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PLANETARY AERONOMY X: ATOMIC POLARIZABILITIES AND SHIELDING FACTORS

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PLANETARY AERONOMY X:
ATOMIC POLARIZABILITIES AND SHIELDING FACTORS

A. Dalgarno

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TABLE OF CONTENTS

Table of Contents (Continued)

SECTION I

INTRODUCTION

Atomic polarizabilities describe the changes in the charge distribution of an atom when it interacts with an electric field and because of its close relationship to dielectric constants, the study of dipole polarizabilities has a lengthy history. Interest in atomic shielding factors is of more recent origin and was stimulated by attempts to determine nuclear quadrupole moments from observations of hyperfine structure. To a first approximation, atomic hyperfine structure is due to the interaction between the nucleus and the valence electrons and the inner closed shells of electrons act merely to screen the nuclear charge and so to modify the electrostatic field in which the valence electrons move. However, another type of shielding occurs because the valence electrons distort the spherical symmetry of the closed shells and the distorted shells then interact with the nucleus. Alternatively, the nuclear multipole moments induce equivalent moments in the charge distribution of the closed shells and these moments then interact with the valence electrons.

Although they refer to different phenomena, polarizabilities and shielding factors are examined together in this review since the mathematical procedures for calculating them are very similar and a larger body of experimental data becomes available for assessing the accuracy of the methods used.

1.1 DEFINITIONS

When an atom is placed in the field of an external charge Z', it is polarized and the resulting distribution of charge can be characterized by a series of induced electric multipole moments, each of which is proportional to Z' provided Z' is small. The induced dipole moment is related to the electric field of the charge through the atomic dipole polarizability, α_d. The induced quadrupole moment, α_q, is related to the gradient of the electric field of the charge through the atomic (field-gradient) polarizability.* Similar relations involving higher order derivatives of the electric field apply to the higher pole polarizabilities.*

The electric field of the external charge is also modified by the charge distribution of the atom and the dipole shielding factor, β_∞, can be defined as the ratio of the change in the electric field at the nucleus due to the charge distribution of the atom to the electric field at the nucleus due to the external charge alone. The quadrupole shielding factor, γ_∞, is the ratio of the change in the gradient of the electric field at the nucleus due to the charge distribution of the atom

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*Occasionally a different meaning is attached to quadrupole (and higher pole polarizabilities). The uniform part of the electric field induces, by a second order dipole-dipole coupling, a quadrupole moment which is proportional to Z'^2. The constant of proportionality is also referred to as a quadrupole polarizability.

to the gradient due to the external charge alone. Similar definitions involving higher order derivatives of the electric field apply to higher pole shielding factors. Shielding factors can be defined alternatively as the ratio of the multipole moment induced in the electron charge distribution to the nuclear multipole moment which gives rise to it.

When the atomic system is not spherically symmetric, the distortion of its electron distribution by the electric charge will depend upon the orientation of the atomic system. In such cases, it is convenient to average the polarizabilities and shielding factors over all orientations.

1.2 QUANTAL FORMULAE

Suppose the unperturbed atom has N electrons with position vectors $\underset{\sim}{r}_i$ referred to the nucleus as origin and let Z be the nuclear charge. The unperturbed Hamiltonian is given in atomic units by

$$H = - \sum_{i=1}^{N} \left(\nabla_i^2 + Z/r_i \right) + \sum_{i<j}\sum \frac{1}{|\underset{\sim}{r}_i - \underset{\sim}{r}_j|} \tag{1}$$

and the unperturbed eigenfunction ψ_o (r), when $\underset{\sim}{r}$ denotes collectively all the position vectors $\underset{\sim}{r}_i$, satisfies the Schrödinger equation

$$(H - E_o) \psi_o (\underset{\sim}{r}) = o, \tag{2}$$

E_o being the unperturbed eigenvalue.

Suppose also that the external charge Z' is located at $\underset{\sim}{r}'$ and that r' is large. Then the interaction potential

$$V(\underset{\sim}{r}, \underset{\sim}{r}') = \frac{ZZ'}{r'} - Z' \sum_{i=1}^{N} \frac{1}{|\underset{\sim}{r}_i - \underset{\sim}{r}'|} \tag{3}$$

may be expanded in the form

$$V(\underset{\sim}{r}, \underset{\sim}{r}') = \frac{Z'(Z - N)}{r'} - Z' \sum_{i=1}^{N} \sum_{k=1}^{\infty} \frac{r_i^{\,k}}{r'^{\,k+1}} P_k(\cos\theta_i) \tag{4}$$

where (r_i, θ_i, ϕ_i) are the spherical polar co-ordinates of $\underset{\sim}{r}_i$, the polar axis being chosen such that the co-ordinates of $\underset{\sim}{r}'$ are (r', o, o) and $P_k\ (\cos\theta_i)$ is the Legendre polynominal of order k. The constant spherically symmetric part of $V(\underset{\sim}{r}, \underset{\sim}{r}')$ is of no interest here and we replace (4) by

$$V(r, r') = -Z' \sum_{i=1}^{N} \sum_{k=1}^{\infty} \frac{r_i^{\,k}}{r'^{\,k+1}} P_k(\cos\theta_i). \tag{5}$$

Let $\psi\ (\underset{\sim}{r} \mid r')$ be the wave function of the system when a charge Z' is placed at $\underset{\sim}{r}'$. Provided the unperturbed state is not degenerate (as we shall assume), the perturbed wave function may be written in the form

$$\psi(\underset{\sim}{r} \mid r') = \psi_o\ (\underset{\sim}{r}) + Z' \sum_{k=1}^{\infty} \frac{\psi_1^{(k)}}{r'^{\,k+1}} + O(Z'^2), \tag{6}$$

$\psi_1^{(k)}$ being chosen so that

$$(\psi_1^{(k)}, \psi_o) = o \tag{7}$$

for all values of k. The requirement (7) ensures that ψ is normalized to the order of Z'.

We shall define the electric multipole moment of order 2^L of a charge distribution as

$$\Omega_{2^L} = - \left(\psi, \sum_{i=1}^{N} r_i^{\,L} P_L (\cos \theta_i) \psi \right) . \tag{8}$$

To the order of Z', (8) is

$$\Omega_{2^L} = -2 Z' \sum_{k=1}^{\infty} \frac{1}{r'^{\,k+1}} \left(\psi_1^{(k)}, \sum_{i=1}^{N} r_i^{\,L} P_L (\cos \theta_i) \psi_o \right)^{*} \tag{9}$$

The electric field strength at the nucleus due to the charge Z' is $-Z'/r'^2$ and the dipole polarizability is given by

$$\alpha_d = 2 \left(\psi_1^{(1)}, \sum_{i=1}^{N} r_i P_1 (\cos \theta_i) \psi_o \right) . \tag{10}$$

The gradient of the electric field at the nucleus is $-2Z'/r'^3$ and the quadrupole polarizability is given by

$$\alpha_q = 2 \left(\psi_1^{(2)}, \sum_{i=1}^{N} r_i^{\,2} P_2(\cos \theta_i) \psi_o \right), \tag{11}$$

the factor of 2 being inserted so that (11) conforms with the definition of α_q employed in most of the literature (c.f. Sternheimer 1954).

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*We are assuming that the wave functions are real. If they are not, the real part of the expression is to be taken.

In general, the $2^{\underline{L}}$ pole polarizability is given by

$$\alpha_2 L = 2 \left(\psi_1^{(L)}, \sum_{i=1}^{N} r_i^{\ L} P_L \ (\cos \theta_1) \ \psi_o \right) \tag{12}$$

in units of a_o^{2L+1}, as being the Bohr radius 5.292 x 10^{-9} cm. With this definition, the polarizabilities of any atom in its ground state are all positive quantities.

The electrostatic potential at the nucleus due to the atomic charge distribution and to the external charge is

$$\phi \ (\underset{\sim}{r}, \underset{\sim}{r}') = - \sum_{L=1}^{N} \frac{1}{r_i} + \frac{Z'}{r'} \tag{13}$$

and the expectation value of the electric field at the nucleus is accordingly

$$\left(\psi, \sum_{i=1}^{N} \frac{P_1 \ (\cos \theta_i)}{r_i^{\ 2}} \ \psi \right) - \frac{Z'}{r'^2} \tag{14}$$

which to first order in Z is

$$2Z' \sum_{k=1}^{\infty} \frac{1}{r'^{\ k+1}} \left(\psi_1^{(k)}, \sum \frac{P_1 (\cos \ \theta_i)}{r_i^{\ 2}} \ \psi_o \right) - \frac{Z'}{r'^2} \tag{15}$$

The dipole shielding factor is therefore

$$\beta\infty = 2 \left(\psi_1^{(1)}, \sum_{i=1}^{N} \frac{P_1 (\cos \ \theta_i)}{r_i^{\ 2}} \ \psi_o \right) \tag{16}$$

Feynman (1939) has shown that the force on a nucleus of charge Z is Z times the electric field at the nucleus due to all the electrons plus the fields from the external charge. The force of an ion charge Z' acting on an ion of net charge $(Z - N)$ is simply $-(Z-N)\, Z'/r'^2$ in the positive r' direction and the corresponding total electric field is $-(Z - N)\, Zr'^2$. Comparing with (15), it follows that

$$\beta = \frac{N}{Z}\,, \tag{17}$$

an argument first published by Sternheimer (1954). The dipole shielding factor is consequently a known quantity. Its interest lies in the fact that (16) contains the first-order perturbed function $\psi_1\,(\underset{\sim}{r})$ which is required for the evaluation of the dipole polarizability. The relationship (17) provides an assessment of the accuracy of the calculated first-order functions.

The expectation value of the gradient of the electric field at the nucleus is

$$\left(\psi, \sum_{i=1}^{N} \frac{2P_2(\cos\,\theta_i)}{r_i^{\,3}}\,\psi\right) - \frac{2Z'}{r'^3} \tag{18}$$

which to first order in Z' is

$$2Z' \sum_{k=1}^{\infty} \frac{1}{r'^{\,k+1}} \left(\psi_1^{(k)},\ \sum_{i=1}^{N} \frac{2P_2(\cos\,\theta_i)}{r_i^{\,3}}\ \psi_o\right)$$

$$- \frac{2Z'}{r'^3}\ . \tag{19}$$

The quadrupole shielding factor is therefore

$$\gamma_{\infty} = 2 \left(\psi_1^{(2)}, \sum_{i=1}^{N} \frac{P_2(\cos\theta_i)}{r_i^{\,3}} \psi_o \right). \qquad (20)$$

In general, the 2^L - pole shielding factor is given by

$$\gamma_{2^L} = 2 \left(\psi_1^{(L)}, \sum_{i=1}^{N} \frac{P_L(\cos\,\theta_i)}{r_i^{\,L+1}} \psi_o \right), \qquad (21)$$

which is dimensionless. With this definition, a positive value of γ_{2^L} corresponds to shielding and a negative value to antishielding.

SECTION II

PERTURBATION THEORY

2.1 THE FIRST ORDER EQUATION

The description of the determination of $\psi_1^{(k)}(\underset{\sim}{r})$ can be simplified by treating each term of $V(\underset{\sim}{r}, \underset{\sim}{r}')$ as a separate perturbing potential. Thus, writing

$$v_k(\underset{\sim}{r}) = - \sum_{i=1}^{N} r_i^{\,k} P_k (\cos \theta_i), \tag{22}$$

the perturbed wave function $\psi_k(\underset{\sim}{r})$ can be expanded in the form

$$\psi_k(\underset{\sim}{r}) = \psi_o(\underset{\sim}{r}) + Z' \psi_1^{(k)}(\underset{\sim}{r}) + Z'^2 \psi_2^{(k)}(\underset{\sim}{r}) + 0(Z'^3) \tag{23}$$

and the perturbed eigenvalue in the form

$$\mathcal{E}_k = E_o + Z' \mathcal{E}_1^{(k)} + Z'^2 \mathcal{E}_2^{(k)} + 0(Z'^3). \tag{24}$$

Then the wave equations of the perturbed system

$$(H + Z'v_k - \mathcal{E}_k) \psi_k = 0 \tag{25}$$

may be replaced by the sequence

$$(H - E_o) \psi_o = 0 \tag{26}$$

$$(H - E_o) \psi_1^{(k)} + (v_k - \mathcal{E}_1^{(k)} \psi_o = 0 \tag{27}$$

$$(H - E_o) \psi_2^{(k)} + (v_k - \mathcal{E}_1^{(k)}) \psi_1^{(k)} - \mathcal{E}_2^{(k)} \psi_o = 0 \tag{28}$$

From (27)

$$\mathcal{E}_1^{(k)} = (\psi_o, v_k \psi_o) \tag{29}$$

and from (28),

$$\mathcal{E}_2^{(k)} = (\psi_1^{(k)}, v_k \psi_o) \tag{30}$$

But from (12)

$$\alpha_2 L = -2 (\psi_1^{(L)}, v_L \psi_o) \tag{31}$$

so that

$$\mathcal{E}_2^{(L)} = - \frac{1}{2} \alpha_2 L \tag{32}$$

The shielding factor (21) may be written

$$\gamma_2 L = 2(\psi_1^{(L)}, v'_L \psi_o) \tag{33}$$

where

$$v'_k(\underset{\sim}{r}) = \sum_{i=1}^{N} \frac{P_k(\cos\theta_i)}{r_i^{\,k+1}} \tag{34}$$

