PHYSICAL REVIEW VOLUME 162, NUMBER 1 5 OCTOBER 1967

Magnetoelectric Susceptibilities of S-State Atomic Systems*

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(Received 19 April 1967)

A study is made of the effect on ${}^1S_0$ atomic systems of the simultaneous interaction of uniform electric and magnetic fields. It is found that in addition to the conventional magnetic-susceptibilities and electric-polarizability terms there exists an interaction term in which the energy depends quadratically on both fields. The coefficient of this term in the energy is defined here as the *magnetoelectric susceptibility*. The magnetoelectric susceptibilities of a large number of two-, four-, ten-, twelve-, eighteen-, and twenty-electron atomic systems are calculated. Analytical Hartree-Fock wave functions are used. The calculations are carried out using double-perturbation theory within the Hartree-Fock framework. The results show that the energy terms described by the magnetoelectric susceptibilities are of the same order of magnitude as those corresponding to the hyperpolarizabilities for magnetic fields of the order of 10^6 G. The magnetoelectric susceptibility effect is dependent on the relative orientation of the two fields, and its behavior with respect to field orientation is described by a property defined as the anisotropy. It is found that the magnetoelectric susceptibilities of the inert-gas isoelectronic-series systems are all negative and decrease in magnitude as the fields are rotated from perpendicular to parallel. The alkaline-earth systems show considerable variation: some are positive, some are negative, and in some the sign depends upon the relative orientation of the fields.

I. INTRODUCTION

When an atom is placed in an external electric field, its electronic charge distribution is distorted. If the applied field is uniform, then as a first approximation, the distortion may be described as an induced electric dipole moment proportional to the field strength. As the field strength is increased, a term cubic in field strength will begin to contribute significantly to the induced moment. These are the electric-polarizability and hyperpolarizability terms, respectively.

If now this system is placed in a magnetic field, the charge distribution will undergo a further distortion. The resulting change in the induced moment may be ascribed to a magnetic-field-induced polarizability. Of course one could just as easily consider these fields to be applied in the reverse order, in which case it might be more appropriate to refer to this as an electric-field-induced magnetic susceptibility. Since this property has apparently been given no name in the literature, the authors propose that it be called the *magnetoelectric susceptibility*. The symbol, $\beta^{\perp}$ is used for the magnetoelectric susceptibility when the electric and magnetic fields are perpendicular. The corresponding quantity in the case of parallel fields is called $\beta^{\parallel}$.

It is the purpose of this paper to calculate the magnetoelectric susceptibilities of a number of S-state atomic systems. These calculations are carried out for the two-, ten-, and eighteen-electron inert-gas isoelectronic series as well as the four-, twelve-, and twenty-electron alkaline-earth atoms and the corresponding isoelectronic ions. The method used is a one-electron double perturbation theory development of the Hartree-Fock procedure.

The case considered here is that of static, uniform electric and magnetic fields. For these spherically symmetric systems, the energy of the system in the fields must be invariant to simultaneous reversal of the electric and magnetic fields. Thus the lowest-order energy term in which the interaction of the two fields will be exhibited will be quadratic in both the electric and magnetic fields.

There are a number of previous investigations of effects resulting from the simultaneous presence of electric and magnetic fields. Among these are the effect of a magnetic field on the dielectric constants of certain anisotropic liquids,[1] the Cotton-Mouton effect,[2] and the magnetoelectric effect in antiferromagnetic materials.[3] Van Vleck[4] showed in 1932 that the magnetoelectric distortion in simple atomic systems would be quadratic rather than linear and he estimated that the magnitude of this term was such that it could not be observed experimentally at that time.

The only previous calculation of the magnetoelectric susceptibility is an exact calculation for the hydrogen atom by Buckingham and Pople.[5] They obtained

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* Work supported by the U. S. Air Force Office of Scientific Research, Grant No. AF-AFOSR-191-67.

[1] W. Kast, Ann. Physik **73**, 145 (1924); E. Friedel, Compt. Rend. **180**, 269 (1925); Jezewski, J. Phys. **5**, 59 (1924); L. S. Ornstein, Z. Physik **35**, 394 (1926).

[2] A. Cotton and H. Mouton, J. Phys. **1**, 5 (1911); Ann. Chim. Phys. **19**, 153 (1910); **20**, 194 (1910). See also A. D. Buckingham and J. A. Pople, Proc. Phys. Soc. (London) **B69**, 1133 (1956).

[3] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1960), p. 119; S. Foner and M. Hanabusa, J. Appl. Phys. 34, 1226 (1963); 34, 1246 (1963).

[4] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 118.

[5] A. D. Buckingham and J. A. Pople, Proc. Cambridge Phil. Soc. **53**, 262 (1957).

perturbed hydrogen wave functions in the same manner as given by Sewell.[6] Using these perturbed wave functions and ignoring spin, they obtained values for the magnetoelectric susceptibility when the electric and magnetic fields are parallel or perpendicular. In atomic units their results are

$$\beta^{\parallel}=-159f^2/8,\quad \beta^{\perp}=-797f^2/24, \tag{1}$$

where f is the fine-structure constant.

No other previous calculation and no measurement of the magnetoelectric susceptibility has appeared in the literature. However, the authors have learned that measurements of this property are currently in progress.[7]

II. THEORETICAL DEVELOPMENT

The energy of an atom in the presence of uniform electric and magnetic fields is a function of the magnitudes of the two fields. This dependence may be written as a Taylor series in the components of the fields. For spherical systems the nonvanishing terms of this series up to fourth order in the field strengths are

$$\begin{aligned}U=U_0-\tfrac{1}{2}\alpha_{\alpha\beta}E_\alpha E_\beta-\tfrac{1}{2}\chi_{\alpha\beta}H_\alpha H_\beta\\ -(1/24)\gamma_{\alpha\beta\gamma\delta}E_\alpha E_\beta E_\gamma E_\delta-\tfrac{1}{4}\beta_{\alpha\beta:\gamma\delta}E_\alpha E_\beta H_\gamma H_\delta\\ -(1/24)\xi_{\alpha\beta\gamma\delta}H_\alpha H_\beta H_\gamma H_\delta-\cdots.\end{aligned} \tag{2}$$

Here $\alpha_{\alpha\beta}$ is the conventional polarizability tensor, $\chi_{\alpha\beta}$ is the magnetic-susceptibility tensor, and $\gamma_{\alpha\beta\gamma\delta}$, $\beta_{\alpha\beta:\gamma\delta}$ and $\xi_{\alpha\beta\gamma\delta}$ are fourth-rank tensors representing the hyperpolarizability, magnetoelectric susceptibility, and hypersusceptibility, respectively.

