

Rayleigh Scattering and the Electromagnetic Susceptibility of Atoms*

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Rayleigh scattering of light by atoms is considered from the point of view of relativistic electron theory. The relationship between the coherent S -matrix element and the frequency-dependent electric and magnetic multipole susceptibilities of the atom is established. Single-particle radial equations are derived for the perturbed electron orbitals, assuming that the atom is described by a relativistic Hartree-Fock-Slater (RHFS) wave function. These equations reduce to the inhomogeneous Schrödinger equations commonly used to evaluate electric polarizabilities when relativistic (fine-structure) effects are neglected. Numerical solutions to the radial equations are obtained for the noble gases. The electric- and magnetic-dipole susceptibilities are compared with previous nonrelativistic calculations as well as with experimental values. The magnetic susceptibilities are found to be essentially independent of frequency, and to agree to within 1% with static experimental values for all of the noble gases except He. The accuracy of the electric polarizability decreases from about 5% for He and Ne to about 50% for Xe. Relativistic effects are almost entirely negligible for magnetic susceptibilities; they are noticeable only in the case of Xe. In the electric polarizability calculations, relativistic effects are completely masked by the crude nature of the RHFS computational techniques.

I. MULTIPOLE DECOMPOSITION OF THE RAYLEIGH-SCATTERING MATRIX ELEMENT

THE cross section for Rayleigh scattering by an atom can be written¹

$$\frac{d\sigma}{d\Omega} = \alpha^2 |M|^2, \quad (1.1)$$

where²

$$M = \sum_n \left[\frac{\langle g|A'|n\rangle\langle n|A|g\rangle}{E_g + \omega - E_n} + \frac{\langle g|A|n\rangle\langle n|A'|g\rangle}{E_g - \omega - E_n} \right]. \quad (1.2)$$

In Eq. (1.2), $|g\rangle$ and $|n\rangle$ refer to the ground state and the excited states of an N -electron atom, while E_g and E_n are the corresponding energies. We use A and A' to designate the operators (in electron spin space) associated with the absorption and emission of a photon of frequency ω . Adopting the point of view of relativistic electron theory, we write

$$A = \hat{\epsilon} \cdot \sum_{j=1}^N \alpha_j e^{i\mathbf{k} \cdot \mathbf{r}_j},$$

$$A' = \hat{\epsilon}' \cdot \sum_{j=1}^N \alpha_j e^{-i\mathbf{k}' \cdot \mathbf{r}_j}, \quad (1.3)$$

where \mathbf{r}_j is the position vector of the j th electron and α_j is the corresponding Dirac matrix. The wave vectors \mathbf{k} and \mathbf{k}' refer to the incident and scattered photon, respectively; $\hat{\epsilon}$ and $\hat{\epsilon}'$ are the photon polarization vectors.

The individual terms in Eq. (1.3) can be expanded in a multipole series,

$$\hat{\epsilon} e^{i\mathbf{k} \cdot \mathbf{r}} = \sum_{JM\lambda} C_{JM\lambda}(\hat{k}) \mathbf{a}_{JM\lambda}(\mathbf{r}). \quad (1.4)$$

Here J and M are the multipole angular-momentum indices and $\lambda = 0, 1$ characterizes the parity of the multipole ($\lambda = 0$ refers to a magnetic multipole and $\lambda = 1$ refers to an electric multipole, the parity of the multipole is $J + \lambda - 1$). The multipole components of the vector potential are³

$$\mathbf{a}_{JM^0}(\mathbf{r}) = j_J(\omega r) \mathbf{Y}_{JM}(\hat{r}) = j_J(\omega r) \mathbf{Y}_{JM}^{(0)}(\hat{r}),$$

$$\mathbf{a}_{JM^1}(\mathbf{r}) = \left(\frac{J+1}{2J+1} \right)^{1/2} j_{J-1}(\omega r) \mathbf{Y}_{J-1M}(\hat{r})$$

$$- \left(\frac{J}{2J+1} \right)^{1/2} j_{J+1}(\omega r) \mathbf{Y}_{J+1M}(\hat{r}). \quad (1.5)$$