It follows from symmetry considerations that (33) is identical to the alternative form

$$\gamma_2 L = 2(\psi_1^{(L)'},\ v_L\ \psi_o) \tag{35}$$

where

$$(H - E_o)\ \psi_1^{(k)'} + (v'_k - \mathcal{E}_1^{(k)'})\ \psi_o = 0 \tag{36}$$

such that

$$(\psi_1^{(k)'},\ \psi_o) = 0 \tag{37}$$

and

$$\mathcal{E}_1^{(k)'} = (\psi_o,\ v'_k\ \psi_o) \tag{38}$$

A formal proof of the identity of (33) and (35) follows from the use of (26) to yield

$$(\psi_1^{(L)'},\ v_L\ \psi_o) = -\ (\psi_1^{(L)'}\ |\ H - E_o\ |\ \psi_1^{(L)}) \tag{39}$$

and (36) to yield

$$-(\psi_1^{(L)} \mid H - E_o \mid \psi_1^{(L)'}) = (\psi_1^{(L)}, v'_L \ \psi_o) . \qquad (40)$$

2.2 THE HYDROGEN ATOM

As a demonstration of the theory of § 2.1, we consider a hydrogen atom in its ground state. Equation (26) for $\psi_1^{(k)}$ can be simplified by writing

$$\psi_1^{(k)} (\underset{\sim}{r}) = f^{(k)} (\underset{\sim}{r}) \ \psi_o (\underset{\sim}{r}) . \qquad (41)$$

Then $f^{(k)} (\underset{\sim}{r})$ satisfies the equation

$$- \frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 f^{(k)} - \sum_{i=1}^{N} \nabla_i f^{(k)} \cdot \frac{\nabla_i \psi_o}{\psi_o} + v_k - E_1^{(k)} = 0: \qquad (42)$$

For a hydrogenic atom in its ground state

$$\psi_o (\underset{\sim}{r}) = (Z^3/ \pi)^{\frac{1}{2}} \exp (-Zr) \qquad (43)$$

and (42) reduces to

$$- \frac{1}{2} \nabla^2 f^{(k)} + Z \frac{df^{(k)}}{dr} - r^k P_k (\cos \theta) = 0. \qquad (44)$$

with solution (Dalgarno and Lewis 1955)

$$f^{(k)}(\underset{\sim}{r}) = \frac{1}{Z} \left(\frac{r^{k+1}}{k+1} + \frac{r^{k}}{kZ} \right) P_k (\cos \theta) . \tag{45}$$

From (30) the multipole polarizability is

$$\alpha_{2^L} = \frac{(2L+2)! \qquad (L+2)}{2^{2L+1} \quad Z^{2L+2} L(L+1)} \tag{46}$$

and from (33) the multipole shielding factor is

$$\gamma_{2^L} = \frac{2}{L(L+1)\ Z} \tag{47}$$

The solution (45) for k = 1 was first obtained by Waller (1926), who calculated the dipole polarizability of atomic hydrogen.

2.3 UPPER BOUNDS

Except for one-electron systems it is not possible to solve (27) exactly. It may be solved formally by substituting the expansion

$$\psi_1^{(k)} (\underset{\sim}{r}) = \underset{t}{\underset{\sim}{S}}{}^{\prime} \; a_t^{(k)} \; \psi_t (\underset{\sim}{r}) \tag{48}$$

where $\psi_t(\underset{\sim}{r})$ is the eigenfunction of the t th excited state of the unperturbed atomic system, satisfying the wave equation

$$(H - E_t) \quad \psi_t(\underset{\sim}{r}) = 0 \tag{49}$$

and the prime on the summation indicates that the term $t = 0$ is excluded. Then the expansion coefficients $a_t^{(k)}$ are given by

$$a_t^{(k)} = - \frac{(\psi_t,\ v_k\ \psi_o)}{E_t - E_o} \tag{50}$$

and

$$\alpha_2L = 2 \mathop{\mathrm{S}'}_{\tilde{t}} \frac{|(\psi_t,\ v_L\ \psi_o)|^2}{E_t - E_o}\ , \tag{51}$$

which is clearly positive for all ground state atomic systems.

The convergence of the summation over t as the number of terms is increased is usually slow, as Tillieu and Guy (1954) have explicitly demonstrated for atomic hydrogen. If transitions to continuum states are unimportant, the convergence can be made more rapid by using the equivalent formula (Lennard - Jones 1930)

$$\alpha_2L = \overset{u}{\alpha_2L} + 2 \mathop{\mathrm{S}'}_{\tilde{t}} \frac{(E_1^{(L)} - E_t)\ |(\psi_t, v_L\ \psi_o)|^2}{(E_1^{(L)} - E_o)\ (E_t - E_o)} \tag{52}$$

where

$$\overset{u}{\alpha_2L} = \frac{2}{(E_1^{(L)} - E_o)} \left\{ (\psi_o,\ v_L^2\ \psi_o) - (\psi_o,\ v_L\ \psi_o)^2 \right\}, \tag{53}$$

and the prime on the summation indicates that the term t = 0 is excluded. Then the expansion coefficients $a_t^{(k)}$ are given by

$$a_t^{(k)} = - \frac{(\psi_t, v_k \psi_o)}{E_t - E_o} \tag{50}$$

and

$$\alpha_2 L = 2 \mathop{S'}_{\tilde{t}} \frac{|(\psi_t, v_L \psi_o)|^2}{E_t - E_o} , \tag{51}$$

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$$\alpha_2 L = \alpha_2 \overset{u}{L} + 2 \mathop{S'}_{\tilde{t}} \frac{(E_1^{(L)} - E_t) \; |(\psi_t, v_L \psi_o)|^2}{(E_1^{(L)} - E_o) \; (E_t - E_o)} \tag{52}$$

where

$$\alpha_2 \overset{u}{L} = \frac{2}{(E_1^{(L)} - E_o)} \left\{ (\psi_o, v_L^2 \psi_o) - (\psi_o, v_L \psi_o)^2 \right\}, \tag{53}$$

$E_1^{(L)}$ being the eigenvalue of the lowest excited state for which $(\psi_1, v_L \psi_o)$ does not vanish. With few exceptions, neither (51) nor (52) provides a useful means of computing α_{2L}, but it is valuable to note that, since $E_1^{(L)} - E_t$ is negative $\alpha_{2L}{}^u$ is an upper bound

$$\alpha_{2L} \leq \alpha_{2L}{}^u \tag{54}$$

2.4 OSCILLATOR STRENGTH FORMULA

Formula (51) may be used to derive accurate values of the dipole polarizabilities for the few atomic systems for which reliable oscillator strengths are available. The electric dipole oscillator strength corresponding to the transition from the state ψ_o to the state ψ_t is defined by

$$f_{ot} = \frac{2}{3} (E_t - E_o) \quad (\psi_t, \sum_i \underset{\sim}{r}_i \psi_o)^2 \tag{55}$$

and in terms of it,

$$\alpha_{ot} = \mathop{S}_{\tilde{t}}{}' \; f_{ot}/(E_t - E_o)^2. \tag{56}$$

Dalgarno and Kingston (1959) have used (56) to predict the polarizabilities of the alkali metals and their results are given in Table 1. The error is unlikely to exceed 10%. Their predictions disagree with early measurements but have been confirmed by the recent experiments of Salop, Pollack and Bederson (1961) whose results are also included in Table 1.

The dipole polarizabilities of metastable helium in the 2^1S and 2^3S states (Dalgarno and Kingston 1958) and of the negative hydrogen ion (Bates and Lewis 1955, Geltman 1962, Dalgarno and Ewart 1962) have also been obtained by summing the individual terms of (56) but because of the contribution from transitions to the continuum, the method is rarely convenient. Donath (1962) has essentially used (56) to predict the dipole polarizabilities of F^-, Ne and Na^+, the wave functions of a number of discrete states being determined by variational methods. The results are not encouraging and a direct variational attack on the complete summation is usually to be preferred.

2.5 APPROXIMATE FORMULAE

Approximate evaluations of (51) can be made by replacing $E_t - E_o$ in the denominator by a mean excitation energy $\bar{E}$, yielding

$$\alpha_{2L} \sim \frac{2}{\bar{E}} \left\{ (\psi_o, v_L^2 \psi_o) - (\psi_o, v_L \psi_o)^2 \right\}. \tag{57}$$

A common choice for $\bar{E}$ is the ionization potential of the atom and the resulting formula usually yields values of α_{2L} which are correct to within an order of magnitude.

TABLE 1

DIPOLE POLARIZABILITIES OF THE ALKALI METALS IN UNITS OF 10^{-24} cm^3

	Li	Na	K	Rh	Cs
Formula (56)	24.4 ± 2.4	24.6 ± 2.5	41.6 ± 4.2	43.9 ± 4.4	53.8 ± 5.4
Measured	20 ± 3.0	20 ± 2.5	40 ± 5.0	40 ± 5.0	52.5 ± 6.5

A more interesting choice of $\bar{E}$ is such that

$$\mathop{S'}_{\tilde{t}} (E_t - E_o) \mid (\psi_t, v_L \psi_o) \mid^2 = \bar{E} \mathop{S'}_{\tilde{t}} \mid (\psi_t, v_L \psi_o) \mid^2 \quad (58)$$

(Vinti 1932). We shall demonstrate in §3 that it leads to a lower bound for α_{2L}.

It is apparent from the form of (57) that (56) is valuable for those systems in which

$$(\psi_1, v_L \psi_o)^2 \gg (\psi_2, v_L \psi_o)^2 \gg (\psi_3, v_L \psi_o)^2 \ . \ . \ . \quad (59)$$

(Vinti 1932), as is often the case.

The procedure of replacing $E_t - E_o$ by a mean energy $\bar{E}$ also yields approximate formulae for shielding factors

$$\alpha_2 L \sim \frac{-2}{E} \left\{ (\psi_o, v_L v_L' \psi_o) - (\psi_o, v_L \psi_o) (\psi_o, v_L' \psi_o) \right\} \qquad (60)$$

but they may be very misleading; the condition analogous to (59) is not satisfied, transitions to continuum states being of great importance. This is reflected in variational calculations by the sensitivity of shielding factors to the assumed trial functions.

SECTION III

VARIATIONAL METHODS

3.1 APPROXIMATE FORMULAE

As (32) demonstrates, electric polarizabilities are directly related to the change in energy due to the perturbation and they may be determined therefore by application of the conventional Rayleigh-Ritz variational methods. Many of the early studies proceeded by substituting a trial wave function ψ_t for the perturbed system into the expression for the total energy

$$\mathcal{E} = (\psi_t | H + V | \psi_t) \tag{61}$$

and minimizing, the final expression being expanded in powers of the preturbing potential. It may be shown (Slater and Kirkwood 1932, Dalgarno and Lewis 1956) that provided ψ_o is the exact unperturbed eigenfunction this procedure is equivalent to the simpler one of minimizing the functional

$$\mathcal{E}_2^{(L)} = (\psi_{1_t}^{(L)} | (H - E_o | \psi_{1_t}^{(L)}) + 2 (\psi_{1_t}^{(L)} | v_L - \mathcal{E}_1^{(L)} | \psi_o) \tag{62}$$

with respect to a trial first order perturbed function ${\psi_1}_t^{(L)}$. In practice, ψ_o is not the exact eigenfunction and the former method introduces spurious terms, which if retained may seriously affect the derived polarizability. If they are ignored, the procedure is again equivalent to the use of (62).

The variational trial wave function

$$ {\psi_1}_t^{(L)}\ (\underset{\sim}{r}) = \left\{ v_L - \mathcal{E}_1^{(L)} \right\} \psi_o(\underset{\sim}{r}) \tag{63} $$

if of special interest. Writing

$$ \bar{v}_L = v_L - \mathcal{E}_1^{(L)} , \tag{64} $$

it follows that

$$ \lambda_L = \frac{-(\psi_o,\ \bar{v}_L^{\,2}\ \psi_o)}{(v_L\ \psi_o | H - E_o |\ v_L\ \psi_o)} \tag{65} $$

and

$$ \mathcal{E}_2^{(L)} = \frac{-(\psi_o,\ \bar{v}_L^{\,2}\ \psi_o)^2}{(v_L\ \psi_o | H - E_o |\ v_L\ \psi_o)} \quad . \tag{66} $$

Thus

$$ \alpha^{\ell}_{2L} = \frac{2(\psi_o,\ v_L^{\,2}\ \psi_o)^2}{(v_L\ \psi_o | H - E_o |\ v_L\ \psi_o)} \tag{67} $$

is a lower bound for α_{2L}.

It is a simple matter to show that the denominator of (68) is equal to the infinite summation (59)

$$\underset{\tilde{t}}{S'} (E_t - E_o)|(\psi_t, v_L \psi_o)|^2 = (v_L \psi_o |H - E_o| v_L \psi_o) \qquad (68)$$

(Vinti 1932, Dalgarno and Lewis 1957), thereby proving that the choice of $\ddot{E}$ described by (59) leads to a lower bound.