For spherically symmetric systems[8,9] these five tensors are isotropic. Thus, since the only isotropic tensor of order 2 is a scalar multiple of $\delta_{\alpha\beta}$ we can write

$$\alpha_{\alpha\beta}=\alpha\delta_{\alpha\beta},\quad \chi_{\alpha\beta}=\chi\delta_{\alpha\beta}. \tag{3a}$$

Further, one can show that any component of an isotropic fourth-order tensor $U_{\alpha\beta\gamma\delta}$ is zero unless α, β, γ, and δ occur in pairs and that the remaining nonzero components satisfy

$$U_{1122}=U_{1133}=U_{2233}=U_{2211}=U_{3322}=U_{3311}=\lambda, \tag{3b}$$

$$U_{1212}=U_{1313}=U_{2323}=U_{2121}=U_{3232}=U_{3131}=\mu+\nu, \tag{3c}$$

$$U_{2112}=U_{3113}=U_{3223}=U_{1221}=U_{2332}=U_{1331}=\mu-\nu, \tag{3d}$$

$$U_{1111}=U_{2112}+U_{1212}+U_{1122}=\lambda+2\mu. \tag{3e}$$

Then, summarizing the results listed as Eqs. (3b)–(3e) the most general isotropic tensor of order 4 can be written as

$$\begin{aligned}U_{\alpha\beta\gamma\delta}=\lambda\delta_{\alpha\beta}\delta_{\gamma\delta}+\mu(\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})\\ +\nu(\delta_{\alpha\gamma}\delta_{\beta\delta}-\delta_{\alpha\delta}\delta_{\beta\gamma}).\end{aligned} \tag{3f}$$

From Eq. (3f) then one finds that the hyperpolarizability term reduces to

$$\begin{aligned}-(1/24)\gamma_{\alpha\beta\gamma\delta}E_\alpha E_\beta E_\gamma E_\delta=-(1/24)(\lambda+2\mu)E^4\\ =-(1/24)\gamma E^4,\end{aligned} \tag{4a}$$

where

$$\gamma=\gamma_{1111}\quad\text{and}\quad E^4=(E_\alpha E_\alpha)(E_\beta E_\beta). \tag{4b}$$

Similarly for the hypersusceptibility term we have

$$-(1/24)\xi_{\alpha\beta\gamma\delta}H_\alpha H_\beta H_\gamma H_\delta=-(1/24)\xi H^4, \tag{4c}$$

where

$$\xi=\xi_{1111}\quad\text{and}\quad H^4=(H_\alpha H_\alpha)(H_\beta H_\beta). \tag{4d}$$

The magnetoelectric susceptibility term becomes

$$-\tfrac{1}{4}\beta_{\alpha\beta:\gamma\delta}E_\alpha E_\beta H_\gamma H_\delta=-\tfrac{1}{4}[\lambda E^2H^2+2\mu(\mathbf{E}\cdot\mathbf{H})^2]. \tag{4e}$$

If the electric and magnetic field parameters are adjusted, without rotation of coordinates, so that **E** and **H** are orthogonal we have

$$-\tfrac{1}{4}\beta_{\alpha\beta:\gamma\delta}E_\alpha E_\beta H_\gamma H_\delta=-\tfrac{1}{4}\lambda E^2H^2=-\tfrac{1}{4}\beta^{\perp}E^2H^2. \tag{4f}$$

Similarly if **E** and **H** are adjusted so that they become parallel we have

$$\begin{aligned}-\tfrac{1}{4}\beta_{\alpha\beta:\gamma\delta}E_\alpha E_\beta H_\gamma H_\delta=-\tfrac{1}{4}(\lambda+2\mu)(E^2H^2)\\ =-\tfrac{1}{4}\beta^{\parallel}E^2H^2.\end{aligned} \tag{4g}$$

From Eqs. (4f) and (4g) we conclude

$$\begin{aligned}-\tfrac{1}{4}\beta_{\alpha\beta:\gamma\delta}E_\alpha E_\beta H_\gamma H_\delta=-\tfrac{1}{4}\beta^{\perp}E^2H^2\\ -\tfrac{1}{4}(\beta^{\parallel}-\beta^{\perp})(\mathbf{E}\cdot\mathbf{H})^2.\end{aligned} \tag{4h}$$

In the above equations $\beta^{\perp}$ corresponds to the tensor component for which the electric and magnetic fields are perpendicular and $\beta^{\parallel}$ corresponds to the case of parallel **E** and **H** fields. The magnetoelectric susceptibility $\beta(\eta)$ is then defined as

$$\beta(\eta)=\beta^{\perp}+(\beta^{\parallel}-\beta^{\perp})\cos^2\eta, \tag{5}$$

where η is the angle between the **E** and **H** fields.

Using the results of Eqs. (3a), (4a), (4c), and (5) the interaction energy, Eq. (2), may be written

$$\begin{aligned}U=U_0-\tfrac{1}{2}\alpha E^2-\tfrac{1}{2}\chi H^2-(1/24)\gamma E^4\\ -\tfrac{1}{4}\beta(\eta)E^2H^2-(1/24)\xi H^4-\cdots.\end{aligned} \tag{6}$$

In Eq. (6) it is clear that the total energy does not depend on the direction of the electric or magnetic field except in the magnetoelectric susceptibility term as must be the case physically. Also, as is further required by symmetry, $\beta(\eta)$ depends only upon the relative orientation of the two fields.

In order to calculate $\beta(\eta)$, the behavior of the atomic system must be known. This behavior in the presence of uniform electric and magnetic fields may be deter-

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[6] G. L. Sewell, Proc. Cambridge Phil. Soc. **45**, 678 (1949).

[7] A. D. Buckingham (private communication).

[8] L. L. Boyle, A. D. Buckingham, R. L. Disch, and D. A. Dunmur, J. Chem. Phys. **45**, 1318 (1966); A. D. Buckingham and M. J. Stephen, Trans. Faraday Soc. **53**, 884 (1957). See also H. Jeffreys, *Cartesian Tensors* (Cambridge University Press, London, 1952), p. 68.

