$ $\left(\frac{\text{Hz}}{(\text{V}/\text{cm})^2} \right)$	α_1 $\left(\frac{\text{Hz}}{(\text{V}/\text{cm})^2} \right)$	$\bar{\alpha}$ $\left(\frac{\text{Hz}}{(\text{V}/\text{cm})^2} \right)$
$3^2\text{S}_{1/2}$		(0.885)	(0.0396)	—	0.0400
$4^2\text{S}_{1/2}$		(0.202)	—	—	0.7678
$5^2\text{S}_{1/2}$		(0.0776)	5.2	—	5.384
$6^2\text{S}_{1/2}$		0.0345	23.6	—	23.36
$7^2\text{S}_{1/2}$		0.0233	76.4	—	75.98
$8^2\text{S}_{1/2}$		—	206	—	203.4
$4^2\text{D}_{5/2}$	(1.0283)		156.1	-53.2	152.4
$4^2\text{D}_{3/2}$	(1.0283)		155.3	-38.5	152.6
$5^2\text{D}_{5/2}$	0.617		1033	-337	1014
$5^2\text{D}_{3/2}$	0.617		994	-252	1015
$6^2\text{D}_{5/2}$	0.388		4054	-1322	3981
$6^2\text{D}_{3/2}$	0.388		3985	-995	3985

^a S_0 is the zero-field fine structure interval and HIC is the hyperfine interaction constant. The calculated values were obtained using the method of Bates and Damgaard (1949). Values in parentheses were taken from other sources and included for comparison to the measured polarizabilities. Note that α (\AA^3) = $595.52 \times \alpha$ [$\text{Hz}/(\text{V}/\text{cm})^2$].

¹ Our symbols $\bar{\alpha}$ for the average polarizability and α_1 for the tensor part are usually replaced by α_0 and α_2 , respectively, in the optical literature.

polarizabilities of the D states from the neighboring P and F states to be uniquely separated. The polarizabilities found in this work are given in Table VIII, along with values the authors have calculated using the Coulomb approximation of Bates and Damgaard (1949). The ground state Stark shifts are negligible compared to the measured shifts.

Gallagher *et al.* (1977) have measured α_1 for the $n = 15, 16, 17$ D states of sodium. For the $n = 17, 18, 19$ P states of sodium, they observed a faster change in energy with electric field strength than could be fit against E^2 and have evaluated the anisotropic part of the hyperpolarizability tensor γ_1 , as well as α_1 . Their results are given in Table IX along with values of $\bar{\alpha}$ and α_1 .

TABLE IX

THE RESULTS OF GALLAGHER *et al.* (1977) FOR THE POLARIZABILITIES OF RYDBERG LEVELS OF SODIUM^a

State	Experiment			Calculated	
	S_0	α_1	C	α_1	$\bar{\alpha}$
	(GHz)	$\left(\frac{\text{kHz}}{(\text{V/cm})^2} \right)$	$\left(\frac{\text{Hz}}{(\text{V/cm})^2} \right)$	$\left(\frac{\text{kHz}}{(\text{V/cm})^2} \right)$	$\left(\frac{\text{kHz}}{(\text{V/cm})^2} \right)$
16p	1.5487	22	0.017	19.8	-224
17p	1.2792	32	0.078	31.3	-349
18p	1.0684	50	0.221	49.0	-542
19p	0.9029	74	0.590	74.1	-809
15d	-0.0286	-1060	0	-940	2950
16d	-0.0240	-1470	0	-1490	4710
17d	-0.0198	-2780	0	-2290	7170

^a The principal quantum number is n , the zero-field fine structure interval is S_0 , and C is a coefficient determined when the data are fit to the expression $\nu = S_0 + \alpha_1 E^2/2 + CE^4$, where ν is the observed microwave frequency and E the applied electric field strength. Both the $d_{3/2}$ and $d_{5/2}$ states have the same $\bar{\alpha}$. The values of α_1 are for the $d_{5/2}$ states and $\alpha_1(\frac{3}{2}) = \frac{1}{9}\alpha_1(\frac{5}{2})$. The calculated values were obtained using the method of Bates and Damgaard (1949). Note that $\alpha(\text{\AA}^3) = \alpha[\text{Hz}/(\text{V/cm})^2]$.

that they calculated using the method of Bates and Damgaard (1949). Since the experimental and calculated values of α_1 agree so well, it may be assumed that the calculated values of $\bar{\alpha}$ are good.