The denominator of (68) can be written in the simple form

$$(v_L \psi_o|H - E_o|v_L \psi_o) = - (v_L \psi_o, \sum_{i=1}^{N} \nabla_i v_L \cdot \nabla_i \psi_o). \qquad (69)$$

For L = 1, integration by parts shows that

$$(v_1 \psi_o|H - E_o|v_1 \psi_o) = \frac{1}{2} N \qquad (70)$$

(this being the Thomas-Kuhn oscillator strength sum rule when taken with (68)), so that

$$\alpha_d \geq \frac{4 (\psi_{o_1} , v_1^2 \psi)^2}{N} \qquad (71)$$

(Kirkwood 1931, Vinti 1932). For heavy atoms, the lower bound given by (71) is very much less than the actual value and a better indication is of the possible magnitude of α_d is provided by replacing N by the number of electrons in the outmost shell.

For most atomic system in states of zero orbital angular momentum (but not all),

$$(\psi_o, \sum_{i \neq j} \sum \underset{\sim}{r}_i \cdot \underset{\sim}{r}_j \; \psi_o) < 0 \qquad (72)$$

and (70) can be replaced by the expression

$$\alpha_d \geq \frac{4}{9N} \; (\psi_o, \sum_{i=1}^{N} r_i^2 \; \psi_o)^2 \; . \qquad (73)$$

The diamagnetic susceptibility of a gas is

$$X = - \frac{e^2 L \, a_o^2}{6 \; mc^2} \; (\psi_o, \sum_{i=1}^{N} r_i^2 \; \psi_o) \qquad (74)$$

where L is Loschmidt s number (c.f. Van Vleck, 1932) and Kirkwood (1931) proposed the semi-empirical formula

$$X = \frac{Le^2 \; a_o^{1/2}}{4 \; mc^2} \; (N \, \alpha)^{1/2}, \qquad (75)$$

later modified by Vinti (1932) to take account of the $\underset{\sim}{r}_i \cdot \underset{\sim}{r}_j$ terms and by Buckingham (1937) to give more precise significance to the value of N. The formula is surprisingly successful (Brindley 1933, Buckingham 1937).

Simple formulae can also be derived for higher order polarizabilities. Thus for atoms in S states,

$$\mathop{\underset{\sim}{S}'}\limits_{t} (E_t - E_o)|\ (\psi_t,\ v_2\ \psi_o)|^2 = \frac{8}{3}\ (\psi_o,\ \sum_{i=1}^{N}\ r_i^{\ 2}\ \psi_o) \tag{76}$$

(Dalgarno and Lewis 1957) so that

$$\alpha_q \geq \frac{3(\psi_o,\ v_2^{\ 2}\ \psi_o)}{4(\psi_o,\ \sum_{i=1}^{N}\ r_i^{\ 2}\ \psi_o)} \tag{77}$$

Dalgarno and Lewis (see also Stewart 1961) have suggested several formulae for estimating the order of magnitude of α_q, which are based on (77). They suggest, in particular,

$$\alpha_q \sim \frac{d\ (E_1^{\ (1)} - E_o}{2(E_1^{\ (2)} - E_o)^2} \tag{78}$$

which has the merit that it does not require a knowledge of any wave functions.

The reliability of these various approximate formulae depends upon the degree with which condition (59) is satisfied and there is little value in carrying through a similar development for shielding factors.

An interesting generalization of (63) has been proposed by Pople and Schofield (1957). They use as trial function for the calculation of dipole polarizabilities

$$\psi_{1_t}^{(L)} = \psi_o\,(\underset{\sim}{r}) \sum_{i=1}^{N} f(r_i)\cos\theta_i \qquad (79)$$

where $f(r_i)$ is allowed to vary arbitrarily. They show that if $\psi_o(\underset{\sim}{r})$ is represented by the Hartree-Fock approximation the optimum form of $f(r_i)$ is the solution of a simple differential equation which may be integrated numerically. The computation involved is less than that of the Sternheimer procedure (Para. 4.4) and the method does not encounter any difficulties arising from exchange effects, (79) being a properly antisymmetrized function. For argon, Pople and Schofield obtain a dipole polarizability of $2.03\overset{o}{A}^3$ compared to $2.40\overset{o}{A}^3$ given by the Sternheimer procedure (Kaneko 1959) and to $1.64\overset{o}{A}^3$ given by extrapolation of refractive index data (Dalgarno and Kingston 1960). Because of its simplicity, the method merits further application though it is less accurate than the uncoupled and coupled Hartree-Fock approximations (Para. 4).

3.2 TWO-ELECTRON SYSTEMS

More complex trial wave functions have been used for the two-electron systems H^-, He and Li^+. It is clear from the work of Hasse' (1930, 1931) and of Barber and Hasse' (1937) that α_d is sensitive to the adopted representation of the unperturbed wave function ψ_o but that provided the form of the trial perturbed wave function $\psi_1^{(1)}$ is carefully chosen, convergence of α_d is obtained with a small number of parameters. Using the six-parameter representation of ψ_o due to Hylleraas (1929) and the trial wave function

$$\psi_1^{(1)}\ (\underset{\sim}{r}_1,\ \underset{\sim}{r}_2) = \left\{ (ar_1 + br_1^{\ 2} + cr_1^{\ 3}) \cos\theta_1 + (ar_2 + br_2^{\ 2} + cr_2^{\ 3}) \cos\theta_2 \right\} \psi_o, \qquad (80)$$

Baber and Hasse' obtained (0.2045 ± 0.0005) x 10^{-24} cm^3 for the dipole polarizability of helium. More recently Schwartz (1961) has used an 18-parameter representation of ψ_o and a much more flexible trial function $\psi_1^{(1)}$ and he computes a value of (0.2050 ± 0.0001) x 10^{-24} cm^3. This value does not agree with the most recent directly measured value of (0.2068 ± 0.0002) x 10^{-24} cm^3 (Johnson, Oudemans and Cole 1960) but it is in harmony with the value of 0.2051 x 10^{-24} cm^3 obtained by Dalgarno and Kingston (1960) from a careful extrapolation of refractive index data.

A different type of trial function has been investigated for helium by Abbott and Bolton (1954), which is essentially a sum of excited ^1P state wave functions. This choice must share some of the convergence difficulties associated with the evaluation of (56) and compares unfavorably with (80).

Baber and Hasse' (1937) have also obtained a value of 0.02862 x 10^{-24} cm^3 for the dipole polarizability of Li$^+$ which is again based on the 6-parameter representation ψ_o and a trial function (80). The value obtained from an analysis of the spectral term defects (Mayer and Mayer 1933, Sternheimer 1954) is 0.0235 x 10^{-24} cm^3 but the variationally determined value is undoubtedly the more accurate.

Schwartz (1961) has also calculated the dipole polarizability of H$^-$ using wave functions similar to those he adopted for helium. He finds that α_d = 31.4 x 10^{-24} cm^{3*} which agrees well with that obtained, α_d = 30.2 x 10^{-24} cm^3 (Geltman 1962, Dalgarno and Ewart 1962) by evaluating (56) from the photo-detachment cross sections computed by Geltman (1962).

The only refined calculation of a quadrupole polarizability and a quadrupole shielding factor appears to be that of Dalgarno, Davison and Stewart (1960). They employ the Hylleraas representation of ψ_o for helium and a trial function similar to (80) but with an additional parameter and obtain α_q = 0.0942 x 10^{-40} cm^3 and γ_∞ = 0.397. As they demonstrate, α_q is rather sensitive to the adopted form of ψ_o and it is probable that their value is too small, the uncertainty being about 5%. The value of γ_∞ is probably accurate to within an error of 2%.

Detailed variational calculations of the type applied to two-electron systems are scarcely feasible for more complex systems and for them it is natural to seek an extension of the Hartree-Fock scheme for unperturbed atoms.

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*The value published by Schwartz is 26.8 x 10^{-24} cm^3. I am informed by Dr. L. M. Branscomb that this value is incorrect and that Schwart's calculations actually yield the value quoted in the text.

SECTION 4

THE HARTREE-FOCK APPROXIMATION

An extension of the Hartree-Fock approximation scheme to the determination of polarizabilities and shielding factors has been carried out by Dalgarno (1959), Kaneko (1959), and Allen (1960). The essential features are contained in earlier discussions by Peng (1941) and by Temkin (1957). Because of its close connection with earlier work, we begin with a description of the Hartree approximation in which electron exchange effects are ignored.

4.1 THE HARTREE APPROXIMATION

In the Hartree approximation, it is assumed that the unperturbed functions may be written in the form

$$\psi_o(\underset{\sim}{r}) = \prod_{i=1}^{N} u_i^{(o)} (\underset{\sim}{r}_i) \tag{81}$$

where the orbitals $u_i^{(o)} (\underset{\sim}{r}_i)$ are eigenfunctions of the equations

$$H_i u_i^{(o)} (\underset{\sim}{r}_i) = \left(-1/2 \, \nabla_i^2 + V_i(r_i) \right) u_i^{(o)} (\underset{\sim}{r}_i) = \epsilon_i u_i^{(o)} (\underset{\sim}{r}_i), \tag{82}$$

the self-consistent potential $V_i(r_1)$ being defined by

$$V_i(r_i) = -\frac{Z}{r_i} + \sum_{k\neq i} \int \frac{|u_k^{(o)}(\underset{\sim}{r}_k)|^2}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|} d\underset{\sim}{r}_k \tag{83}$$

and the summation being over the occupied orbitals.

The orbitals $u_i^{(o)}(\underset{\sim}{r}_i)$ are written as the product

$$u_i^{(o)}(\underset{\sim}{r}_i) = \frac{P_o(r_i\ \ell_i|r_i)}{r_i} Y_{\ell_i m_i}(\theta_i,\phi_i) \tag{84}$$

where n_i, ℓ_i and m_i are respectively the principal, azimuthal and magnetic quantum numbers specifying the orbital, $P_o(n_i\ell_i|r_i)$ is the radial wave function normalized so that

$$\int_o^\infty P_o(n_i\ell_i|r_i)\, P_o(n_i'\ \ell_i|r_i)\, dr = \delta n_i n_i' \tag{85}$$

and $Y_{\ell_i m_i}(\theta_i,\phi_i)$ is the spherical harmonic of order ℓ_i. Then (82) reduces to

$$\left(-1/2\frac{d^2}{dr^2} + V_i(r_i) + \frac{\ell_i(\ell_i+1)}{2r_i^2} - \epsilon_i^{(o)}\right) P_o(n_i\ell_i|r_i) = 0 \tag{86}$$

The total unperturbed function $\psi_o(\underset{\sim}{r})$ is a solution of

$$(H' - E_o')\,\psi\,(\underset{\sim}{r}) = 0 \tag{87}$$

where

$$H' = \sum_{i=1}^{N} H_i - \sum\sum_{i<k} \iint \frac{|u_i^{(o)}(\underset{\sim}{r}_i)|^2\,|u_k^{(o)}(\underset{\sim}{r}_k)|^2}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|}\, d\underset{\sim}{r}_i\; d\underset{\sim}{r}_k \tag{88}$$

and

$$E_o' = \sum_{i=1}^{N} \epsilon_i^{(o)} - \sum\sum_{i<k} \iint \frac{|u_i^{(o)}(\underset{\sim}{r}_i)|^2\,|u_k^{(o)}(\underset{\sim}{r}_k)|^2}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|}\, d\underset{\sim}{r}_i\; d\underset{\sim}{r}_k . \tag{89}$$

The first order perturbed wave function is written in the form

$$\psi_1(\underset{\sim}{r}) = \sum_{i=1}^{N} \frac{u_i^{(1)}(\underset{\sim}{r}_i)}{u_i^{(o)}(\underset{\sim}{r}_i)}\;\psi_o(\underset{\sim}{r}) \tag{90}$$

where we have suppressed the superscript L. Corresponding to (90), the electric multipole polarizability is given by

$$\alpha_{2L} = 2 \sum_{i=1}^{N} \left(u_i^{(1)},\ r_i^L P_L (\cos \theta_i)\ u_i^{(o)} \right) \tag{91}$$

and the multipole shielding factor is given by

$$\gamma_{2L} = 2 \sum_{i=1}^{N} \left(u_i^{(1)},\ \frac{P_L(\cos \theta_i)}{r_i^{L+1}}\ u_i^{(o)} \right) . \tag{92}$$

The procedure of Pople and Schofield (1957) is equivalent to (90) with the restriction that $u_i^{(1)}/u_i^{(o)}$ be independent of the electron shell.