[9] A. D. Buckingham and J. A. Pople, Proc. Phys. Soc. (London) **B69**, 1133 (1956).

mined by considering the Hamiltonian

$$H=H_0+\mathbf{E}\cdot\sum_{i=1}^{N}\mathbf{r}_i+\tfrac{1}{2}f\mathbf{H}\cdot\mathbf{L}$$
$$+\tfrac{1}{8}f^2\mathbf{H}\cdot\sum_{i=1}^{N}[r_i^2\mathbf{1}-\mathbf{r}_i\mathbf{r}_i]\cdot\mathbf{H}. \quad (7)$$

Here spin is ignored since our present work is concerned with systems for which the total spin is zero.

The Hamiltonian of Eq. (7) contains six independent perturbation parameters corresponding to the Cartesian components of the electric and magnetic fields. As seen in Eq. (4), $\beta(\eta)$ has only two independent components; those corresponding to parallel and perpendicular relative orientation of the two fields. Thus the most general Hamiltonian required to obtain either of the components of $\beta(\eta)$, is the form of Eq. (7) corresponding to the case of either parallel or perpendicular fields. These forms are

$$H^{\parallel}=H_0+E_z\sum_{i=1}^{N}z_i+\tfrac{1}{2}fH_zL_z+\tfrac{1}{8}f^2H_z^2\sum_{i=1}^{N}(x_i^2+y_i^2), \quad (8)$$

$$H^{\perp}=H_0+E_z\sum_{i=1}^{N}z_i+\tfrac{1}{2}fH_xL_x+\tfrac{1}{8}f^2H_x^2\sum_{i=1}^{N}(y_i^2+z_i^2). \quad (9)$$

The two components of $\beta(\eta)$ are obtained through double perturbation Hartree-Fock theory using the Hamiltonians listed as Eqs. (8) and (9).

III. FORMULATION OF METHOD

The magnetoelectric susceptibilities are calculated through Hartree-Fock double perturbation theory. In this method the total wave function ψ is expressed as an antisymmetrized product of one-electron wave functions χ_i. The total energy of an atomic system in the electric and magnetic fields is

$$E=\langle\psi|H|\psi\rangle, \quad (10)$$

where H is either of the Hamiltonians, Eqs. (8) or (9). This energy is minimized with respect to a variation of the one-electron orbitals χ_i. The condition for E to be a minimum is that χ_i must satisfy the perturbed one-electron Fock equation[10]:

$$[h^0+v+\lambda h_E^1+\mu h_H^1+\mu^2h_H^2]\chi_i=\epsilon_i\chi_i. \quad (11)$$

In this equation ϵ_i is the one-electron energy, h^0 contains the kinetic energy and Coulomb potential terms

$$h^0=-\tfrac{1}{2}\nabla^2-Z/r, \quad (12)$$

and the operators, h_E^1, h_H^1, and h_H^2 are the one-electron forms of the electric and magnetic field operators of Eqs. (8) or (9). For the case of parallel fields these may be written

$$h_E^1=z, \quad h_H^1=l_z, \quad h_H^2=\tfrac{1}{2}(x^2+y^2), \quad (13)$$

where l_z is the z component of the one-electron angular-momentum operator. The corresponding operators for the case of perpendicular fields are seen immediately from Eq. (9). The operator v contains the Coulomb and exchange integrals arising from the $1/r_{\mu\nu}$ terms in the Hamiltonian. This operator is defined by

$$v(\mu)\chi_i(\mu)=\sum_{j=1}^{N}[\langle\chi_j(\nu)|1/r_{\mu\nu}|\chi_j(\nu)\rangle\chi_i(\mu)$$
$$-\langle\chi_j(\nu)|1/r_{\mu\nu}|\chi_i(\nu)\rangle\chi_j(\mu)]. \quad (14)$$

In applying perturbation theory to Eq. (11), the orbitals and energies are written

$$\chi_i=\sum_{k,l}\lambda^k\mu^l\chi_i^{k,l}, \quad \epsilon_i=\sum_{k,l}\lambda^k\mu^l\epsilon_i^{k,l}. \quad (15)$$

Substitution of the expansion for χ_i into the operator v gives

$$v=\sum_{k,l}\lambda^k\mu^l\nu^{k,l}, \quad (16)$$

where

$$\nu^{k,l}(\mu)=\sum_{j=1}^{N}\sum_{m=0}^{k}\sum_{n=0}^{l}\langle\chi_j^{m,n}(\nu)|1/r_{\mu\nu}(1-P_{\mu\nu})|$$
$$\times\chi_j^{k-m}(\nu)^{l-n}\rangle. \quad (17)$$

Substitution of the expansions for χ_i, ϵ_i and v, Eqs. (15) and (16), into the Hartree-Fock expression for the total energy,[11]

$$E=\sum_{i=1}^{N}[\epsilon_i-\tfrac{1}{2}\langle\chi_i|v|\chi_i\rangle], \quad (18)$$

gives

$$E=\sum_{k,l}\lambda^k\mu^lE^{k,l}, \quad (19)$$

where

$$E^{k,l}=\sum_{i=1}^{N}[\epsilon_i^{k,l}-\tfrac{1}{2}\sum_{m=0}^{k}\sum_{n=0}^{l}\sum_{q=0}^{k-m}\sum_{r=0}^{l-n}\langle\chi_i^{m,n}|\nu^{q,r}|$$
$$\times\chi_i^{k-m-q,l-n-r}\rangle]. \quad (20)$$

It can be seen upon comparison of Eq. (19) with Eq. (6) that the magnetoelectric susceptibility is obtained from the perturbation energy $E^{2,2}$ according to the relations

$$\beta^{\perp}=-f^2E_{\perp}^{2,2}, \quad \beta^{\parallel}=-f^2E_{\parallel}^{2,2}. \quad (21)$$

Thus the magnetoelectric susceptibility is calculated from the expression for $E^{2,2}$ which is obtained from Eqs. (20). This expression after algebraic manipulation

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[10] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II, p. 288.