It is convenient to introduce the functions

$$\phi_{JM}(\mathbf{r}) = j_J(\omega r) Y_{JM}(\hat{r}), \quad (1.6)$$

and to note that

$$\mathbf{a}_{JM^1}(\mathbf{r}) \approx - \left(\frac{J+1}{J} \right)^{1/2} \nabla \phi_{JM}(\mathbf{r}). \quad (1.7)$$

The error involved in the approximation (1.7), which

³ We adopt the notation of Ref. 2 (pp. 24-29) for the spherical vectors \mathbf{Y}_{JLM} and $\mathbf{Y}_{JM}^{(\lambda)}$, and we use $j_J(\omega r)$ to denote a spherical Bessel function of order J .

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¹ We use natural units throughout: $\hbar = c = 1$, $e^2/4\pi = \alpha$, $\alpha^{-1} = 137.0388$.

² A derivation of Eq. (1.2) for a one-electron system which is easily generalizable to a multielectron atom is given in A. I. Akhiezer and V. B. Beresetskii, *Quantum Electrodynamics* (Interscience Publishers, Inc., New York, 1965), pp. 484-491.

is of order $(\omega a)^2$ (where a is a characteristic atomic radius), is seen to be completely negligible at optical frequencies. The expansion coefficients $C_{JM}^\lambda(\hat{k})$ in Eq. (1.4) are given by

$$C_{JM}^\lambda(\hat{k}) = 4\pi i^{J-\lambda} (\mathbf{Y}_{JM}^{(\lambda)}(\hat{k}) \cdot \hat{\epsilon}). \quad (1.8)$$

Corresponding to the multipole decomposition of the individual terms of Eq. (1.3), there is, of course, an expansion of the emission and absorption operators of the N -electron system:

$$\begin{aligned} A &= \sum_{JM\lambda} C_{JM}^\lambda(\hat{k}) A_{JM}^\lambda, \\ A'^* &= \sum_{JM\lambda} C_{JM}^\lambda(\hat{k}') A_{JM}^\lambda, \end{aligned} \quad (1.9)$$

with

$$A_{JM}^\lambda = \sum_{j=1}^N \alpha_j \cdot \mathbf{a}_{JM}^\lambda(\mathbf{r}_j). \quad (1.10)$$

The matrix element M therefore decomposes as

$$M = \sum_{JM\lambda, J'M'\lambda'} C_{JM}^\lambda(\hat{k}) C_{J'M'}^{\lambda'*}(\hat{k}') M_{JM\lambda, J'M'\lambda'}, \quad (1.11)$$

where

$$\begin{aligned} M_{JM\lambda, J'M'\lambda'} &= \sum_n \left[\frac{\langle g | A_{J'M'}^{\lambda'*} | n \rangle \langle n | A_{JM}^\lambda | g \rangle}{E_g + \omega - E_n} \right. \\ &\quad \left. + \frac{\langle g | A_{JM}^\lambda | n \rangle \langle n | A_{J'M'}^{\lambda'*} | g \rangle}{E_g - \omega - E_n} \right]. \end{aligned} \quad (1.12)$$

The operators A_{JM}^λ are related simply to the multipole moment operators Q_{JM}^λ of the atomic system²:

$$Q_{JM}^\lambda = -ie \left(\frac{J(2J+1)}{J+1} \right)^{1/2} \frac{(2J-1)!!}{\omega^J} A_{JM}^{\lambda*}. \quad (1.13)$$

As $\omega \rightarrow 0$, one easily shows from (1.13) that

$$\langle g | Q_{J0}^1 | g \rangle = \frac{e}{(4\pi)^{1/2}} \langle g | \sum_{j=1}^N r_j^J P_J(\cos\theta_j) | g \rangle, \quad (1.14)$$

$$\langle g | Q_{1M}^0 | g \rangle = \frac{e}{(4\pi)^{1/2}} \langle g | \frac{1}{2} \sum_{j=1}^N [\mathbf{r}_j \times \boldsymbol{\alpha}_j]_M | g \rangle.$$