4.2 THE UNCOUPLED HARTREE APPROXIMATION

There are two procedures for specifying the perturbed orbitals $u_i^{(1)}$ $(\underset{\sim}{r}_i)$ (Dalgarno, 1959). In the simpler procedure, the radial parts of $u_i^{(o)}$ and $u_i^{(1)}$ are allowed to undergo independent but otherwise arbitrary variations. This is equivalent to the assumption that

$$(H' - E_o')\ \ \psi_1(\underset{\sim}{r}) + \overline{v}_L\ \ \psi_o(\underset{\sim}{r}) = 0. \tag{93}$$

Substituting (90), it follows that

$$(H_i - \epsilon_i^{(o)})\ u_i^{(1)}\ (\underset{\sim}{r}_i) + \overline{v_L(\underset{\sim}{r}_i)}\ \ u_i^{(o)}(\underset{\sim}{r}_i) = 0 \tag{94}$$

where

$$\overline{v_L(\underset{\sim}{r}_i)} = r_i{}^L P_L \; (\cos\theta_1) - \left(u_i{}^{(o)}, \; r_i{}^L P_L \; (\cos\theta_i) \; u_i{}^{(o)} \right), \quad (95)$$

it being convenient to require that

$$\left(u_i{}^{(1)}, \; u_i{}^{(o)} \right) = 0 \quad (96)$$

4.2.1. Expressions for α_{2L} and γ_{2L}. Foley, Sternheimer and Tycko (1954) pointed out that (94) can be reduced to a finite set of uncoupled radial equations. Thus, generalizing their procedures, we express the inhomogeneous angular part of (94) as the finite sum

$$P_1(\cos\theta_i) Y_{\ell_i m_i} \; (\theta_i, \; \phi_i) = \sum_{\ell_i{}'} \left(\frac{2\;\ell_i + 1}{2\;\ell_i{}' + 1} \right)^{1/2} C(L\ell_i\ell_i{}'; \; Om_i)$$

$$C(L\ell_i\ell_i{}';oo) \; Y_{\ell_i{}' \; m_i} \; (\theta_i, \; \phi_i) \quad (97)$$

where $C(\ell_1\ell_2\ell;m_1m_2)$ is the Clebsch-Gordon coefficient in the notation of Rose (1957). Accordingly, we may write

$$u_i{}^{(1)} \; (\underset{\sim}{r}_i) = \sum_{\ell'} \left(\frac{2\ell_i + 1}{2\ell_i{}' + 1} \right)^{1/2} C(L\ell_i\ell_i{}'; \; Om_i) \; C(L\ell_i\ell_i{}';oo)$$

$$\times \; Y_{\ell_i', m_i}(\theta_i, \phi_i) \frac{P_1(n_i\ell_i;\ell_i'|r}{r} \tag{98}$$

and (94) becomes

$$\left\{- 1/2 \frac{d^2}{dr^2} + V_i(r_i) + \frac{\ell_i(\ell_i' + 1)}{2r^2} - {}_i^{(o)}\right\} P_1(n_i\ell_i;\ell_i'|r$$

$$+ \left\{r^L - \delta_{\ell_i\ell} \int_o^\infty P_o(n_i\ell_i|r)\, r^L\, P_o(n_i\ell_i|r)dr\right\} P_o(n_i\ell_i|r) = 0 \tag{99}$$

for all values of ℓ_i' included in the sum (97). In solving (99), care must be taken to insure that $\int_o P_1(n_i\ell_i|r)\, P_o(n_i\ell_i|r)dr = 0.$ (100)

The multipole polarizabilities become

$$\alpha_{2L} = 2 \sum_{n_i\ell} \sum_{\ell_i'} \left(\frac{2\ell_i + 1}{2\ell_i' + 1}\right) C(L\ell_i\ell_i';oo)^2 \times I_L(n_i\ell_i;\ell_i')$$

$$\sum_{m_i} C(L\ell i_\ell i';\, om_i)^2 \tag{101}$$

where

$$I_L(n_i\ell_i;\ell_i') = \int_o^\infty P_1(n_i\ell_i;\ell_i'|r)\; r^L\; P_o(n_i\ell_i|r)dr \qquad (102)$$

and the summation is over the occupied orbitals. Averaging over all orientations of the undisturbed atomic system, (101) simplifies to

$$\alpha_{2L} = 2 \sum_{n_i\ell_i} \sum_{\ell_i'} \frac{a(n_i\ell_i)}{(2L+1)}\; C(L\ell_i\ell_i';oo)^2\; I_L(n_i\ell_i;\ell_i') \qquad (103)$$

where $a(n_i\ell_i)$ is the number of electrons in the $(n_i\ell_i)$ shell. The parity C-coefficient $C(L\ell_i\ell_i';oo)$ vanishes unless ℓ_i' lies between $L + \ell_i$ and $|L - \ell_i|$ and unless $L + \ell_i + \ell_i'$ is even. Its value is

$$C(L\ell_i\ell_i';oo) = (-1)^{1/2}\,(L + \ell_i - \ell_i') \left(\frac{2\ell_i' + 1}{L + \ell_i + \ell_i' + 1}\right)^{1/2}$$

$$\times \quad \frac{\tau(L + \ell_i + \ell_i')}{(L + \ell_i - \ell_i')\;\tau\,(L - \ell_i + \ell_i')\;\tau\,(-L + \ell_i + \ell_i')} \qquad (104)$$

where

$$\tau(x) = (1/2x)\,!\ \ /\ \ \sqrt{x}\,! \qquad (105)$$

(Racah 1942).

Straightforward evaluation of (104) yields for closed shell systems, the dipole polarizability formula

$$\alpha_d = \frac{4}{3} \sum_{n\ell} \left\{ (\ell + 1)\ I_1(n\ell;\ell + 1) + \ell I_1(n\ell;\ell - 1) \right\} \tag{106}$$

the quadrupole polarizability formula

$$\alpha_q = \frac{6}{5} \sum_{n\ell} \left\{ \frac{(\ell + 1)\ (\ell + 2)}{(2\ell + 3)}\ I_2(n\ell;\ell + 2) + \frac{2\ell(\ell + 1)\ (2\ell + 1)}{3(2\ell - 1)\ (2\ell + 3)} \right.$$

$$\left. I_2(n\ell;\ell) + \frac{(\ell - 1)\ell}{(2\ell - 1)}\ I_2(n\ell;\ell - 2) \right\}, \tag{107}$$

the octupole polarizability formula

$$\alpha_8 = \frac{7}{10} \underset{n\ell}{\quad} \left\{ \frac{(\ell + 1)\ (\ell + 2)\ (\ell + 3)}{(2\ell + 3)\ (2\ell + 5)}\ I_3(n\ell;\ell + 3) + \frac{3\ell(\ell + 1)\ (\ell + 2)}{5(2\ell - 1)\ (2\ell + 5)} \right.$$

$$I_3\ (n\ell;\ell + 1) + \frac{3}{5}\ \frac{(\ell - 1)\ \ell(\ell + 1)}{(2\ell - 3)\ (2\ell + 3)}\ I_3(n\ell;\ell - 1) + \frac{(\ell - 2)\ (\ell - 1)}{(2\ell - 3)\ (2\ell - 1)}$$

$$\left. I_3(n\ell;\ell - 3) \right\}. \tag{108}$$

and the hexadecapole polarizability formula

$$\alpha_{12} = \frac{35}{18} \sum_{n\ell} \left\{ \frac{(\ell+1)(\ell+2)(\ell+3)(\ell+4)}{(2\ell+3)(2\ell+5)(2\ell+7)} I_4(n\ell;\ell+4) \right.$$

$$+ \frac{4}{7} \frac{\ell(\ell+1)(\ell+2)(\ell+3)}{(2\ell-1)(2\ell+3)(2\ell+7)} I_4(n\ell;\ell+2)$$

$$+ \frac{18}{35} \frac{(\ell-1)\ell(\ell+1)(\ell+2)(2\ell+1)}{(2\ell-3)(2\ell-1)(2\ell+3)(2\ell+5)} I_4(n\ell;\ell)$$

$$+ \frac{4}{7} \frac{(\ell-2)(\ell-1)\ell(\ell+1)}{(2\ell-5)(2\ell-1)(2\ell+3)} I_4(n\ell;\ell-2)$$

$$\left. + \frac{(\ell-3)(\ell-2)(\ell-1)}{(2\ell-5)(2\ell-3)(2\ell-1)} I_4(n\ell;\ell-4) \right\} . \tag{109}$$

Some of the terms of (106), (107), and (109) for small values of ℓ have been derived previously by Foley, Sternheimer and Tycko (1954) and Sternheimer (1954, 1961).

The multipole shielding factors are given by expressions identical to (101) - (109) except that $I(n\ell;\ell')$ is replaced by

$$J(n\ell;\ell') = \int_0^\infty P_1'(n\ell;\ell'|r) \frac{1}{r^{L+1}} P_o(n\ell|r)dr. \tag{110}$$

Alternatively, $I(n\ell;\ell')$ may be replaced by

$$J'(n\ell;\ell') = \int_0^\infty P_1'(n\ell;\ell'|r) r^L P_o(n\ell|r) dr \tag{111}$$

where $P_1'(n\ell;\ell'|r)$ is the solution of

$$\left\{- 1/2 \frac{d^2}{dr^2} + V_i(r) + \frac{\ell'(\ell' + 1)}{r^2} - \epsilon_i^{(o)}\right\} P_1'(n\ell;\ell'|r)$$

$$+\left\{\frac{1}{r^{L+1}} - \delta_{\ell\ell'} \int_0^\infty P_o(n\ell|r) \frac{1}{r^{L+1}} P_o(n\ell|r)\, dr\right\}$$

$$P_o(n\ell|r) = 0. \tag{112}$$

<u>4.2.2. Solution of First Order Equation.</u> Equation (99) may be solved by direct numerical integration and Sternheimer (1954, 1957) has described in detail a suitable computational procedure. He points out that the labor involved in a direct evaluation of $V_i(\underset{\sim}{r}_i)$ can be avoided by using the relationship

$$V_i(\underset{\sim}{r}_i) - \epsilon_i^{(o)} = 1/2 \left\{\frac{1}{P(n_i\ell_i|r_i)} \frac{d^2P(n_i\ell_i|r_i)}{dr_i^2} - \frac{\ell_i(\ell_i + 1)}{r_i^2}\right\}. \tag{113}$$

The method of numerical integration usually involves several iterations and is tedious to apply.

Equation (99) may also be solved by variational methods. It is instructive to return to Equation (94) and to construct the functional

$$\epsilon_i^{(2)} = \left(u_i^{(1)} \mid H_i - \epsilon_i^{(o)} \mid u_i^{(1)} \right) + 2 \left(u_i^{(1)} \mid \overline{v_L(\underset{\sim}{r}_i)} \mid u_i^{(o)} \right) . \tag{114}$$

Minimizing $\epsilon_i^{(2)}$ with respect to the trial function

$$u_i^{(1)} \; (\underset{\sim}{r}_i) = \lambda \, \overline{v_1(\underset{\sim}{r}_i)} \;\; u_i^{(o)} \; (\underset{\sim}{r}_i) \tag{115}$$

leads to the dipole polarizability formula

$$\alpha_d = \frac{4}{9} \sum_{n=1}^{N} \left(u_i^{(o)}, \; r_i^{\,2} \, u_i^{(o)} \right)^2 \tag{116}$$

which was derived by Hellman (1935) and by Buckingham (1937) by superficially different methods. Several of the other more complicated formulae derived by Buckingham (1937) and by Bravin (1953, 1954) also follow directly from (114) using the more flexible trial functions

$$u_i^{(1)} \; (\underset{\sim}{r}_i) = (a + br_i + cr_i^{\,2}) \; v_1(\underset{\sim}{r}_i) \; u_i^{(o)}(\underset{\sim}{r}_i) \tag{117}$$

It is clear from (98) that, except when $\ell = 0$, (117) has the wrong angular dependence.

The simplest trial orbital with the correct angular dependence is given by (98) with

$$P_1(n_i\ell_i;\ell_i'|r) = \lambda(n_i\ell_i;\ell_i') \, r \, P_o(n_i\ell_i|r), \tag{118}$$

but it leads to negative polarizabilities (except when $\ell = 0$). With more complicated trial wave functions, it is possible to obtain solutions of (94) of comparable accuracy to those obtained from numerical integration and with less labor. It has been common practice in recent years to select trial functions of the form

$$P_1(n_i\ell_i;\ell_i'|r) = \sum_s a^s r^s P_o(n_i\ell_i|r), \tag{119}$$

a choice which has the advantage that by using (84) the potential $V_i(r)$ can be removed from the calculation. It has the disadvantage that it forces nodes into $P_1(n_i\ell_i;\ell_i|r)$ which should not occur (Sternheimer 1959). The effect on the derived polarizabilities is usually not serious, partly because the polarizabilities are determined by the distortion at large distances from the nucleus, but many of the variationally determined shielding factors are of uncertain accuracy.

4.2.3. The Helium Isoelectronic Sequence.

The only systems to which the Hartree approximation may properly be applied are those comprising the helium isoelectronic sequence. The dipole and quadrupole polarizabilities and shielding factors have been obtained by numerical integration of (99) (Sternheimer 1957, 1959) and by variational methods using (117) (Das and Bersohn 1956, Wikner and Das 1957). There are small discrepancies between the two sets of values which can be attributed to the different representations employed for the unperturbed orbitals. The results are given in Table 2 which includes also the most accurate estimates available of the various quantities.

With the notable exception of H^-, the accuracy of the uncoupled approximation is good. It improves rapidly with increasing nuclear charge and it is better for polarizabilities than for shielding factors, suggesting that the approximation provides a more accurate description of the distortion in the electron density in regions far from the nucleus than in regions near to the nucleus.

For more complex systems, the influence of exchange effects requires consideration.