[11] H. A. Bethe, *Intermediate Quantum Mechanics* (W. A. Benjamin, Inc., New York, 1964), p. 41.

$$\langle\chi_j^{m,n}(\nu)|(1/r_{\mu\nu})(1-P_{\mu\nu})|\chi_j^{k-m,k-n}(\nu)\rangle\phi(\mu)$$
$$=\langle\chi_j^{m,n}(\nu)(1/r_{\mu\nu})\chi_j^{k-m,k-n}(\nu)\rangle\phi(\mu)$$
$$-\langle\chi_j^{m,n}(\nu)(1/r_{\mu\nu})\phi(\nu)\rangle\chi_j(\mu)^{k-m,k-n}$$

for any function $\phi(\mu)$.

reduces to

$$E^{2,2}=\sum_{i=1}^{N}[2\langle\chi_i^{2,0}|h_H^2|\chi_i^{0,0}\rangle+\langle\chi_i^{1,0}|h_H^2|\chi_i^{1,0}\rangle-\langle\chi_i^{1,1}|h^0+\nu^{0,0}-\epsilon_i^{0,0}|\chi_i^{1,1}\rangle+2\langle\chi_i^{2,0}|h_H^1+\nu^{0,1}-\epsilon_i^{0,1}|\chi_i^{0,1}\rangle$$
$$+\langle\chi_i^{0,1}|\nu^{2,0}-\epsilon_i^{2,0}|\chi_i^{0,1}\rangle+\langle\chi_i^{1,0}|\nu^{1,1}-\epsilon_i^{1,1}|\chi_i^{0,1}\rangle-\langle\chi_i^{1,1}|\nu^{1,1}-\epsilon_i^{1,1}|\chi_i^{0,0}\rangle]. \quad (22)$$

In order to obtain $E^{2,2}$, the perturbed orbitals $\chi_i^{1,0}$, $\chi_i^{0,1}$, $\chi_i^{2,0}$, and $\chi_i^{1,1}$ and the corresponding orbital energies must be known. These are obtained as solutions to certain equations of the perturbation sequence of equations which result when expansions (14) and (15) are used with Eq. (11). The equations which must be solved are

$$(h^0+\nu^{0,0}-\epsilon_i^{0,0})\chi_i^{0,0}=0, \quad (23)$$

$$(h^0+\nu^{0,0}-\epsilon_i^{0,0})\chi_i^{1,0}=-(h_E^1+\nu^{1,0}-\epsilon_i^{1,0})\chi_i^{0,0}, \quad (24)$$

$$(h^0+\nu^{0,0}-\epsilon_i^{0,0})\chi_i^{0,1}=-(h_H^1+\nu^{0,1}-\epsilon_i^{0,1})\chi_i^{0,0}, \quad (25)$$

$$(h^0+\nu^{0,0}-\epsilon_i^{0,0})\chi_i^{2,0}=-(h_E^1+\nu^{1,0}-\epsilon_i^{1,0})\chi_i^{1,0}$$
$$-(\nu^{2,0}-\epsilon_i^{2,0})\chi_i^{0,0}, \quad (26)$$

$$(h^0+\nu^{0,0}-\epsilon_i^{0,0})\chi_i^{1,1}=-(h_E^1+\nu^{1,0}-\epsilon_i^{1,0})\chi_i^{0,1}$$
$$-(h_H^1+\nu^{0,1}-\epsilon_i^{0,1})\chi_i^{1,0}$$
$$-(\nu^{1,1}-\epsilon_i^{1,1})\chi_i^{0,0}. \quad (27)$$

The solutions to the zero-order problem, Eq. (23), are the analytical Hartree-Fock wave functions available in the literature. The solutions to Eqs. (24)–(27) are obtained by a variational procedure. In solving Eqs. (24)–(27) an important simplifying assumption is made. This is that these equations may be "uncoupled" through the neglect of the interaction terms $v^{1,0}$, $v^{0,1}$, $v^{2,0}$, and $v^{1,1}$. This simplification, though greatly reducing the complexity of the numerical problem required in solving these equations, is expected to have only a small effect on the magnetoelectric susceptibility.[12,13]

The perturbed orbitals are obtained as the function which yields the minimum value of a functional corresponding to each of the perturbation equations, Eqs. (24)–(27). These functionals for the four perturbed orbitals of interest are

$$J_{1,0}(\phi)=\langle\phi|h^0+\nu^{0,0}-\epsilon_i^{0,0}|\phi\rangle$$
$$+2\langle\phi|h_E^1-\epsilon_i^{1,0}|\chi_i^{0,0}\rangle, \quad (28)$$

$$J_{0,1}(\phi)=\langle\phi|h^0+\nu^{0,0}-\epsilon_i^{0,0}|\phi\rangle$$
$$+2\langle\phi|h^1-\epsilon_i^{0,1}|\chi_i^{0,0}\rangle, \quad (29)$$

$$J_{2,0}(\phi)=\langle\phi|h^0+\nu^{0,0}-\epsilon_i^{0,0}|\phi\rangle+2\langle\phi|h_E^1-\epsilon_i^{1,0}|\chi_i^{1,0}\rangle$$
$$-2\epsilon_i^{2,0}\langle\phi|\chi_i^{0,0}\rangle, \quad (30)$$

$$J_{1,1}(\phi)=\langle\phi|h^0+\nu^{0,0}-\epsilon_i^{0,0}|\phi\rangle+2\langle\phi|h_E^1-\epsilon_i^{1,0}|\chi_i^{0,1}\rangle$$
$$+2\langle\phi|h_H^1-\epsilon_i^{0,1}|\chi_i^{1,0}\rangle-2\epsilon_i^{1,1}\langle\phi|\chi_i^{1,0}\rangle, \quad (31)$$

where ϕ is a function which contains arbitrary variation parameters. The functionals $J_{s,t}(\phi)$ are minimized with respect to these variational parameters of ϕ. The perturbed orbital $\chi_i^{s,t}$ is the function ϕ when the variation parameters in ϕ have the values which minimize $J(\phi)$. This procedure is derived and explained in the literature.[14]

In the Hartree-Fock derivation of Eq. (11), it is required that all orbitals satisfy an orthonormality condition, namely,

$$\langle\chi_i|\chi_j\rangle=\delta_{i,j};\quad i,j=1,2,\cdots,N. \quad (32)$$

When the expansion for χ_i, Eq. (15), is substituted into Eq. (32), a sequence of equations results. Each member of this sequence is an orthogonality condition on one of the perturbed orbitals $\chi_i^{s,t}$. The conditions on the orbitals of interest are

$$\langle\chi_i^{1,0}|\chi_j^{0,0}\rangle=0, \quad (33)$$

$$\langle\chi_i^{0,1}|\chi_j^{0,0}\rangle=0, \quad (34)$$

$$\langle\chi_i^{2,0}|\chi_j^{0,0}\rangle+\tfrac{1}{2}\langle\chi_i^{1,0}|\chi_j^{1,0}\rangle=0, \quad (35)$$

$$\langle\chi_i^{1,1}|\chi_j^{0,0}\rangle+\langle\chi_i^{1,0}|\chi_j^{0,1}\rangle=0. \quad (36)$$