Gallagher *et al.* used two-photon pumping of a sodium beam in this work. They used rf radiation to induce transitions between levels in the presence of a weak electric field (~ 10 V/cm) in order to determine the differential Stark shifts. Field ionization in a stronger, pulsed electric field was used to detect the rf resonance. (It is possible to distinguish different m_l states by varying

the field ionization potential.) The polarizabilities of the Rydberg states scale as n^7 , and the values reported are on the order of 10^9 \AA^3 .

Gallagher *et al.* (1976) have measured the $nf-ng$ and $ng-nh$ splittings in sodium for $n = 13-17$. Freeman and Kleppner (1976) have used these measurements to determine effective (dynamic) dipole and quadrupole polarizabilities of the closed-shell ion core of sodium. This work is significant because of the accuracy with which these quantities may be determined. Using a quantum defect analysis, Freeman and Kleppner find $(0.14841 \pm 0.00022) \times 10^{-24} \text{ cm}^3$ and $(20 \pm 6) \times 10^{-43} \text{ cm}^5$ for effective dipole and quadrupole polarizabilities of the sodium core. They expect that further experiments will allow the determination of the dipole and quadrupole polarizabilities of the atomic core to a few parts in 10^4 , and even higher order moments may be revealed. Kleppner (1975) believes that these ideas may lead to an experimental value of the Rydberg accurate to better than 1 part in 10^{10} . Gallagher *et al.* have recently obtained results for lithium splittings and core polarizabilities.

E. SIMPLE MOLECULES

We do not wish to enter into a full discussion of molecular polarizabilities (see Hirschfelder *et al.*, 1954). However, it seems relevant to mention some research with simple diatomic molecules. Kolos and Wolniewicz (1967) have calculated the polarizability of H_2 as a function of internuclear distance using a variational perturbation method and have used the results to tabulate $\bar{\alpha}$ and γ for $v = 0$, $0 \leq J \leq 31$, and $0 \leq v \leq 8$, $J = 0$. Here, γ is the polarizability anisotropy, v is the vibrational quantum number, and J is the rotational quantum number. They also tabulated results for HD and D_2 . This calculation is regarded as highly accurate (few parts per thousand) by other workers. Kolos and Wolniewicz refer to several experimental measurements in their paper, and the agreement is very good between theory and experiment. H_2 is unique in that it is trivial to produce a gas for which $v = 0$ and $J = 0, 1$ (the para and ortho modifications) and with extra effort one can obtain a pure parahydrogen gas.

Nelissen *et al.* (1969) used the $E-H$ gradient balance method and electric deflection to study H_2 . They determined $\gamma/3\bar{\alpha}$ for $v = 0$, $J = 1$ H_2 , and $\bar{\alpha}$ for (75% $v = 0$, $J = 1$ and 25% $v = 0$, $J = 0$) H_2 . Schwartz (1970) used the $E-H$ balance method to find $\bar{\alpha}$ for $v = 0$, $J = 1$ H_2 . These beam measurements yielded results that are lower than the calculated values of Kolos and Wolniewicz (1967), but the uncertainties in the beam results are such that a discrepancy is not clear.

English and MacAdam (1970) and MacAdam and Ramsey (1972) used an atomic beam resonance apparatus in a direct measurement of the polarizabil-

ity anisotropy in H_2 and D_2 for $v = 0, J = 1$. MacAdam and Ramsey found $\gamma(H_2) = (0.3016 \pm 0.0005) \times 10^{-24} \text{ cm}^3$ and $\gamma(D_2) = (0.2917 \pm 0.0004) \times 10^{-24} \text{ cm}^3$. These values differ from the results of Kolos and Wolniewicz by 0.17 and 0.3%, respectively, for H_2 and D_2 . The difference is increased to 0.56% for both H_2 and D_2 if a correction to the theoretical results is made for diabatic effects, i.e., failure of the Born–Oppenheimer approximation (Karl and Poll, 1975).

Besides hydrogen, the study of the polarizabilities of loosely bound molecules is relevant to our discussion. Dagdigian *et al.* (1971), Graff *et al.* (1972), and Dagdigian and Wharton (1972) have used deflection and resonance methods to study the heteronuclear alkali metal dimers. In the case of NaLi, they were able to determine both $\bar{\alpha}$ and α_i since the polarizability was an important contribution to the overall electric dipole moment in their experiment. They found $\bar{\alpha} = (40 \pm 5) \times 10^{-24} \text{ cm}^3$ and $\gamma = (24 \pm 2) \times 10^{-24} \text{ cm}^3$ for $v = 0$ NaLi.