4.3 EXCHANGE EFFECTS

Buckingham (1937) found that (116) yielded dipole polarizabilities in better agreement with experiment if the unperturbed Hartree wave functions were replaced by the unperturbed Hartree-Fock wave functions and following Sternheimer (1954) it has been common practice to similarly modify the uncoupled Hartree approximation. Thus, in (99) and in (113),

TABLE 2

DIPOLE AND QUADRUPOLE POLARIZABILITIES AND SHIELDING FACTORS OF THE HELIUM ISOELECTRONIC SEQUENCE

	$\alpha_d(10^{-24}\ \text{cm}^3)$			$\alpha_q(10^{-40}\ \text{cm}^5)$		
	Uncoupled Approximation	Coupled Approximation	Accurate	Uncoupled Approximation	Coupled Approximation	Accurate
H^-	13.4	~11.8	31.4	66.5	-	-
He	0.220	0.196	0.205	0.0979	0.0965	
Li^+	0.0304	0.0281	0.0286	0.00472	0.00464	-
Be^{++}	0.00820	-	-	0.000637	-	-
		β_∞			γ_∞	
H^-	3.25	2.00	2.00	-	-	-
He	1.23	1.00	1.00	0.417	0.388	0.397
Li^+	0.763	0.667	0.667	0.257	0.248	-
Be^{++}	0.569	0.500	0.500	0.185	-	-

$P_o(n_i \ell_i | r)$ is taken to be the appropriate Hartree-Fock orbital. Dalgarno and Parkinson (1959) have made the further modification of forming antisymmetrical combinations of the product type solutions (81) and (90) and using them to calculate the polarizabilities. It is of interest to note that the application of this procedure to (114) with the variational solution (115) yields for the dipole polarizability

$$\alpha_d = \frac{4}{9} \sum_{i=1}^{N} (u_i^{(o)}, r^2 u_i^{(o)}) \left\{ (u_i^{(o)}, r^2 u_i^{(o)}) - \sum_{j \neq i} |(u_i^{(o)}, \underset{\sim}{r} u_j^{(o)}|^2 \right\}, \tag{120}$$

a formula given by Hellman (1935), and application of it to the variational solution (115) and the functional (114) yields

$$\alpha_d = \frac{4}{9} \sum_{i=1}^{N} \left\{ (u_i^{(o)}, r_i^2 u_i^{(o)}) - \sum_{j \neq i} | (u_i^{(o)}, \underset{\sim}{r}_i u_j^{(o)}|^2 \right\}^2 , \tag{121}$$

a formula given by Buckingham (1937).

We shall derive the correct version of (120) and (121) in Para. 4.5. They differ because of the inconsistency involved in using a Hartree-Fock orbital in an equation derived from the Hartree approximation scheme. This inconsistency is also reflected by the occurrence of infinities in the potential derived from (113), wherever the Hartree-Fock orbital $P_o(n_i \ell_i \,|r)$ has a node. In variational calculations, the difficulties presented by these unwanted singularities are suppressed by choosing trial wave functions of the form (119).

In calculations using numerical integration, they are presumably treated by smoothing $V_i\ (r_i)$ through the singularities (Dalgarno and Parkinson 1959). The presence of the singularities introduces some arbitrariness into the derived values of polarizabilities and shielding factors.

4.4 THE STERNHEIMER PROCEDURE

An instructive analysis of the Sternheimer procedure is obtained by formally solving (94) as an expansion in terms of the eigenfunctions of (82), which we label more explicitly by the principal and azimuthal quantum numbers $u_i = u\ (n\ell)$ (Sternheimer 1954). Then as in the derivation of (52), we obtain

$$\alpha_{2L} = \sum_{n\ell} \alpha_{2L}\ (n\ell) \tag{122}$$

where

$$\alpha_{2L}\ (n\ell) = -2 \underset{n'\ell'\neq n\ell}{\underset{\sim}{S}} \frac{\left|\left(u\ (n'\ell'),\ \overline{v_L}\ u(n\ell)\right)\right|^2}{\epsilon^{(o)}\ (n'\ell') - \epsilon^{(o)}\ (n\ell)} \tag{123}$$

and

$$\gamma_{2L} = \sum_{n\ell} \gamma_{2L} (n\ell) \tag{124}$$

where

$$\gamma_{2L} (n\ell) = -2 \mathop{S}_{n'\ell' \neq n\ell} \frac{\Big(u(n'\ell'), \overline{v_L}\, u(n\ell)\Big) \Big(u(n'\ell'), v_L{}'\, u(n\ell)\Big)}{\epsilon^{(o)}_{(n'\ell')} - \epsilon^{(o)}_{(n\ell)}} \tag{125}$$

where the $(n\ell)$ summation is over the occupied orbitals and the $(n'\ell')$ summation is over all possible orbitals and includes an integration over the continuum.

It is apparent from the form of (123) or (125) that in the evaluation of (106) - (109) the contribution to the polarizability or the shielding factor from a particular electron shell may be positive or negative but that in summing over all shells there will occur a nearly complete cancellation of contributions from transitions between occupied orbitals. The cancellation is not quite complete because $V_i (r_i)$ differs for different electron shells and $u(n\ell)$ are not members of the same complete set. The Hartree approximation, with or without Sternheimer's modification, gives rise to spurious contributions from transitions between occupied orbitals.

Because of the energy denominators in (129) and (131) it is to be expected that upward transitions from the outermost shells will provide the major contributions to the polarizabilities and shielding factors and this has been confirmed by explicit calculations (cf. Sternheimer 1954, 1957, Wikner and Das 1956).

The summations over ℓ' in (123) or (125) can be written out explicitly as in (103). Thus

$$\alpha_d\ (n\ell) = -2 \underset{\tilde{n}'}{S}{}' \ \frac{\left|\left(u^{(o)}\ (n'\ell \pm 1),\ \bar{v}_1\ u^{(o)}\ (n\ell)\right)\right|^2}{\epsilon^{(o)}\ (n'\ell \pm 1) - \epsilon^{(o)}\ (n\ell)}$$

$$= \alpha_d\ (n\ell - \ell + 1) + \alpha_d\ (n\ell - \ell - 1),\ \text{say} \qquad (126)$$

or

$$\gamma_\infty\ (n\ell) = -2 \underset{\tilde{n}'}{S} \frac{\left(u^{(o)}\ (n\ell)\ \bar{v}_2\ u^{(o)}\ (n'\ell \pm 2)\right)\left(u^{(o)}(n'\ell \pm 2),\ \bar{v}_2{}'\ u^{(o)}(n\ell)\right)}{\epsilon^{(o)}\ (n'\ell \pm 2)\ -\ \epsilon^{(o)}\ (n\ell)}$$

$$-2 \underset{\tilde{n}}{S} \frac{\left(u^{(o)}\ (n\ell),\ \bar{v}_2\ u^{(o)}\ (n'\ell)\right)\left(u^{(o)}\ (n'\ell),\ \bar{v}_2{}'\ u^{(o)}(n\ell)\right)}{\epsilon^{(o)}\ (n'\ell)\ -\ \epsilon^{(o)}\ (n\ell)} \qquad (127)$$

$$= \gamma_\infty\ (n\ell - \ell + 2) + \gamma_\infty(n\ell - \ell) + \gamma_\infty\ (n\ell - \ell - 2),\ \text{say}$$

As an illustration of the cancellation of contributions from transitions between occupied orbits, Sternheimer (1959) finds that for Na^+, $\alpha_d(2s - p) = 0.117\,\mathrm{\AA}^3$ and $\alpha_d(2p - s) = -0.098\,\mathrm{\AA}^3$, the largest contribution to $\alpha_d(2s - p)$ and $\alpha_d(2p - s)$ arising from the 2s - 2p transition. The most important contribution to α_d is $\alpha_d(2p - d) = 0.133\,\mathrm{\AA}^3$ giving a net polarizability of $0.152\,\mathrm{\AA}^3$.

For polarizabilities, transitions involving an increase in the azimuthal quantum number are usually the most important, especially for heavy ions with closed shell configurations. For Cs^+ (Sternheimer 1959), $\alpha_q(5p - f) = 5.21\,\mathrm{\AA}^5$ and $\alpha_q(5p - p) = 1.70\,\mathrm{\AA}^5$. For shielding factors, transitions involving no change in the azimuthal quantum number are usually much more important. For the quadrupole shielding factor of Na^+, Sternheimer (1959) obtains 0.30 for $\gamma_\infty(2p - f)$ and -5.16 for $\gamma_\infty(2p - p)$ while for K^+, he obtains -17.15 for $\gamma_\infty(3p - p)$, -1.22 for $\gamma_\infty(2p - p)$ and 1.05 for the sum of the remaining terms all of which involve a change in ℓ.

For moderate and heavy ions then, the major contribution to γ_∞ comes from the radial modes of excitation $\gamma_\infty(n\ell - \ell)$, the contribution from the angular modes $\gamma_\infty(n\ell - \ell \pm 2)$ being comparatively small. The radial modes produce a negative shielding factor and so give rise to antishielding. A similar behavior occurs for hexadecapole moments (Sternheimer 1961).

There is a real physical distinction between radial and angular modes of excitation which can be understood by considering a non-spherical nucleus placed at the center of a spherical shell of electric charge (cf. Kopfermann 1958). There will occur an angular redistribution which will concentrate the charge in the regions closest to the nuclear charge, screening the nuclear multipole moments and leading to a reduction in the total coupling. There will also occur a radial redistribution, the shell being distorted inwards by the electrostatic interaction between the positive nucleus and the negative electric charge. This radial redistribution gives an apparent increase in the nuclear coupling and is antishielding.

4.5 THE UNCOUPLED HARTREE-FOCK APPROXIMATION

The unphysical transitions between occupied orbitals can be excluded and the inconsistencies of the Sternheimer procedure can be removed by using total wave functions which satisfy the Pauli principle. To avoid mathematical complexity, we shall restrict further development to closed shell systems.

The unperturbed wave function is written as

$$\psi_o(\underset{\sim}{r}) = \mathcal{A} \prod_{i=1}^{N} u_i^{(o)} (\underset{\sim}{r}_i) \tag{128}$$

where $\mathcal{A}$ is the normalized antisymmetrizing operator and the unperturbed orbitals $u_i^{(o)}$ satisfy the eigenvalue equations

$$H_i u_i^{(o)}(\underset{\sim}{r}_i) = \epsilon_i^{(o)} \; u_i^{(o)}(\underset{\sim}{r}_i) \tag{129}$$

where

$$H_i u_t(\underset{\sim}{r}_i) = \left(- 1/2 \; \nabla_i^2 - \frac{Z}{r_i} \right) u_t \; (\underset{\sim}{r}_i) + \sum_{k=1}^{N} \int \frac{|u_k^{(o)}(\underset{\sim}{r}_k)|^2}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|}$$

$$d\underset{\sim}{r}_k \; u_t \; (\underset{\sim}{r}_i) \; - \sum_{k=1}^{N}{}_{||} \int \frac{u_k^{(o)}(\underset{\sim}{r}_k) \; u_t \; (\underset{\sim}{r}_k)}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|} \; d\underset{\sim}{r}_k \; u_k^{(o)} \; (\underset{\sim}{r}_i), \tag{130}$$

the second summation being restricted to pairs of orbitals with parallel spins. The total unperturbed wave function $\psi_o(r)$ satisfies the equation

$$(H' - E_o') \;\; \psi_o(r) = 0 \tag{131}$$

where

$$H' = \sum_{l=1}^{N} H_i - \sum_{i<k}\sum \int \frac{|u_i^{(o)}(\underset{\sim}{r}_i)|^2 |u_k^{(o)}(\underset{\sim}{r}_k)|^2}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|} \, d\underset{\sim}{r}_i \, d\underset{\sim}{r}_k$$

$$+ \sum_{i<k}\sum{}_{||} \int \frac{u_i^{(o)}(\underset{\sim}{r}_i) \; u_k^{(o)}(\underset{\sim}{r}_i) \; u_i^{(o)}(\underset{\sim}{r}_k) \; u_k^{(o)}(\underset{\sim}{r}_k)}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|} \, d\underset{\sim}{r}_i \, d\underset{\sim}{r}_k \tag{132}$$

and

$$E_o' = \sum_{i=1}^{N} \epsilon_i^{(o)} - \sum\sum_{i<k} \int \frac{|u_i^{(o)}(\underset{\sim}{r}_i)|^2 |u_k^{(o)}(\underset{\sim}{r}_k)|^2}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|} d\underset{\sim}{r}_i \, d\underset{\sim}{r}_k$$

$$+ \sum\sum_{i<k} \; | \; | \int \frac{u_i^{(o)}(\underset{\sim}{r}_i)\, u_k^{(o)}(\underset{\sim}{r}_i)\, u_i^{(o)}(\underset{\sim}{r}_k)\, u_k^{(o)}(\underset{\sim}{r}_k)}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|} d\underset{\sim}{r}_i \, d\underset{\sim}{r}_k .$$

(133)

Proceeding as for the uncoupled Hartree approximation, we solve

$$(H' - E_o') \; \psi_1 (\underset{\sim}{r}) + \bar{v}_L \; \psi_o (\underset{\sim}{r}) = 0 \qquad (134)$$

by the substitution

$$\psi_1 (\underset{\sim}{r}) = \sum_{i=1}^{N} \mathcal{A} \prod_{i \neq j} u_i^{(o)} (\underset{\sim}{r}_i) \, u_j^{(1)} (\underset{\sim}{r}_j).$$

(135)

Then (Dalgarno 1959)

$$(H_i - \epsilon_i^{(o)}) \, u_i^{(1)} (\underset{\sim}{r}_i) + v_L (\underset{\sim}{r}_i) \, u_i^{(o)} (\underset{\sim}{r}_i)$$

(136)

$$= \sum_{j=1}^{N} \left\{ (\epsilon_j^{(o)} - \epsilon_i^{(o)}) \, (u_i^{(1)}, u_j^{(o)}) + (u_j^{(o)}, \bar{v}_L \, u_i^{(o)}) \right\} u_j^{(o)} (\underset{\sim}{r}_i)$$

and

$$\alpha_{2L} = -2 \sum_{i=1}^{N} \left\{ (u_i^{(o)}, \bar{v}_L (\underset{\sim}{r}_i) u_i^{(1)}) - \sum_{k=1}^{N} {}_{||} (u_k^{(o)}, \bar{v}_L (\underset{\sim}{r}_i) u_i^{(o)}) \right.$$

$$\left. (u_i^{(1)}, u_k^{(o)}) \right\}, \tag{137}$$

$$\gamma_{2L} = -2 \sum_{i=1}^{N} \left\{ (u_i^{(o)}, \bar{v}_{L'} (\underset{\sim}{r}_i) u_i^{(1)}) - \sum_{k=1}^{N} {}_{||} (u_k^{(o)}, \bar{v}_{L'} (\underset{\sim}{r}_i) u_i^{(o)}) \right.$$

$$\left. (u_k^{(1)}, u_k^{(o)}) \right\}. \tag{138}$$

If we now solve (136) formally as an expansion in the set of eigenfunctions of (131), we obtain expressions identical to (123) and (125) except that the $(n'\ell')$ summation now excludes all the occupied orbitals.