These constraints are satisfied by subjecting the perturbed orbitals to transformations of the form

$$\chi_i^{s,t}=\phi_i^{s,t}-\sum_{j=1}^{N}C_{ij}^{s,t}\chi_j^{0,0}. \quad (37)$$

The $C_{ij}^{s,t}$ are then evaluated from Eqs. (33) to (36). The functions $\phi_i^{s,t}$ are unconstrained forms of the orthogonalized perturbed orbitals $\chi_i^{s,t}$. The four functionals, Eqs. (28)–(31), may be reexpressed in terms of the $\phi_i^{s,t}$ instead of the $\chi_i^{s,t}$. They may then be minimized by freely varying $\phi_i^{s,t}$ without any constraint.

The trial forms of the orbitals $\phi_i^{s,t}$ must be selected carefully. It is clear from the perturbation equations, Eqs. (24)–(27), that only certain types of angular symmetry may be present in the solutions to those equations. After determining from these equations which types of angular symmetry are allowed in each of the perturbed orbitals, trial functions are chosen by multiplying radial functions with spherical harmonics of the appropriate symmetries. These trial functions

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[12] P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. 44, 505 (1966).

[13] J. D. Lyons, Ph.D. dissertation, State University of New York at Buffalo, 1967 (unpublished).

[14] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 122; P. W. Langhoff, Ph.D. dissertation, State University of New York at Buffalo, 1965, p. 31 (unpublished).

all have the following general form:

$$\phi_i^{s,t}(r,\theta,\phi)=\eta_i(r)\sum_{\nu} P_{i\nu}^{s,t}(r)Y_{l_\nu}^{m_\nu}(\theta,\phi)\,, \tag{38}$$

where the unperturbed orbital $\chi_i^{0,0}$ is

$$\chi_i^{0,0}(r,\theta,\phi)=\eta_i(r)Y_{l_i}^{m_i}(\theta,\phi)\,. \tag{39}$$

In Eq. (38) the allowable spherical harmonics are determined from Eqs. (24)–(27) as explained above and the sum over ν contains all symmetries thus allowed. The radial part of $\phi_i^{s,t}$ contains the product of $\eta_i(r)$, the radial part of the unperturbed form of the ith orbital, and $P_{i\nu}^{s,t}(r)$, an arbitrary polynomial in r of the form

$$P_{i\nu}^{s,t}(r)=\sum_{k=1}^{N_0} C_k r^k\,. \tag{40}$$

Here the C_k are the variation parameters and N_0 is determined as the number of terms in $P_{i\nu}^{s,t}(r)$ for which the value of the functional has converged to desired accuracy. Through the variational procedure a set of C_k is determined for each type of angular symmetry in each of the perturbed orbitals. The radial functions are chosen in this particular form for flexibility and for computational convenience. In Table I the type of angular symmetry which must be included in each of the perturbed orbitals are summarized.

IV. RESULTS AND DISCUSSION

The trial orbitals $\phi_i^{s,t}$ are substituted into the appropriate functional, which is minimized to yield the perturbed orbitals $\chi_i^{1,0}$, $\chi_i^{0,1}$, $\chi_i^{2,0}$, and $\chi_i^{1,1}$. Once these orbitals are obtained $E^{2,2}$ is evaluated according to Eq. (22). The two components required to specify the magnetoelectric susceptibility $\beta(\eta)$ are obtained by carrying out this procedure for the cases of perpendicular and parallel electric and magnetic fields. These calculations were carried out on an IBM 7044 computer. Further details concerning these calculations are given elsewhere.[14]

In Table II the calculated magnetoelectric susceptibilities for neutral atoms are given for several choices of ground-state function. The size of the basis set of the outermost orbitals and the zero-order energy are tabulated to show the relationship between these quantities and the calculated properties for the various functions for the same atom. It is seen that the variation among the calculated values of β is much greater than that in the zero-order energies. This is not surprising since the zero-order wave functions $\chi_i^{0,0}$ are obtained subject to the requirement that the energy be a minimum. Since the part of the wave function which contributes the major share of the zero-order energy is the region nearest the nucleus, while the largest contribution to the magnetoelectric susceptibility comes from the outermost shell of the atom, these two properties are able to convey quite different information about the wave function.

TABLE I. Spherical harmonics required in perturbed orbitals.[a]

	Symmetry of unperturbed orbital		
	s	p_0	$p_{\pm1}$
$\chi_i^{1,0}$	p_0	s, d	$d_{\pm1}$
$\chi_i^{0,1}$	None	p_1, p_{-1}	p_0
$\chi_i^{2,0}$	s, d_0	p_0, f_0	$p_{\pm1}, f_{\pm1}$
$\chi_i^{1,1}$	p_1, p_{-1}	d_1, d_{-1}	$s, d_0, d_{\pm2}$

[a] See Eq. (38) of text.

TABLE II. Sensitivity of magnetoelectric susceptibility to the choice of zeroth-order function.