Molof *et al.* (1974b) have used an electric deflection technique to measure $\bar{\alpha}$ for Li_2 , Na_2 , K_2 , Rb_2 , and Cs_2 . The work was described in Section III,C,3. Their values of $\bar{\alpha}$ correspond to thermal averages over the rotational and vibrational states at the experimental temperatures $\sim 650^\circ\text{K}$. However, the ground-state polarizabilities differ from these thermal averages by only a few percent (Miller and Molof, 1977). No measurements for α_i have been made for the homonuclear alkali dimers. Calculations indicate that $\alpha_{\parallel}/\alpha_{\perp}$ is between 1.4 and 2.0 for the alkali dimers. Molof *et al.* (1974b) found the following average polarizabilities, in units of 10^{-24} cm^3 : Li_2 (990°K), 34 ± 3 ; Na_2 (736°K), 30 ± 3 ; K_2 (569°K), 61 ± 5 ; Rb_2 (534°K), 68 ± 7 ; and Cs_2 (515°K), 91 ± 7 .

Greene and Milne (1968) obtained preliminary results for Na_2 ($37 \times 10^{-24} \text{ cm}^3$) and for Na_2Cl_2 ($32 \times 10^{-24} \text{ cm}^3$).

van der Waals molecules can be formed in nozzle beams, and their study provides an interesting link between atomic and molecular structure. In Table I we gave approximate formulas for the van der Waals C_6 and C_8 coefficients in terms of the dipole and quadrupole polarizabilities of the separated atoms. Stwalley (1970) and Li and Stwalley (1973) have used these concepts in order to analyze spectra obtained for Mg_2 , for example. Dalgarno and Davison (1966) have reviewed van der Waals interactions. Kramer and Hershbach (1970) have discussed approximate formulas for van der Waals constants.

IV. Future Possibilities for Polarizabilities

We have pointed out that little experimental research has been possible with the open-shell atoms other than the alkali metals and some of the

alkaline earths. This situation could improve if an efficient detector of neutral atoms is developed for beam work, e.g., laser fluorescence or cryo-pumped ionizers. Supersonic beams of atoms have not yet been used in polarizability experiments. Another possibility is the further use of shock tubes to produce atomic gases. Precision measurements of the index of refraction and of the depolarization of scattered light in shock tube interferometry should be possible today. (Thus far, shock tube interferometry has utilized lamps rather than lasers.) The experimentalists have two goals: (1) to achieve a level of accuracy such that electron correlation effects may be observed, and (2) to measure polarizabilities *and* polarizability anisotropies for the open shell atoms.

Theorists have held an advantage over experimentalists at the present time. Sophisticated calculations are enabling us to understand the effects of electron correlation on polarizabilities. (The same is true in other areas of atomic physics, such as in electron scattering.) However, once experimentalists break through present limitations, they will be able to tackle the heavy atoms as easily as the light ones. The same is not true for theory, and there is already an indication (with the alkali metals) that the heavy atoms will be troublesome.

Research on the polarizabilities of excited atoms is expected to proceed rapidly. The accuracy with which these measurements can be made makes it possible to specify the role of the ionic core precisely—both its multipole polarization and the effect of penetration by the valence electron.

Further research on molecular polarizabilities (insofar as relevant to this article) might be seen to delve into the determination of polarizability anisotropies and the internuclear dependence of α_{\parallel} and α_{\perp} , whether through state selection or with beams of different temperatures. Supersonic molecular beams are found to have low internal energies, and the internal energy can be controlled somewhat in “seeded” beams.