Averaging $M_{JM\lambda, J'M'\lambda'}$ over the angular-momentum orientations of the atomic ground state we obtain

$$\begin{aligned} \langle M_{JM\lambda, J'M'\lambda'} \rangle_{\text{av}} &= -\frac{1}{4\pi\alpha} \frac{J+1}{J(2J+1)} \frac{\omega^{2J}}{[(2J-1)!!]^2} \\ &\quad \times \chi_{2J}^\lambda(\omega) \delta_{JJ'} \delta_{MM'} \delta_{\lambda\lambda'}, \end{aligned} \quad (1.15)$$

where

$$\begin{aligned} \chi_{2J}^\lambda(\omega) &= -\sum_n \left[\frac{\langle g | Q_{JM}^\lambda | n \rangle \langle n | Q_{J'M'}^{\lambda'*} | g \rangle}{E_g + \omega - E_n} \right. \\ &\quad \left. + \frac{\langle g | Q_{J'M'}^{\lambda'*} | n \rangle \langle n | Q_{JM}^\lambda | g \rangle}{E_g - \omega - E_n} \right] \end{aligned} \quad (1.16)$$

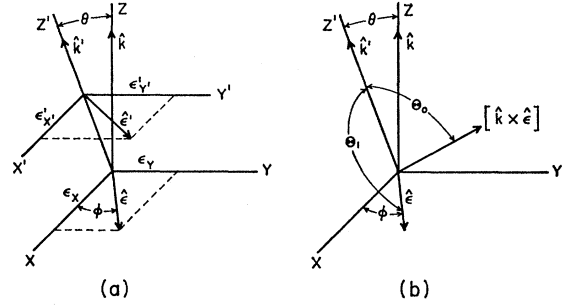


FIG. 1. (a) The coordinate system X', Y', Z' is attached to the vector k' (which is in the X, Z plane); the Y' axis is parallel to the Y axis. (b) The angles Θ_0 and Θ_1 occurring in the differential cross section are the angles of ϵ and $k \times \epsilon$ measured relative to k' .

is the 2^J -pole electric or magnetic⁴ susceptibility of the atom.

In the following section, we will reduce Eq. (1.11) to a form suitable for the evaluation of the Rayleigh-scattering cross section for closed subshell atoms in terms of the susceptibilities $\chi_{2J}^\lambda(\omega)$. Equation (1.12) is brought into a form appropriate to the numerical evaluation of the susceptibilities of arbitrary multi-electron atoms in Sec. III. In Sec. IV the formulas developed in Sec. III are shown to reduce to their familiar forms in the nonrelativistic limit. Some numerical results for the electric and magnetic susceptibilities of the noble gases are presented in Sec. V and compared with previous calculations as well as with experimental values.

II. RAYLEIGH SCATTERING OF POLARIZED PHOTONS

Choosing the coordinate system illustrated in Fig. 1(a) and making use of the explicit expressions for $C_{JM}^\lambda(\hat{k})$ given in Eq. (1.8) we can write the Rayleigh-scattering matrix element for an atom with closed subshells as

$$M = M_x \epsilon_x \epsilon_{x'} + M_y \epsilon_y \epsilon_{y'}, \quad (2.1)$$

where

$$\begin{aligned} M_x &= \frac{1}{2} \sum_{J=1}^{\infty} (2J+1) \left[\left(P_J - \frac{P_{J^2}}{J(J+1)} \right) X_{J^1} \right. \\ &\quad \left. + \left(\frac{1}{2} (P_{J-1} + P_{J+1}) + \frac{P_{J-1^2} + P_{J+1^2}}{2J(J+1)} \right) X_{J^0} \right], \\ M_y &= \frac{1}{2} \sum_{J=1}^{\infty} (2J+1) \left[\left(\frac{1}{2} (P_{J-1} + P_{J+1}) \right. \right. \\ &\quad \left. \left. + \frac{P_{J-1^2} + P_{J+1^2}}{2J(J+1)} \right) X_{J^1} + \left(P_J - \frac{P_{J^2}}{J(J+1)} \right) X_{J^0} \right]. \end{aligned} \quad (2.2)$$