Atom[a]	No. of basis functions in orbitals s	p	Field free energy[b] $(-E_0)$	Magnetoelectric susceptibility[b] $(\beta^{\perp})$	$(\beta^{\parallel})$
He[c]	4	···	2.8616785	-0.100×10^{-3}	-0.888×10^{-4}
He[c]	5	···	2.861680	-0.988×10^{-4}	-0.878×10^{-4}
He[d]	12	···	2.861680	-0.988×10^{-4}	-0.879×10^{-4}
He[e]	3	···	2.861680	-0.991×10^{-4}	-0.880×10^{-4}
Be[c]	5	···	14.573014	0.104×10^{-1}	-0.258×10^{-1}
Be[d]	12	···	14.57302	0.122×10^{-1}	-0.245×10^{-1}
Be[e]	5	···	14.57302	0.124×10^{-1}	-0.244×10^{-1}
Be[f]	6	···	14.57302	0.122×10^{-1}	-0.245×10^{-1}
Ne[g]	7	5	128.54318	-0.162×10^{-2}	-0.912×10^{-3}
Ne[c]	5	4	128.54698	-0.424×10^{-3}	-0.233×10^{-3}
Ne[f]	6	4	128.5470	-0.423×10^{-3}	-0.232×10^{-3}
Ne[h]	7	6	128.5470	-0.377×10^{-3}	-0.207×10^{-3}
Ne[e]	5	4	128.5471	-0.396×10^{-3}	-0.217×10^{-3}
Mg[c]	7	3	199.61432	0.112	-0.483×10^{-1}
Mg[c]	8	5	199.61458	0.181	-0.513×10^{-1}
A[i]	3	2	525.76526	-0.568×10^{-3}	-0.202×10^{-3}
A[j]	6	4	526.78407	-0.206×10^{-2}	-0.112×10^{-2}
A[k]	9	7	526.81401	0.584×10^{-1}	-0.605×10^{-2}
A[c]	7	5	526.81706	-0.641×10^{-3}	-0.192×10^{-2}
A[c]	8	8	526.81734	-0.343×10^{-3}	-0.242×10^{-2}
A[l]	7	7	526.81743	-0.144×10^{-2}	-0.226×10^{-2}

[a] References for Hartree-Fock functions.
[b] All numerical quantities are given in atomic units.
[c] E. Clementi, IBM J. Res. Develop. **9**, 2 (1965).
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Thus the magnetoelectric susceptibilities are useful along with the energies in assessing the quality of zero-order wave functions. Another purpose for compiling the quantities of Table II is to provide a check on the value of β. It is felt that if several values of β are similar and one or two differ somewhat from these, the similar values are most reliable. This is quite clearly illustrated in the case of $\beta^{\parallel}$ for beryllium. In this case three values are about −0.0245 atomic units (au) while a fourth is −0.0258 au. Thus the value $\beta^{\parallel}$ −0.0245 au is considered most reliable.

As shown above, the perturbed orbitals $\chi_i^{s,t}$ contain arbitrary polynomials in r, $P_{i,\nu}^{s,t}$ as given in Eq. (40). The effect of the number of terms included in this polynomial on the calculated properties is investigated. Some results of this test are given as Table III. Here the values of the fourth-order energy $E^{2,2}$ for the case of parallel electric and magnetic fields are given for the total energy and for the major orbital contributions to the energy when the polynomial contains two, three, four, and five terms. This number of terms is referred to as N_0 in Eq. (40). Convergence to three places seems assured with the inclusion of five terms in the polynomial with the possible exception of calcium. In the case of calcium, which seems to show the poorest convergence, two digits appear to be reliable.

The calculated values of the magnetoelectric susceptibilities for all systems considered are given as Table IV. The results are given for the case in which the electric and magnetic fields are perpendicular as well as that in which they are parallel. The values given in this table are those judged most reliable for each of the systems considered. Thus, as indicated above, the value tabulated for $\beta^{\parallel}$ in beryllium is −0.0245 au.

TABLE III. Convergence of the trial perturbed orbitals. The mixed fourth-order energy $E^{2,2}$ is given with increasing number of terms in the polynomial in r, $P_{i,\nu}^{s,t}$.

Atom[a]	Contribution	Number of terms[b] 2	3	4	5
He[c]	Total	0.216×10^{-4}	0.220×10^{-4}	0.220×10^{-4}	0.220×10^{-4}
Be[d]	$2s$	0.5347×10^{-2}	0.6662×10^{-2}	0.6438×10^{-2}	0.6438×10^{-2}
	Total	0.535×10^{-2}	0.666×10^{-2}	0.644×10^{-2}	0.644×10^{-2}
Ne[e]	$2p_1$	0.1407×10^{-4}	0.1531×10^{-4}	0.1518×10^{-4}	0.1518×10^{-4}
	$2p_0$	0.2738×10^{-4}	0.2674×10^{-4}	0.2726×10^{-4}	0.2724×10^{-4}
	Total	0.560×10^{-4}	0.579×10^{-4}	0.581×10^{-4}	0.581×10^{-4}
Mg[d]	$3s$	0.9475×10^{-2}	0.1355×10^{-1}	0.1285×10^{-1}	0.1284×10^{-1}
	Total	0.948×10^{-2}	0.136×10^{-1}	0.129×10^{-1}	0.128×10^{-1}
A[d]	$3s$	0.2328×10^{-5}	0.1370×10^{-4}	0.1038×10^{-4}	0.1063×10^{-4}
	$3p_1$	0.1243×10^{-3}	0.1331×10^{-3}	0.1326×10^{-3}	0.1326×10^{-3}
	$3p_0$	0.2117×10^{-3}	0.1998×10^{-3}	0.2036×10^{-3}	0.2045×10^{-3}
	Total	0.463×10^{-3}	0.480×10^{-3}	0.479×10^{-3}	0.480×10^{-3}
Ca[d]	$4s$	0.2252×10^{-1}	0.4280×10^{-1}	0.3789×10^{-1}	0.3837×10^{-1}
	Total	0.226×10^{-1}	0.429×10^{-1}	0.379×10^{-1}	0.384×10^{-1}

[a] References to the zero-order Hartree-Fock functions are given under Table II.
[b] See Eqs. (38) and (40) of text.
[c] See Ref. d of Table II.
[d] See Ref. c of Table II.
[e] See Ref. f of Table II.

These results follow certain general trends. Within an isoelectronic series the values decrease as the degree of ionization increases. This is of course simply a manifestation of the fact that the inner electrons are more tightly bound and thus the positive ions are less

TABLE IV. Magnetoelectric susceptibilities of S-state atomic systems.