The solution can be achieved by methods similar to those employed in deriving the unperturbed orbitals, the substitution (98) again effecting a reduction to sets of radial equations. Alternatively a variational method can be employed based on the functionals

$$\epsilon_i^{(2)} = (u_i^{(1)}|\bar{H}_i - \epsilon_i^{(o)}|u_i^{(o)}) - \sum_{j=1}^{N} (\epsilon_j^{(o)} - \epsilon_i^{(o)})|(u_j^{(o)}, u_i^{(1)})|^2$$

$$+ 2 \left\{(u_i^{(1)}, \bar{v}_L (\underset{\sim}{r}_i) u_i^{(o)}) - \sum_{j=1}^{N} (u_j^{(o)}, \bar{v}_L (\underset{\sim}{r}_i) u_i^{(o)}) (u_i^{(1)}, u_j^{(o)})\right\} . \tag{139}$$

The trial function

$$u_i^{(1)} (\underset{\sim}{r}_i) = \overline{\lambda\, v_1(\underset{\sim}{r}_i)}\; u_i^{(o)} (\underset{\sim}{r}_i) \tag{140}$$

yields the approximate formula for the dipole polarizability

$$\alpha_d = \frac{4}{9} \sum_{i=1}^{N} \frac{\left\{(u_i^{(o)}, r_i^{2} u_i^{(o)}) - \sum_{j\neq i} | (u_i^{(o)}, r_i u_j^{(o)}) |^2 \right\}^2}{D_i} \tag{141}$$

where

$$D_i = 1 - \frac{2}{3} \sum_{j=1}^{N} (\epsilon_j^{(o)} - \epsilon_i^{(o)}) | (u_j^{(o)}, r_i^2 u_i^{(o)}) |^2$$

$$+ \frac{2}{3} \sum_{k=1}^{N} \| \iint \frac{u_i^{(o)} (\underset{\sim}{r}_i) u_k^{(o)}(\underset{\sim}{r}_i) u_i^{(o)}(\underset{\sim}{r}_k) u_k^{(o)}(r_j) \left[\underset{\sim}{r}_i^{2} - \underset{\sim}{r}_i \circ \underset{\sim}{r}_k \right]}{| \underset{\sim}{r}_i - \underset{\sim}{r}_k |} d\underset{\sim}{r}_i \, d\underset{\sim}{r}_k, \tag{142}$$

first derived by Knipp (1939) from arguments based upon perturbation theory. The summation

$$\sum_i D_i = N + \frac{2}{3} \sum_{i=1}^{N} \sum_{k=1}^{N} {}_{||} \iint \frac{u_i^{(o)}(\underset{\sim}{r}_i) u_k^{(o)}(\underset{\sim}{r}_i) u_i^{(o)}(\underset{\sim}{r}_k) \left[\underset{\sim}{r}_i^{\,2} - \underset{\sim}{r}_i \, \underset{\sim}{r}_k\right]}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|} \, d\underset{\sim}{r}_i \, d\underset{\sim}{r}_k \qquad (143)$$

is the dipole oscillator strength sum rule appropriate to the eigenfunctions of the Hartree-Fock Hamiltonian (132). Knipp (1939) has also given a generalization of (141) which follows from (139) and the trial function (118), but it must considerably underestimate α_d.

The solution of (137) has been obtained only for beryllium (Dalgarno and McNamee 1961) and their results are shown in Table 3. The values obtained from the uncoupled approximation are much smaller than those obtained by the Sternheimer procedure and it seems that many of the shielding factors used in the interpretation of experimental data may be seriously in error. Beryllium is a special case, however, in that antishielding does not occur (within the Hartree-Fock approximation) whereas in cases of greatest experimental interest the antishielding is dominant.

TABLE 3

PROPERTIES OF B_e $(1s^2\ 2s^2)\ ^1S$

	$\alpha_d(\overset{o}{A})^3$	β_∞	$\alpha_q(\overset{o}{A})^5$	γ_∞
Sternheimer procedure	9.5	4.4	15.1	1.24
Fully-coupled approximation	4.5	1.8	9.1	0.77

A modification of (136) has been used by Khubchandani, Sharma and Das (1962) to calculate the radial antishielding in $C\ell^-$ and K^+. In place of the exchange operator

$$\sum_{k=1}^{N}{}_{||} \int \frac{u_k^{(o)}(\underset{\sim}{r}_k)\, u_i^{(1)}(\underset{\sim}{r}_k)}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|}\, d\underset{\sim}{r}_k\, u_k^{(o)}(\underset{\sim}{r}_i) \qquad (144)$$

they write, in effect,

$$\sum_{k=1}^{N}{}_{||} \int \frac{u_k^{(o)}(\underset{\sim}{r}_k)\, u_i^{(o)}(\underset{\sim}{r}_k)}{|\underset{\sim}{r}_i - \underset{\sim}{r}_k|}\, d\underset{\sim}{r}_k\, \frac{u_k^{(o)}(\underset{\sim}{r}_i)}{u_i^{(o)}(\underset{\sim}{r}_i)}\, u_i^{(1)}(\underset{\sim}{r}_i). \qquad (145)$$

The procedure can be regarded as an extension of the uncoupled Hartree approximation for determining $u_i^{(1)}$ in which the inconsistencies arising from the use of unperturbed Hartree-Fock orbitals are eliminated. Khubchandani et al. find that compared to the predictions of the Sternheimer procedure, the magnitude of γ_∞ for K^+ is increased by 30% and for Cl^- by 11% but there is an insignificant alteration of the quadrupole polarizabilities.

4.6 THE COUPLED HARTREE-FOCK APPROXIMATION

The previous formulae (137) and (138) for polarizabilities and shielding factors remain valid in the fully-coupled Hartree-Fock approximation, the only differences arising in the specification of the perturbed orbitals. The theoretical development has been given by Dalgarno (1959), Kaneko (1959) and Allen (1960). It follows from writing the wave function $\Psi(\underset{\sim}{r})$ of the perturbed system as

$$\Psi(\underset{\sim}{r}) = \mathcal{A} \prod_{i=1}^{N} \left\{ u_i^{(o)}(\underset{\sim}{r}_i) + u_i^{(1)}(\underset{\sim}{r}_i) + \dots \right\} \qquad (146)$$

and minimizing the total energy with respect to arbitrary variations of $u_i^{(o)}$ and $u_i^{(1)}$. Then expanding in powers of the perturbation, the first order perturbed orbitals satisfy the equation

$$(H_i - \epsilon_i^{(o)})\; u_i^{(1)}(\underset{\sim}{r}_i) + \left\{ v_L(\underset{\sim}{r}_i) - \epsilon_i^{(1)} \right\} u_i^{(o)}(\underset{\sim}{r}_i)$$

$$= \; -2 \sum_{k=1}^{N} \int \frac{u_k^{(1)}(\underset{\sim}{r}_k)\; u_k^{(o)}(\underset{\sim}{r}_k)}{|\, \underset{\sim}{r}_i - \underset{\sim}{r}_k \,|} \; d\underset{\sim}{r}_k \; u_i^{(o)}(\underset{\sim}{r}_i)$$

$$+ \sum_{k=1}^{N}{}_{||} \left\{ \int \frac{u_k^{(o)}(\underset{\sim}{r}_k)\; u_i^{(o)}(\underset{\sim}{r}_k)}{|\, \underset{\sim}{r}_i - \underset{\sim}{r}_k \,|} \; d\underset{\sim}{r}_k \; u_k^{(1)}(\underset{\sim}{r}_i) + \int \frac{u_k^{(1)}(\underset{\sim}{r}_k)\; u_i^{(o)}(\underset{\sim}{r}_k)}{|\, \underset{\sim}{r}_i - \underset{\sim}{r}_k \,|} \right.$$

$$\left. d\underset{\sim}{r}_k \; u_k^{(o)}(\underset{\sim}{r}_i) \right\} \qquad (147)$$

and

$$\epsilon_i^{(1)} = (u_i^{(o)},\; v_L(\underset{\sim}{r}_i)\; u_i^{(o)}) + 2 \sum_{k=1}^{N} \int \frac{u_k^{(1)}(\underset{\sim}{r}_k)\; u_k^{(o)}(\underset{\sim}{r}_k)\; |\, u_i^{(o)}(\underset{\sim}{r}_i) \,|^2}{|\, \underset{\sim}{r}_i - \underset{\sim}{r}_k \,|}$$

$$d\underset{\sim}{r}_i \; d\underset{\sim}{r}_k \; - 2 \sum_{k=1}^{N}{}_{||} \int \frac{u_k^{(o)}(\underset{\sim}{r}_k)\; u_i^{(o)}(\underset{\sim}{r}_k)\; u_k^{(1)}(\underset{\sim}{r}_i)\; u_i^{(o)}(\underset{\sim}{r}_i)}{|\, r_i - r_k \,|} \; d\underset{\sim}{r}_i \; d\underset{\sim}{r}_k .$$

$$(148)$$

In (147), the perturbed orbitals are coupled together both by direct and exchange interactions. The substitution (98) reduces (147) to coupled sets of radial equations but the solution involves laborious computation and it has been carried out only for the helium sequence. The fully-coupled approximation is, however, much more accurate than the uncoupled approximation. Thus, if the difference between the Hartree-Fock Hamiltonian (132) and the actual Hamiltonian of the system is regarded as a small perturbation, then in the absence of degeneracies the polarizabilities derived from the fully-coupled approximation are correct to first order whereas for the polarizabilities derived from the uncoupled approximation there is a non-vanishing first order correction (Dalgarno 1959). By an obvious extension of the arguments given by Cohen and Dalgarno (1961), it may be shown that the theorem applies also to the calculation of shielding factors. In addition, the fully coupled approximation will usually yield lower bounds for the polarizabilities (Dalgarno and McNamee 1961a).

For the helium sequence, (147) simplifies to

$$\left(- 1/2\, \nabla_i^{\,2} + V_i(r_i) - \epsilon_i^{(o)} \right) u^{(1)}(\underset{\sim}{r}_i) + v_L(\underset{\sim}{r}_i)$$

$$= - 2 \int \frac{u^{(1)}(\underset{\sim}{r}_k)\, u^{(o)}(\underset{\sim}{r}_k)}{\left| \underset{\sim}{r}_i - \underset{\sim}{r}_k \right|}\, d\underset{\sim}{r}_k\, u^{(o)}(\underset{\sim}{r}_i). \tag{149}$$

Solutions of (149) for dipole and quadrupole perturbations have been obtained by Dalgarno (1959), Kaneko (1959) and Dalgarno and McNamee (1961) and the resulting values of the polarizabilities and shielding factors are given in Table 2. The results are encouraging (again with the exception of H^-), especially for the quadrupole shielding factor. The dipole shielding factors of the helium sequence are actually given exactly by the fully-coupled approximation and serve merely as a computational check.

Since the effect of correlation is usually to reduce the polarizabilities, the uncoupled Hartree approximation probably overestimates α_q as it does α_d. Accordingly, for He

$$0.0965\mathring{A}^5 \leq \alpha_q \leq 0.0979\mathring{A}^5 \qquad (150)$$

and for Li^+

$$0.00464\mathring{A}^5 \leq \alpha_q \leq 0.00472\mathring{A}^5 . \qquad (151)$$

The lower bound for helium is larger than the value given by the more refined variational calculation of Dalgarno, Davison and Stewart (1960), suggesting that their adopted six-parameter representation of the unperturbed wave function does not provide an accurate description of the electron density at large distances from the nucleus.

Watson and Freeman (1962) have pointed out that calculations of shielding factors can be carried out within the framework of the Hartree-Fock method, provided two constraints are relaxed. Relaxing the constraint that the orbitals be separable into products of radial and angular factors gives the angular excitation contribution and relaxing the constraint that the radial wave functions be the same for electrons with different magnetic quantum numbers in a particular electron shell gives the radial excitation contributions. They have applied their method to the calculation of the radial excitation contributions to the quadrupole shielding factors of Cl^-, Cu^+, Br^-, Rb^+, Cs^+, I^- and Ce^{3+}. For Cu^+, they obtain - 17.6 in good agreement with the value of - 17.1 computed by Sternheimer and Foley (1956) but for Cl^-, they obtain - 88.9 which is much larger in magnitude than the value of - 56.5 computed by Sternheimer and Foley.* It would be interesting to compare the results of Watson and Freeman with those given by the fully-coupled approximation.