In Eqs. (2.2) $P_J^m(\cos\theta)$ is an associated Legendre func-

⁴ The diamagnetic susceptibility of atoms is determined from the "A²" term in the interaction Hamiltonian by a first-order perturbation calculation in nonrelativistic theory. In a relativistic theory there is no A² term and the corresponding contribution to χ_2^0 is contained in the second-order matrix element (1.16).

tion ($P_J = P_J^0$), normalized as in Ref. 2. To simplify the notation somewhat we have used

$$X_{J^\lambda} = \frac{1}{4\pi} M_{JM\lambda}; J_{M\lambda}. \quad (2.3)$$

If we square M and sum over the polarization states of the outgoing photon we obtain an expression for the Rayleigh scattering of polarized photons,

$$\frac{d\sigma}{d\Omega} = \alpha^2 (|M_x|^2 \cos^2\phi + |M_y|^2 \sin^2\phi). \quad (2.4)$$

Integrating (2.4) over the outgoing photon directions, we obtain a general formula for total cross section,

$$\sigma(\omega) = 2\pi\alpha^2 \sum_{J\lambda} (2J+1) |X_{J^\lambda}|^2. \quad (2.5)$$

At optical frequencies, by far the most important contributions to Eqs. (2.4) and (2.5) arise from the dipole terms $J=1$. In the dipole approximation

$$\begin{aligned} M_x &\approx \frac{3}{2} [\cos\theta X_1^1 + X_1^0], \\ M_y &\approx \frac{3}{2} [X_1^1 + \cos\theta X_1^0], \end{aligned} \quad (2.6)$$

and therefore, using expression (1.15) to relate X_1^λ to the dipole susceptibilities $\chi_2^\lambda(\omega)$, we find

$$\begin{aligned} \frac{d\sigma}{d\Omega} &\approx \omega^4 \{ \sin^2\Theta_1 [\chi_2^1(\omega)]^2 \\ &+ 2 \cos\theta \chi_2^1(\omega)\chi_2^0(\omega) + \sin^2\Theta_0 [\chi_2^0(\omega)]^2 \}. \end{aligned} \quad (2.7)$$

The angles Θ_1 and Θ_0 are illustrated in Fig. 1(b). Since for the noble gases the magnetic susceptibilities are about -10^{-5} of the electric polarizability (at optical frequencies), Eq. (2.7) reduces to the first term only, which is the well-known classical formula for Rayleigh scattering.

It is amusing to note that an interference of the type expressed by the second term in Eq. (2.7) has been observed⁵ recently in the Rayleigh scattering of polarized light from a Ruby laser (6943 Å) on the noble gases Ar and Xe. Because of the small size and sign of $\chi_2^0(\omega)$ it is apparent that effects of the observed magnitude and sign are not explained on atomic grounds.

III. RELATIVISTIC THEORY OF ELECTRIC AND MAGNETIC SUSCEPTIBILITIES

We are interested in obtaining expressions for $\chi_2^{J^\lambda}(\omega)$ which are amenable to more detailed study. To this end, we approximate the atomic states $|g\rangle$ and $|n\rangle$ by antisymmetric relativistic Hartree-Fock-Slater (RHFS) product wave functions. The individual electron orbitals satisfy single-particle Dirac equations with a self-consistent potential. This potential is constructed by

⁵ T. V. George, L. Goldstein, L. Slama, and M. Yokoyama, *Phys. Rev.* **137**, A369 (1965).

making the Slater approximation for the exchange term and by spherically averaging the direct part of the electron-electron interaction (a procedure which is of course unnecessary for atoms with completely closed subshells). A technique for evaluating RHFS wave functions numerically is described by Liberman, Waber, and Cromer.⁶

The advantages of using relativistic orbitals in the expressions for $\chi_2^{J^\lambda}(\omega)$ are twofold. First, the fine structure of the atomic levels is included automatically in the calculation; and second, the individual electron excitation energies are determined much more accurately for heavy atoms using the relativistic theory. The advantage of using the Slater variation of the Hartree-Fock method is mainly its simplicity. It should be noted, however, that application of simple relativistic Hartree (RH) wave functions (dropping exchange terms entirely) leads to complications similar to those pointed out by Dalgarno⁷ in connection with the nonrelativistic theory. These complications are associated with the fact that the individual terms connecting two occupied orbitals in Eq. (3.5) do not cancel in a RH calculation, as they must according to the Pauli principle.