Atom or ion[a]	Magnetoelectric susceptibility[b] $\beta^{\perp}$	$\beta^{\parallel}$	Atom or ion[a]	Magnetoelectric susceptibility[b] $\beta^{\perp}$	$\beta^{\parallel}$
H^{-} [c]	-0.158×10^{1}	-0.127×10^{1}			
He [d]	-0.988×10^{-4}	-0.878×10^{-4}	Li^{-} [d]	-0.199×10^{3}	-0.161×10^{3}
Li^{+} [d]	-0.153×10^{-5}	-0.142×10^{-5}	Be [e]	0.122×10^{-1}	-0.245×10^{-1}
Be^{2+} [d]	-0.105×10^{-6}	-0.976×10^{-7}	B^{+} [d]	0.130×10^{-2}	-0.571×10^{-3}
B^{3+} [d]	-0.137×10^{-7}	-0.129×10^{-7}	C^{2+} [d]	0.192×10^{-3}	-0.374×10^{-4}
C^{4+} [d]	-0.270×10^{-8}	-0.257×10^{-8}	N^{3+} [d]	0.396×10^{-4}	-0.464×10^{-5}
N^{5+} [d]	-0.699×10^{-9}	-0.671×10^{-9}	O^{4+} [d]	0.105×10^{-4}	-0.850×10^{-6}
			F^{5+} [d]	0.338×10^{-5}	-0.200×10^{-6}
O^{2-} [f]	-0.770×10^{2}	-0.490×10^{2}			
F^{-} [g]	-0.150×10^{-1}	-0.851×10^{-2}	Na^{-} [h]	-0.384×10^{2}	-0.567×10^{2}
Ne [g]	-0.396×10^{-3}	-0.217×10^{-3}	Mg [d]	-0.181	-0.513×10^{-1}
Na^{+} [g]	-0.467×10^{-4}	-0.252×10^{-4}	Al [d]	0.149×10^{-1}	-0.159×10^{-2}
Mg^{2+} [d]	-0.956×10^{-5}	-0.512×10^{-5}	Si^{2+} [d]	0.349×10^{-2}	0.808×10^{-4}
Al^{3+} [d]	-0.261×10^{-5}	-0.139×10^{-5}	P^{3+} [d]	0.108×10^{-2}	0.867×10^{-4}
Si^{4+} [d]	-0.874×10^{-6}	-0.463×10^{-6}	S^{4+} [d]	0.401×10^{-3}	0.430×10^{-4}
P^{5+} [d]	-0.339×10^{-6}	-0.179×10^{-6}	Cl^{5+} [d]	0.170×10^{-3}	0.215×10^{-4}
Cl^{-} [h]	-0.654×10^{-1}	-0.346×10^{-1}	K^{-} [i]	-0.444×10^{3}	-0.449×10^{3}
A [j]	-0.144×10^{-2}	-0.226×10^{-2}	Ca [d]	0.727	-0.154
K^{+} [d]	-0.775×10^{-3}	-0.357×10^{-3}			
Ca^{2+} [d]	-0.207×10^{-3}	-0.915×10^{-4}			
Sc^{3+} [d]	-0.693×10^{-4}	-0.293×10^{-4}			
Ti^{4+} [d]	-0.272×10^{-4}	-0.111×10^{-4}			
V^{5+} [d]	-0.120×10^{-4}	-0.473×10^{-5}			

[a] References are to the zero-order Hartree-Fock functions.
[b] The magnetoelectric susceptibilities are given in atomic units.
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[j] See Ref. 1 of Table II.

TABLE V. Properties determined by the anisotropy K.

Range of K	Relative size	Change in β[a]	Sign of β[a]
$K<-2$	$\lvert\beta^{\parallel}\rvert > \lvert\beta^{\perp}\rvert$	Decrease	Changed
$-2<K<-1$	$\lvert\beta^{\parallel}\rvert < \lvert\beta^{\perp}\rvert$	Decrease	Changed
$-1<K<0$	$\lvert\beta^{\parallel}\rvert < \lvert\beta^{\perp}\rvert$	Decrease	Unchanged
$0<K<1$	$\lvert\beta^{\parallel}\rvert < \lvert\beta^{\perp}\rvert$	Increase	Unchanged
$1<K<2$	$\lvert\beta^{\parallel}\rvert < \lvert\beta^{\perp}\rvert$	Increase	Changed
$2<K$	$\lvert\beta^{\parallel}\rvert > \lvert\beta^{\perp}\rvert$	Increase	Changed

[a] These changes in β are those which occur as the fields are rotated from perpendicular to parallel relative orientation.

deformable in a field. Also the magnetoelectric susceptibilities of the neutral inert-gas atoms increase with Z as do the values for the alkaline-earth neutral atoms. However, the values for the second group systems are considerably larger than those of the inert-gas atoms. This demonstrates the greater stability of the systems, which consist entirely of filled shells over those which contain an additional doubly occupied subshell.

These general trends are also observed in the linear multipole polarizabilities,[15] the uniform-field quadrupole polarizabilities,[16] and the hyperpolarizabilities.[17] However, in all but the hyperpolarizabilities the variations are less pronounced than with β.

TABLE VI. Characteristics of magnetoelectric susceptibility. (Demonstration of the dependence of β upon the angle between the two field directions for all systems considered.)

Atom or ion[a]	Anisotropy (K) [b]	Atom or ion	Anisotropy (K) [b]	Null angle (η_0) [c]
H^{-} [d]	-0.20			
He [e]	-0.11	Li^{-} [e]	-0.14	...
Li^{+} [e]	-0.072	Be [f]	3.0	55°
Be^{2+} [e]	-0.070	B^{+} [e]	1.4	35°
B^{3+} [e]	-0.058	C^{2+} [e]	1.2	25°
C^{4+} [e]	-0.048	N^{3+} [e]	1.1	20°
N^{5+} [e]	-0.040	O^{4+} [e]	1.1	15°
		F^{5+} [e]	1.1	15°
O^{2-} [g]	-0.36			
F^{-} [h]	-0.43	Na^{-} [i]	0.48	...
Ne [h]	-0.45	Mg [e]	1.3	30°
Na^{+} [h]	-0.46	Al^{+} [e]	1.1	20°
Mg^{2+} [e]	-0.46	Si^{2+} [e]	0.98	...
Al^{3+} [e]	-0.47	P^{3+} [e]	0.92	...
Si^{4+} [e]	-0.47	S^{4+} [e]	0.89	...
P^{5+} [e]	-0.47	Cl^{5+} [e]	0.87	...
Cl^{-} [i]	-0.47	K^{-} [j]	0.01	...
A [k]	0.57	Ca [e]	1.2	25°
K^{+} [e]	-0.54			
Ca^{2+} [e]	-0.56			
Sc^{3+} [e]	-0.58			
Ti^{4+} [e]	-0.59			
V^{5+} [e]	-0.61			

[a] References are to the list of zero-order Hartree-Fock functions given under Tables II and IV.
[b] The quantity K is defined by: $K=(\beta^{\perp}-\beta^{\parallel})/\lvert\beta^{\perp}\rvert$.
[c] The null angle η_0 is the angle at which $\beta=0$.
[d] See Ref. c of Table IV.
[e] See Ref. c of Table II.
[f] See Ref. f of Table II.
[g] See Ref. f of Table IV.
[h] See Ref. e of Table II.
[i] See Ref. h of Table IV.
[j] See Ref. i of Table IV.
[k] See Ref. 1 of Table II.