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*I am indebted to Dr. A. Freeman for providing me with this description of his work in advance of publication.

SECTION 5

EXPANSION METHODS

An assessment of the accuracy of the various methods of calculating polarizabilities and shielding factors can be obtained by expanding the wave functions as series in inverse powers of the nuclear charge, a procedure which uncouples the perturbed orbitals and leads to equations which can be solved analytically. Its usefulness in predicting polarizabilities and shielding factors depends upon the rapidity of convergence of the derived series expansions. In general, the convergence will be more rapid for shielding factors, which depend upon the distortion near the nucleus, than for polarizabilities, which depend upon the distortion far from the nucleus. The method has the advantage that results for all members of an isoelectronic sequence are obtained in a simple calculation.

5.1 THE HELIUM SEQUENCE

Expansion methods have been used by Dalgarno and Stewart (1958) and Dalgarno, Davison and Stewart (1960) to solve the exact Schrödinger equations appropriate to the dipole and quadrupole polarizations of the helium sequence. They expand

$$\psi_n = \sum_s \phi_n^{(s)}, \quad E_n = \sum_s E_n^{(s)} \tag{152}$$

where

$$\phi_o\ (\underset{\sim}{r}_1, \underset{\sim}{r}_2) = (Z^3/\pi)\ \exp\ \left\{-Z(r_1 + r_2)\right\} \tag{153}$$

$$E_o{}^o = -Z^2, \tag{154}$$

the unperturbed Hamiltonian being

$$H'' = -\frac{1}{2}\ \nabla_1{}^2 - \frac{1}{2}\nabla_2{}^2 - \frac{Z}{r_1} - \frac{Z}{r_2}\ . \tag{155}$$

To first order in Z^{-1},

$$\alpha_{2L} = 2\ \left(\ \phi_1{}^{(o)}\ |v_L - E_1{}^{(o)}|\ \phi_o{}^o\ \right)$$

$$+\ 2\left\{\left(\ \phi_1{}^{(o)}\ |v_L - E_1{}^{(o)}|\phi_o{}^{(1)}\right) + \left(\phi_1{}^{(1)}|v_L - E_1{}^{(o)}|\ \phi_o{}^o\right)\right\}$$

(156)

with a similar expression for γ_{2L}. The first order functions $\phi_1{}^{(o)}$, $\phi_o{}^{(1)}$ and $\phi_o{}^o$ are solutions of

$$(H'' - E_o{}^{(o)})\ \phi_o{}^{(1)} + \left(\frac{1}{|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|} - E_o{}^{(1)}\right)\phi_o{}^o = 0$$

(157)

$$(H'' - E_o^{(o)})\, \phi_1^{(o)} + \left(\gamma_L - E_1^{(o)}\right) \phi_o^{o} = 0 \qquad (158)$$

$$\left(H'' - E_o^{(o)}\right)\phi_1^{(1)} + \left(\frac{1}{|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|} - E_o^{(1)}\right)\phi_1^{(o)} + \left(v_L - E_1^{(o)}\right)$$

$$\phi_o^{(1)} - \left\{\left(\phi_o^{o}\ \frac{1}{|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|} - E_o^{(1)} | \phi_1^{(o)}\right) + \left(\phi_o^{o} | v_L - E_1^{(o)} | \phi_o^{(1)}\right)\right\}$$

$$\phi_o^{o} = 0. \qquad (159)$$

The solution $\phi_1^{(o)}$ of (158) can be obtained immediately but, because of the electron interaction term, the solutions of (157) and (159) present great difficulty. However, using the methods of Dalgarno and Stewart (1956), (156) can be written in the alternative form

$$\alpha_{2L} = 2\left(\phi_1^{(o)} \mid v_L - E_1^{(o)} \mid \phi_o^{o}\right)$$

$$+ 2\left\{ 2\left(\phi_o^{(o)} \mid \frac{1}{|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|} - E_o^{(1)} \mid \phi_2^{(o)}\right)\right.$$

$$\left. + \left(\phi_2^{(o)} \mid \frac{1}{|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|} - E_o^{(1)} \mid \phi_1^{(o)}\right)\right\} \qquad (160)$$

where

$$(H'' - E_o^o)\,\phi_2^{(o)} + (v_L - E_1^{(o)})\,\phi_1^{(o)}$$

$$- (\phi_o^o |\, v_L - E_1^{(o)} | \phi_1^{(o)})\,\phi_o^o = 0 \qquad (161)$$

and the solution of (161) can be achieved by elementary means. The analogous expression for γ_{2L} is (Dalgarno, Davison and Stewart 1960)

$$\gamma_{2L} = 2(\phi_1^{(o)} \mid v_L - E_1^{(o)} \mid \phi_o^o\ )$$

$$+ 2 \left\{ (\phi_1^{(o)} \mid \frac{1}{|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|} - E_o^{(1)} | \phi_1^{(o)}) \right.$$

$$\left. + \ (\phi_{11} \mid \frac{1}{|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|} - E_o^{(1)} \mid \phi_o^o) \right\} \qquad (162)$$

where

$$(H'' - E_o^o)\,\phi_{11} + (v'_L - E_1^{(o)\prime})\,\phi_1^{(o)} + (v_L - E_1^{(o)})\,\phi_1^{(o)\prime}$$

$$- \left\{ (\phi_o^{(o)} \mid v_L' - E_1^{(o)\prime} \mid \phi_1^{(o)}) + (\phi_o^o | v_L - E_1^{(o)} | \phi_1^{(o)\prime}) \right\} \phi_o^o = 0,$$

$$(163)$$

and the solution of (163) can also be achieved by elementary means.

The details can be found in the papers cited. The results are that to first order in Z^{-1}

$$\alpha_d = \frac{9}{Z^4} + \frac{207}{16Z^5} + 0(Z^{-6}) \tag{164}$$

$$\beta_\infty = \frac{2}{Z} \tag{165}$$

$$\alpha_q = \frac{30}{Z^6} + \frac{10381}{128Z^7} + 0(Z^{-8}) \tag{166}$$

$$\gamma_\infty = \frac{2}{3Z} + \frac{1}{18Z^2}(480 \ln 2 - 329) + 0(Z^{-3}) \tag{167}$$

Applying the screening approximation which takes some account of higher order terms (Dalgarno and Stewart 1960), we obtain

$$\alpha_d = 9/(Z-0.3594)^4 \tag{168}$$

$$\beta_\infty = 2/Z \tag{169}$$

$$\alpha_q = 30/(Z-0.4506)^6 \tag{170}$$

$$\gamma_\infty = 2/3(Z-0.3092). \tag{171}$$

The accuracy of the simple formulae is superior to that of the uncoupled Hartree approximation and is comparable to that of the coupled Hartree approximation. Thus (171) gives a value of 0.394 for the quadrupole shielding factor of helium compared to the (probably) accurate value of 0.396. The accuracy of the formulae increases rapidly with increasing nuclear charge.

A similar analysis can be applied to the Hartree-Fock approximation (Cohen and Dalgarno 1961). For the helium sequence, it is found that the uncoupled approximation is equivalent to the formulae

$$\alpha_d = \frac{9}{Z^4} + \frac{1923}{128Z^5} + 0(Z^{-6}) \qquad (172)$$

$$\beta_\infty = \frac{2}{Z} + \frac{3}{4\ Z^2} + 0(Z^{-3}) \qquad (173)$$

(Cohen and Dalgarno 1961, unpublished)

$$\alpha_q = \frac{30}{Z^6} + \frac{10485}{128Z^7} + 0(Z^{-8}) \qquad (174)$$

$$\gamma_\infty = \frac{2}{3Z} + \frac{13}{48Z^2} + 0(Z^{-3}) \qquad (175)$$

(Cohen, Dalgarno and McNamee 1962), whereas the coupled approximation is equivalent to formulae identical to (168), (169), (170) and (171). The coupled approximation therefore leads to results which are correct to first order in harmony with the assertions in Para. 4.6. For β_∞ the coupled approximation actually leads to results which are correct to all orders of Z^{-1}.

5.2 THE BERYLLIUM SEQUENCE

Cohen, Dalgarno and McNamee (1962) have also conducted an analysis of the calculation of the quadrupole polarizabilities and nuclear shielding factors of the beryllium sequence using the uncoupled and coupled Hartree-Fock approximations. According to the uncoupled approximation, they find that

$$\alpha_q = \frac{32670}{Z^6} \left(1 + \frac{8.002}{Z}\right) \tag{176}$$

$$\gamma_\infty = \frac{2}{Z} \left(1 + \frac{1.263}{Z}\right) \tag{177}$$

and according to the coupled approximation they find that

$$\alpha_q = \frac{32670}{Z^6} \left(1 + \frac{9.199}{Z}\right) \tag{178}$$

$$\gamma_\infty = \frac{2}{Z} \left(1 + \frac{1.220}{Z}\right) \tag{179}$$

It appears from these comparisons that only a small improvement in accuracy will result from using the coupled approximation in place of the uncoupled approximation. It will be of interest to extend the comparison to cases where antishielding can occur.

The series expansions for α_q converge too slowly to be quantitatively useful but we may obtain values of γ_∞ of acceptable accuracy from (177) and (179). Applying the screening approximation (Dalgarno and Stewart 1960), we obtain for the uncoupled approximation

$$\gamma_{\infty} = 2/(Z-1.263) \tag{180}$$

which yields a value of 0.73 for beryllium in good agreement with the value of 0.77 obtained by numerical integration by Dalgarno and McNamee (1961b). The coupled approximation yields the more accurate formulae

$$\gamma_{\infty} = 2/(Z-1.220) \tag{181}$$

according to which γ_{∞} is 0.72 for beryllium.

Contrary to the case of the helium sequence, (178) and (179) are not identical to the exact expansions. This occurs because the Hartree-Fock approximation does not take account of the degeneracy in the limit of infinite Z of the substates common to a particular quantum number (Layzer 1959, Linderberg and Shull 1960). Thus the correct zero order wave function for the ground states of the beryllium sequence is not $\psi_o(1s^2\ 2s^2)\ ^1S$ as the Hartree-Fock approximation asserts but the linear combination

$$\psi_o\ (^1S) = a\ \psi_o(1s^2\ 2s^2)\ ^1S + b\ \psi_o(1s^2\ 2p^2)\ ^1S \tag{182}$$

where a and b are constants so chosen that the matrix of the Hamiltonian is diagonal. The modification is important for the second component of the wave function introduces the possibility of antishielding. Cohen et al. (1962) have calculated the zero order changes in the quadrupole polarizability and shielding factor and they find that the leading term of (178) should be $31541/Z^6$ in place of $32670/Z^6$ and that the leading term of (179) should be $1.784/Z$ in place of $2/Z$. It appears that the coupled approximation may overestimate α_q by about 4% and γ_∞ by about 11%.

In the case of the dipole polarizability of beryllium the calculation would be further complicated because the dipole perturbation itself couples the two components of (182) to $\psi_o(1s^2\ 2s2p)\ ^1P$, with which they are degenerate. To obtain reliable values of α_d, it seems necessary to adopt a multi-configuration approach of the kind explored by Donath (1961).

SECTION 6

STATISTICAL METHODS

Calculations of polarizabilities (Gombas 1944, 1956) and of shielding factors (Sternheimer 1950, 1951, 1954, 1957, 1961; Sternheimer and Foley 1953) have been carried out based upon the Thomas-Fermi model of the atom. A comparison of the dipole polarizabilities computed by Gombas (1944) with the most accurate values available (cf. Table 5) is given in Table 4. The method overestimates α_d considerably for neutral atoms but its accuracy improves with increasing mass and with increasing excess charge.

A similar behaviour may be anticipated for shielding factors but as currently employed the statistical description does not yield any information on the radial antishielding which is dominant for heavy systems.