We are of course neglecting all effects of electron-electron correlation. The importance of these effects can be seen by comparing a nonrelativistic calculation of the electric susceptibility of He including correlation⁸ and a corresponding calculation neglecting correlation⁹ with the experimental measurements.¹⁰ Since correlation effects are less important in heavier atoms we should expect our calculations to agree with experiment more accurately as the atomic number increases. We find, however, an increasing discrepancy in the electric susceptibilities with increasing atomic number, whereas the corresponding magnetic calculations agree with experiment more or less uniformly for $N=2$ to 54. The peculiarity is probably explained by the fact that the magnetic susceptibility (in the dipole approximation) is sensitive to $\langle r^2 \rangle$ for the one-electron orbitals while the electric susceptibilities depend on the higher moments of the one-electron orbitals as well.

Let us label the one-electron orbitals by a principal quantum number n , an angular quantum number $\kappa = \mp(j + \frac{1}{2})$ for $j = l \pm \frac{1}{2}$ (where j and l are the total and "orbital" angular momenta), and an angular-momentum projection quantum number m . Each orbital $|n\kappa m\rangle$ is assumed to satisfy a central field Dirac equation

$$\begin{aligned} H|n\kappa m\rangle &= \epsilon_{n\kappa}|n\kappa m\rangle, \\ H &= \alpha \cdot \mathbf{p} + \beta m + V(r), \end{aligned} \quad (3.1)$$

where $V(r)$ is determined by the self-consistent pro-

⁶ D. Liberman, J. T. Waber, and D. T. Cromer, *Phys. Rev.* **137**, A27 (1965).

⁷ A. Dalgarno, *Advan. Phys.* **11**, 281 (1962).

⁸ Y. M. Chan and A. Dalgarno, *Proc. Phys. Soc. (London)* **85** 227 (1965).

⁹ M. Karplus and H. J. Kolker, *J. Chem. Phys.* **39**, 2997 (1963).

¹⁰ C. Cuthbertson and M. Cuthbertson, *Proc. Roy. Soc. (London)* **A135**, 44 (1932).

cedure described in Ref. 6. We use the representation of Ref. 2, for the Dirac matrices and employ the angular-momentum eigenstates¹¹

$$\Omega_{km}(\hat{r}) = \sum_{\mu} C(l\frac{1}{2}j; m-\mu, \mu) \chi_{\mu} Y_{l, m-\mu}(\hat{r}), \quad (3.2)$$

where $C(l\frac{1}{2}j; m-\mu, \mu)$ is a Clebsch-Gordan coefficient and χ_{μ} is a two-component Pauli spinor. With this notation in mind, we may write $|n\kappa m\rangle$ in the form

$$|n\kappa m\rangle = \frac{1}{r} \begin{pmatrix} iG_{n\kappa}(r)\Omega_{km}(\hat{r}) \\ F_{n\kappa}(r)\Omega_{-km}(\hat{r}) \end{pmatrix}, \quad (3.3)$$

where

$$\begin{aligned} (\epsilon_{n\kappa} - m - V)G_{n\kappa} - \left(\frac{d}{dr} - \frac{\kappa}{r}\right)F_{n\kappa} &= 0, \\ \left(\frac{d}{dr} + \frac{\kappa}{r}\right)G_{n\kappa} + (\epsilon_{n\kappa} + m - V)F_{n\kappa} &= 0. \end{aligned} \quad (3.4)$$

The expression for $X_{J^{\lambda}}$ in terms of single-electron matrix elements is

$$\begin{aligned} X_{J^{\lambda}} &= \frac{1}{4\pi} \sum_{n\kappa m} \sum_q \left[\frac{(n\kappa m | b_{JM^{\lambda}}^{*} | q)(q | b_{JM^{\lambda}} | n\kappa m)}{\epsilon_{n\kappa} + \omega - \epsilon_q} \right. \\ &\quad \left. \times \frac{(n\kappa m | b_{JM^{\lambda}} | q)(q | b_{JM^{\lambda}}^{*} | n\kappa m)}{\epsilon_{n\kappa} - \omega - \epsilon_q} \right], \end{aligned} \quad (3.5)$$

where q refers collectively to the quantum numbers of a one-electron intermediate state (the corresponding energy ϵ_q may be negative as well as positive), and where $b_{JM^{\lambda}} = \alpha \cdot \mathbf{a}_{JM^{\lambda}}$. The sum over m is to be interpreted as an average for subshells which are partially filled.