ACKNOWLEDGMENT

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Appendix

RECOMMENDED VALUES FOR ATOMIC POLARIZABILITIES, EXPRESSED
IN UNITS OF 10^{-24} cm^3

Estimated accuracy (%)	Atom	Average polarizability	Notes
"Exact"	H	0.666793	<i>a</i>
"Exact"	He	0.204956	<i>a</i>
0.5	Li	24.3	<i>b</i>
2	Be	5.60	<i>c</i>
2	B	3.03	<i>d</i>
2	C	1.76	<i>d</i>
2	N	1.10	<i>d</i>
2	O	0.802	<i>d</i>
2	F	0.557	<i>d</i>
2	Ne	0.395	<i>d</i>
2	Na	23.6	<i>e</i>
2	Mg	10.6	<i>d</i>
2	Al	8.34	<i>d</i>
2	Si	5.38	<i>d</i>
2	P	3.63	<i>d</i>
2	S	2.90	<i>d</i>
2	Cl	2.18	<i>d</i>
0.5	Ar	1.64	<i>d</i>
2	K	43.4	<i>e</i>
8	Ca	25.0	<i>c</i>
50	Sc	16.9	<i>f</i>
50	Ti	13.6	<i>f</i>
50	V	11.4	<i>f</i>
50	Cr	6.8	<i>f</i>
50	Mn	8.6	<i>f</i>
50	Fe	7.5	<i>f</i>
50	Co	6.8	<i>f</i>
50	Ni	6.5	<i>f</i>
50	Cu	6.1	<i>f</i>
2	Zn	7.08	<i>d</i>
2	Ga	8.12	<i>d</i>
2	Ge	6.07	<i>d</i>
2	As	4.31	<i>d</i>
2	Se	3.77	<i>d</i>
2	Br	3.05	<i>d</i>
0.5	Kr	2.48	<i>a</i>
2	Rb	47.3	<i>b</i>
8	Sr	27.6	<i>c</i>
50	Y	22	<i>f</i>
50	Zr	18	<i>f</i>

(continued)

APPENDIX—Continued

Estimated accuracy (%)	Atom	Average polarizability	Notes
50	Nb	14	<i>f</i>
50	Mo	13	<i>f</i>
50	Tc	10.0	<i>f</i>
50	Ru	8.6	<i>f</i>
50	Rh	7.6	<i>f</i>
50	Pd	6.9	<i>f</i>
50	Ag	6.3	<i>f</i>
50	Cd	6.0	<i>f</i>
50	In	4.5	<i>a</i>
50	Sn	4.4	<i>f</i>
50	Sb	4.0	<i>f</i>
50	Te	3.9	<i>f</i>
50	I	3.9	<i>f</i>
0.5	Xe	4.04	<i>a</i>
2	Cs	59.6	<i>e</i>
8	Ba	39.7	<i>c</i>
50	La	37	<i>f</i>
50	Ce	36	<i>f</i>
50	Pr	34	<i>f</i>
50	Nd	32	<i>f</i>
50	Pm	30	<i>f</i>
50	Sm	29	<i>f</i>
50	Eu	27	<i>f</i>
50	Gd	26	<i>f</i>
50	Tb	25	<i>f</i>
50	Dy	25	<i>f</i>
50	Ho	23	<i>f</i>
50	Er	23	<i>f</i>
50	Tm	22	<i>f</i>
50	Yb	22	<i>f</i>
50	Lu	20	<i>f</i>
50	Hf	15	<i>f</i>
50	Ta	13	<i>f</i>
50	W	10	<i>f</i>
50	Re	9	<i>f</i>
50	Os	8	<i>f</i>
50	Ir	7	<i>f</i>
50	Pt	6.3	<i>f</i>
50	Au	5.7	<i>f</i>
50	Hg	5.1	<i>a</i>
50	Tl	3.5	<i>a</i>
50	Pb	3.7	<i>f</i>
50	Bi	4.0	<i>f</i>
50	Po	4.6	<i>f</i>

APPENDIX—Continued

Estimated accuracy (%)	Atom	Average polarizability	Notes
50	At	5.1	<i>f</i>
50	Rn	6.3	<i>g</i>
50	Fr	67	<i>h</i>
50	Ra	46	<i>h</i>
50	Ac	53	<i>f</i>
50	Th	50	<i>f</i>
50	Pa	48	<i>f</i>
50	U	46	<i>f</i>
50	Np	45	<i>f</i>
50	Pu	43	<i>f</i>
50	Am	41	<i>f</i>
50	Cm	40	<i>f</i>
50	Bk	39	<i>f</i>
50	Cf	38	<i>f</i>
50	Es	36	<i>f</i>
50	Fm	35	<i>f</i>
50	Md	34	<i>f</i>
50	No	33	<i>f</i>
50	Lw	32	<i>i</i>

^a From Teachout and Pack (1971).

^b From Table III.

^c From Table IV.

^d From Werner and Meyer (1976) and Reinsch and Meyer (1976).

^e From Table V.

^f Scaled from self-consistent-field (SCF) calculations by forcing agreement with better values where available. The SCF calculations are those of Thorhallsson *et al.* (1968a, 1968b) and Saxena and Fraga (1972). The accuracy in the polarizabilities resulting from this scaling is estimated to be $\pm 50\%$, as this is the maximum adjustment in the SCF values that was required.

^g From Tuck (1960).

^h Extrapolated from columns 1A and 2A of the periodic table.

ⁱ Extrapolated from the other actinide polarizabilities.

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