It is also interesting to note the signs in Table IV. Every one of the two-, ten-, and eighteen-electron systems has a negative value of β whatever the orientation of the fields. The situation is quite different for the alkaline-earth systems. The negative ions have negative values of β for all field orientations. For the neutral atoms, the positive four-electron ions, and Al^{+}, the sign of β depends upon the relative orientation of the fields. In fact, for one value of β, the magnetoelectric susceptibility vanishes for these systems. For the other twelve electron, positive ions, β is positive for all relative field orientations. Thus all possible signs are exhibited in the four-, twelve-, and twenty-electron systems.

A convenient way to examine the properties of β more closely is by considering its variation as the angle between the electric and magnetic fields is changed. It is helpful to define the anisotropy of β as

$$K=(\beta^{\perp}-\beta^{\parallel})/\lvert\beta^{\perp}\rvert\,. \tag{41}$$

Much information about β is obtained from a knowledge of K. This information is summarized in Table V.

As shown in Table V, K tells whether $\lvert\beta^{\parallel}\rvert$ or $\lvert\beta^{\perp}\rvert$ is larger, whether β is increased or decreased as the angle η decreases from 90° to 0°, and whether or not the sign of β changes. Throughout this section the changes in β discussed are those which occur as the relative orientation of the fields is changed from perpendicular to parallel.

When the sign of β changes, there must be some value of η for which β vanishes. That "null angle" is called η_0 and is defined by

$$\beta^{\perp}+(\beta^{\parallel}-\beta^{\perp})\cos^2\eta_0=0\,. \tag{42}$$

Thus

$$\cos\eta_0=[\beta^{\perp}/(\beta^{\perp}-\beta^{\parallel})]^{1/2}=1/\sqrt{K}\,. \tag{43}$$

The anisotropies and null angles are tabulated in Table VI.

The general trends shown in this table are quite interesting. All K's in the first column are in the range $-1<K<0$ with the exception of A. Also the values are decreasing as Z increases in the two-electron isoelectronic series, while they increase with Z for the ten- and eighteen-electron series. Again, the only exception is argon. However, while the K values do differ widely among the six argon functions used, those of the three functions judged most reliable by all other standards are consistently positive. The value of the argon anisotropy may be a valid anomaly; however, it

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seems quite possible that the approximations made here and those inherent to the Hartree-Fock framework make the results for an atom with 18 electrons very much in error.[7]

In the alkaline-earth K values there are only three exceptions and these are not entirely unexpected. All values in this column are greater than unity or approximately unity except for the three negative ions. Also, excluding the negative ions again, they all decrease with increasing Z. It would seem most likely that the anomalous behavior of the Li$^-$, Na$^-$, and K$^-$ functions is due to the inherent inadequacy of the Hartree-Fock description of negative ions.

ACKNOWLEDGMENT

It is a pleasure to thank Professor A. David Buckingham for several helpful discussions and suggestions during the course of this work.

PHYSICAL REVIEW VOLUME 162, NUMBER 1 5 OCTOBER 1967

Stark Broadening of H_β, H_γ, and H_δ: An Experimental Study*

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(Received 11 May 1967)

Stark-broadened H_β, H_γ, and H_δ line profiles from a spatially uniform plasma column which was formed in a critically damped discharge tube were recorded with a rapid-scan spectrometer. A plasma temperature of $\sim$2 eV was inferred from both H_β- and H_γ-to-continuum ratios. Values of the electron density were determined to an estimated accuracy of better than $\pm 2\%$ by means of two multiple-pass laser interferometers operating at infrared and visible wavelengths. Systematic errors in recording and analyzing the line profiles are estimated to be less than $\pm 1.5\%$. For interferometric values of the electron density in the range $(1.3-8.5)\times 10^{16}$ cm^{-3}, the measured half-intensity widths of all the recorded H_β profiles agreed to within $\pm 2\%$ of the widths predicted by Stark-broadening theory. In this comparison, the $\pm 2\%$ represents the maximum scatter of the measured half-intensity widths where the theoretical widths were determined using the interferometric values of electron density which were taken as the standard. The total systematic error in this comparison is estimated to be less than $\pm 3.5\%$. For H_γ the measured half-intensity widths ranged from 11 to 25% larger than that predicted by theory for electron densities in the range $(1.3-7.1)\times 10^{16}$ cm^{-3}. For H_δ the measured half-intensity widths are 7% narrower than that predicted by theory for electron densities in the range $(1.3-2.8)\times 10^{16}$ cm^{-3}. Because the H_β, H_γ, and H_δ profiles were recorded from the same plasma, systematic errors in measuring the electron density will affect the comparison of theory and experiment for each line in the same sense. Thus the relative systematic errors between the comparison of all three lines with the theory are estimated to be less than $\pm 1.5\%$.

I. INTRODUCTION

THE dominant line-broadening mechanism in dense plasmas ($N_e > 10^{15}$ cm^{-3}, $T_e < 10$ eV) is Stark broadening caused by the electric microfields of the free electrons and ions which surround the radiating atoms. Because hydrogen is subject to a linear Stark effect, the Balmer lines experience a pronounced Stark broadening which depends almost entirely on the charged-particle density. Thus, experimentally obtained Stark profiles can be used as a measure of electron density provided the relationship between broadening and electron density is well known.

Previous experimental studies of Stark-broadened Balmer lines emitted by arcs[1,2] and shock tubes[3] indicated significant inadequacies in the old Holtzmark theory.[4] The development of a generalized impact approximation by Kolb and Griem[5] and independently by Baranger[6] led to an improved Stark-broadening theory which included the effects of electrons, Debye shielding, and ion-ion correlations.[7,8] Theoretical profiles have been tabulated by Griem[9] which are estimated to have an over-all accuracy of better than 15%. This corresponds to a possible error of $\pm 20\%$ in the electron densities deduced from recorded profiles.[8]

Among the several groups who performed previous experimental checks of the theory, Berg *et al.*[10] found that the Stark theory for H_α, H_β, and H_γ predicted

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* This work was supported by the U. S. Atomic Energy Commission.

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