TABLE 4

DIPOLE POLARIZABILITIES IN UNITS OF 10^{-24} cm^3

System	Statistical Theory	Accurate Value
F^-	6.20	~1.2
Cl^-	7.10	~3
Br^-	8.41	~4.5
I^-	9.21	~7
Ne	2.01	0.40
A	2.88	1.64
Kr	4.00	2.48
Xe	4.61	4.04
Ne^+	0.850	0.15
K^+	1.36	~0.9
Rb^+	2.14	~1.7
Cs^+	2.66	~2.5
Mg^{++}	0.400	0.07
Ca^{++}	0.721	~0.5
Sr^{++}	1.30	~1.1
Ba^{++}	1.70	~1.7

TABLE 5*

DIPOLE POLARIZABILITIES IN UNITS OF 10^{-24} cm^3

System	(a)	(b)	System	(a)	(b)
H^-	14.9(1)	31.4(3)	C	2.1(21)	
	13.4(2)	30.2(4)	O^{2+}	0.3(16)	
He	0.218(1)	0.196(5,6)	Ne^{3+}	0.13(16)	
	0.224(2)	0.2050(3)	N	1.3(21)	1.13(22)
	0.220(5)	0.2051(7)	O^+	0.49(16)	
Li^+	0.0305(1)	0.0286(8)	O	0.89(21)	0.77(22)
	0.0307(2)	0.0281(5)	Ne^{2+}	0.15(16)	
	0.0304(5)	0.08(9,10)	O^-	3.2(16)	
		0.024(11,12)	F	0.6(21)	
Be^{2+}	0.00813(1)	0.00759(14)	Ne^+	0.21(16)	
	0.00825(2)	0.04(9)	F^-	1.9(23)	1.0(9,10)
		0.007(11,12)		1.8(21)	0.76(13)
B^{3+}	0.00303(2)	0.00288(14)			1.2(26)
		0.02(9)	Ne	0.40(21)	0.395(7)
		0.003(11,12)		0.62(6)	0.367(26)
C^{4+}	0.00139(2)	0.00132(14)	Na^+	0.152(23)	0.2(9,10)
		0.0013(8)		0.145(16)	0.26(13)
		0.012(9)			0.154(26)

Li	20(15)	24.4(18)	Mg^{2+}	0.082(16)	0.10(9,11)
	25(16)	20 ± 3(19)			0.072(24)
	24.9(17)	16 ± 3(25)			0.012(10)
Be	9.6(16)	4.5(20)	Al^{3+}	0.050(12)	0.053(11)
	9.5(20)			0.045(16)	0.07(9,10)
B	5.1(21)		Si^{4+}	0.027(16)	0.04(9,10)
O^{3+}	0.3(16)		Na	22.9(17)	24.6(18)
					20 ± 2.5(19)
Cl^{-}	7.19(23)	3.5(9)	Sr^{2+}		1.4(10)
		3.0(10,13)			1.6(13)
A	2.40(6)	1.64(7)	Rb	49.1(17)	43.9(18)
K^{+}	1.24(23)	0.9(9,10)			40 ± 5(19)
		0.8(11)	Ca^{2+}		1.8(13)
		1.2(13)	Sn^{4+}		3.4(13)
Ca^{2+}	0.73(12,15)	0.54(11,9)	I^{-}		7.6(9)
Sc^{3+}		0.35(9)			6.2(10,13)
Ti^{4+}		0.24(9)	Xe		4.04(7)
K	44.4(17)	41.6(18)	Cs^{+}	5.60(23)†	2.7(9,10)
		40 ± 5(19)			2.4(11)
Cs	57(15)				3.1(13)
Sc	154(15)		Ba^{2+}		1.7(9)
Fe^{++}		-1(13)			2.5(13)
Cu^{+}	0.982(23)	1.6(13)	La^{3+}		1.3(9)
Zn^{2+}		0.8(13)	Cs	67.7(17)	53.8(18)

Ge^{4+}		1.0(13)			52.5 ± 6.5(19)
Cu^{2+}		0.2(13)	Ba		62(25)
Br^-		4.97(9)	Pb^{2+}		4.9(13)
		4.15(10,13)	Hg^{2+}	2.78(23)†	
Kr		2.48(7)	Te^+		5.2(13)
Rb^+	2.92(23)†	1.7(9,10)	U^{6+}	1.34(23)†	
		1.8(13)			
Sr^{2+}		0.86(9)			
		1.0(11)			

Footnotes for Table 5

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[*] Values for a few systems not included in Table 4 have been estimated by Pauling (1927) using a screened hydrogenic formula.

[†] These values are computed using Hartree wave functions, which usually overestimate α_d considerably.

(a) Values computed using the Sternheimer procedure. In References (16) and (21), the antisymmetrical version has been used.

(b) Experimental values and more accurate theoretical values.

SECTION 7

NUMERICAL VALUES

7.1 DIPOLE POLARIZABILITIES

A compilation of dipole polarizabilities computed using the Sternheimer procedure or the antisymmetrical version of it is given in Table 5. When the result of a more refined theoretical calculation exists it also is included.

Experimental values of dipole polarizabilities can be obtained from deflection measurements such as those of Salop, Pollack and Bederson (1961), from extrapolation of measurements of refractive indices (cf. Dalgarno and Kingston 1960), from analysis of the Rydberg-Ritz corrections for spectral series (Born and Heisenberg 1924; Mayer and Mayer 1933), from the indices of refraction of salts in aqueous solutions (Fajans and Joos 1924) and from refraction data on crystals (Tessman, Kahn and Shockley 1953). Table 4 includes the experimental values.

An assessment of the accuracy of the theoretical values is confused by defects in the theories used to interpret the experimental data and by environmental effects which cause the polarizability to differ from that of the free atom or ion (Burns and Wikner 1961). The Sternheimer procedure, being essentially a single-electron approximation, should yield accurate dipole polarizabilities for the alkali metals but its accuracy is unlikely to be sustained for many-electron systems, especially those with an outermost shell of electrons described by orbitals with nodes other than at the nucleus. Table 5 is, at least, not in disagreement with this view. It appear that with the exceptions of beryllium and boron the polarizabilities predicted for neutral atoms lighter than sodium are unlikely to be in error by more than 15%, a figure also suggested by some calculations of the induced electric field at the nucleus by Sternheimer (1959). For beryllium, boron and atoms heavier than sodium, the possible error may approach a factor of two. For positive ions the errors are smaller and for negative ions they are larger. It is usually argued that correlation effects act to reduce polarizabilities, suggesting that the predicted polarizabilities are too large. This is probably true in general but not always, as the example of H^- demonstrates.

The table provides clear evidence that environmental effects significantly modify polarizabilities. Thus the dipole polarizability of free Na^+ cannot be very different from 0.15×10^{-24} cm^3 whereas the value derived from the refractivity of ionic crystals is 0.26×10^{-24} cm^3.

7.2 QUADRUPOLE POLARIZABILITIES

A compilation of quadrupole polarizabilities computed using the Sternheimer procedure is given in Table 6. The accuracy of the predicted quadrupole polarizabilities is comparable to but somewhat higher than that of the predicted dipole polarizabilities.

7.3 QUADRUPOLE SHIELDING FACTORS

Quadrupole shielding factors, computed according to the Sternheimer procedure, are collected together in Table 7. The results of more refined theoretical calculations are also included and are given in brackets. The accuracy of the predicted values is comparable to but somewhat lower than that of the dipole polarizabilities.

The significant feature of the table is the large antishielding predicted for heavy systems, to which Foley, Sternheimer and Tycko (1954) first drew attention. Qualitative confirmation of the existence of large antishielding effects has been obtained from nuclear quadrupole coupling data in alkali-halide gases (cf. Townes 1958; Wikner and Das 1958; Burns 1959a) and in ionic solids (cf. Bersohn 1958; Bernheim and Gutowsky 1960; Simmons and Slichter 1961; Hewitt and Taylor 1962), from analysis of nuclear spin transitions in crystals induced by ultrasonic waves (Proctor and Robinson 1956; Jennings, Tanttila and Kraus 1958; Taylor and Bloemberger 1959; Bolef and Mernes 1959), from nuclear magnetic relaxation times in ionic crystals (Van Kranendonk 1954; Das, Roy and Ghosh Roy 1956; Wikner, Blumberg and Hahn 1960), from dislocation studies

TABLE 6*

QUADRUPOLE POLARIZABILITIES IN UNITS OF 10^{-40} cm^5

System		System	
H^-	66.5(27)	Mg^{2+}	0.0223(30)
	67.0(28)	Al^{3+}	0.0101(28)
He	0.0993(27)		0.00915(30)
	0.0949(28)	Si^{4+}	0.00438(30)
	0.0979(5)	Cl^-	13.8(27)
Li^+	0.00473(27)		13.1(29)‡
	0.00471(28)	A	2.19(30)
	0.00472(5)	K^+	0.733(27)
Be^{2+}	0.000637(27)	Ca^{2+}	0.721(31)‡
	0.000633(28)	Cu^+	0.0309(30)
B^{3+}	0.000142(28)	Rb^+	1.28(27)
Be	15.1(20)		2.99(27)†
F^-	2.38(29)	Cs^+	3.03(31)†
Ne	0.370(30)		7.80(27)†
Na^+	0.0670(28)		7.86(31)†
	0.0634(23)		
	0.0649(31)		

*A partial evaluation of α_q has been carried out by Wikner and Das (1958) for Cl^-, K^+, Cu^+, Ga^{3+}, Rb^+, Cs^+, Br^- and I^-.

†Computed using unperturbed Hartree orbitals

‡These values are in harmony with the results of a more refined calculation by Khubchandani et al. (1962).

TABLE 7

QUADRUPOLE SHIELDING FACTORS†

H^-	$1.141^{(28)}$	F^-	$-25.7^{(29)‡}$	Ca^{2+}	$-8.4^{(30)‡}$
	$1.131^{(23)}$	Ne	$-8.99^{(30)‡}$	Mn^{2+}	$-6.81^{(29)}$
He	$0.416^{(28)}$	Na^+	$-4.1^{(34)}$	Fe^{3+}	$-6.17^{(29)}$
	$0.424^{(23)}$		$-4.5^{(28)}$	Cu^+	$-15.0^{(34)}$
	$(0.397)^{(32)}$		$-4.6^{(23)}$		$-13.8^{(35)}$
Li^+	$0.056^{(28)}$	Mg^{2+}	$-2.7^{(30)‡}$		$(-15.1)^{(36)*}$
	$0.263^{(23)}$	Al^{3+}	$-2.6^{(28)}$	Ga^{3+}	$-6.94^{(29)}$
	$(0.249)^{(32)}$	Si^{4+}	$-1.9^{(30)‡}$	Br^-	$-97.0^{(35)**}$
Be^{++}	$0.185^{(28)}$	Cl^-	$-56.6^{(34)}$	Kr	$-41.0^{(29)}$
	$0.189^{(23)}$		$-50.1^{(29)}$	Rb^+	$-49.3^{(35)**}$
	$(0.181)^{(32)}$		$-49.3^{(35)}$		$-70.7^{(34)**}$
B^{3+}	$0.145^{(28)}$		$(-55.5)^{(37)}$	Cd^{2+}	$-15^{(29)††}$
	$(0.142)^{(32)}$		$(-87.5)^{(36)*}$	Ag^+	$-22.1^{(29)}$
Be	$1.24^{(20)}$	A	$-21.2^{(30)*}$	In^{3+}	$-15.3^{(29)**\#}$
	$(0.72)^{(33)}$	K^+	$-17.3^{(23)}$	I^-	$-179^{(35)**}$
B^+	$0.768^{(23)}$		$-12.8^{(35)}$	Cs^+	$-110^{(35)**}$
	$(0.53)^{(33)}$		$(-16.3)^{(37)}$		$-144^{(34)**}$

† A partial evaluation of for Cu^+, V^{++}, Ag^+ and Hg^{++} has been reported recently by Sternheimer (1962b).

‡ The outer shell contribution only has been included.

* In (36), the radial contribution only has been calculated. The value given includes the angular contribution obtained in reference (34).

** These values are computed using Hartree wave functions.

†† This is an interpolated value.

In reference (29), it is suggested that the use of Hartree-Fock wave functions for In^{3+} would give a value of -11.

References to Tables 5, 6, and 7.

(1) Wikner and Das (1957)
(2) Sternheimer (1957)
(3) Schwartz (1961)
(4) Geltman (1962)
(5) Dalgarno and McNamee (1961a)
(6) Kaneko (1959)
(7) Dalgarno and Kingston (1960)
(8) Baber and Hasse′ (1937)
(9) Fajan and Joos (1924)
(10) Born and Heisenberg (1924)
(11) Mayer and Mayer (1933)
(12) Sternheimer (1954)
(13) Tessman, Kahn and Shockley (1953)
(14) Dalgarno and Stewart (1958)
(15) Sundbom (1958)
(16) Parkinson (1960)
(17) Sternheimer (1962)
(18) Dalgarno and Kingston (1959)
(19) Salop, Pollack and Bederson (1961)
(20) Dalgarno and McNamee (1961b)
(21) Dalgarno and Parkinson (1959)
(22) Alpher and White (1959)

References to Tables 5, 6, and 7. (Continued)

(23) Sternheimer (1959)

(24) Bockasten (1956)

(25) Drechsler and Muller (1952)

(26) Donath (1961)

(27) Sternheimer (1957)

(28) Das and Bersohn (1956)

(29) Burns and Wikner (1961)

(30) Burns (1959b)

(31) Burns (1959a)

(32) Dalgarno, Davison and Stewart (1960)

(33) Cohen, Dalgarno and McNamee (1962)

(34) Sternheimer and Foley (1956)

(35) Wikner and Das (1958)

(36) Watson and Freeman (1962)

(37) Khubchandani, Sharma and Das (1962).

(Otsuka 1958), and from mixed crystal experiments (Kawamura, Otsuka and Ishiwatari 1956; Otsuka and Kawamura 1957). There are serious deficiencies in the theories used to interpret the experiments. Some measure of quantitative agreement is found between the predicted and derived values of γ_∞ for positive ions but the predicted values of γ_∞ for negative ions are apparently too large by a factor of about four (Burns and Wikner 1961). Although errors of this order cannot be excluded, the work of Watson and Freeman (1962) suggests that the Sternheimer procedure underestimates $|\gamma_\infty|$ and modification of the negative ion structure by its environment must be a major source of the discrepancies (Burns and Wikner 1961).

7.4 HIGHER ORDER POLARIZABILITIES AND SHIELDING FACTORS

Some calculations of higher order polarizabilities have been reported by Burns (1959a) and by Stewart (1961) and of higher order shielding factors by Sternheimer (1961). The hexadecapole antishielding factors are very large and higher order effects are important (Sternheimer 1962b).

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