As shown in Appendix A, the electric matrix element $X_{J^{\lambda}}$ of Eq. (3.5) can be rewritten in terms of ϕ_{JM} , making use of the approximation (1.7). With this in mind, we may set

$$b_{JM^0} = \alpha \cdot \mathbf{a}_{JM^0}, \quad b_{JM^1} = \left(\frac{J+1}{J}\right)^{1/2} \phi_{JM}. \quad (3.6)$$

It is possible to put Eq. (3.5) into a form more suitable for detailed analysis by introducing the positive and negative frequency perturbations to $|n\kappa m\rangle$;

$$\begin{aligned} |n\kappa m+\rangle &= \sum_q \frac{|q\rangle(q | b_{JM^{\lambda}} | n\kappa m)}{\epsilon_{n\kappa} + \omega - \epsilon_q}, \\ (n\kappa m- | &= \sum_q \frac{(n\kappa m | b_{JM^{\lambda}} | q)(q |}{\epsilon_{n\kappa} - \omega - \epsilon_q}, \end{aligned} \quad (3.7)$$

from which it follows that

$$\begin{aligned} X_{J^{\lambda}} &= \frac{1}{4\pi} \sum_{n\kappa m} [(n\kappa m | b_{JM^{\lambda}}^{*} | n\kappa m+\rangle \\ &\quad + (n\kappa m- | b_{JM^{\lambda}}^{*} | n\kappa m)]. \end{aligned} \quad (3.8)$$

¹¹ M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

The perturbations $|n\kappa m\pm\rangle$ satisfy inhomogeneous Dirac equations¹²

$$\begin{aligned} (\epsilon_{n\kappa} + \omega - H) |n\kappa m+\rangle &= b_{JM^{\lambda}} |n\kappa m\rangle, \\ (n\kappa m- | (\epsilon_{n\kappa} - \omega - H) &= (n\kappa m | b_{JM^{\lambda}}). \end{aligned} \quad (3.9)$$

These equations (which are valid only if all of the atomic electrons interact through a common potential) are the relativistic generalization of the single-particle Schrödinger equations used to describe dispersion effects nonrelativistically.¹³

Equations (3.9) can be reduced to a set of inhomogeneous radial equations and the corresponding matrix elements can be written in terms of radial integrals. The results of these calculations, which are given in Appendix B, are summarized as follows:

$$\begin{aligned} X_{J^{\lambda}} &= \frac{\omega^{2J}}{[(2J+1)!!]^2} \frac{J+1}{J} \sum_{n\kappa} (2j+1) \\ &\quad \times \sum_{\kappa_1} (2j_1+1) R_{n\kappa, \kappa_1, J^{\lambda}}(\omega), \end{aligned} \quad (3.10)$$

where

$$\begin{aligned} R_{n\kappa, \kappa_1, J^1}(\omega) &= \Lambda_{JJ_1} \Pi_{lJl_1} [J_{n\kappa, \kappa_1, J^1}(\omega) + J_{n\kappa, \kappa_1, J^1}(-\omega)], \\ R_{n\kappa, \kappa_1, J^0}(\omega) &= \Lambda_{JJ_1} \Pi_{lJ-1l_1} \left(\frac{\kappa + \kappa_1}{J+1}\right)^2 \\ &\quad \times [J_{n\kappa, \kappa_1, J^0}(\omega) + J_{n\kappa, \kappa_1, J^0}(-\omega)], \end{aligned} \quad (3.11)$$

$$J_{n\kappa, \kappa_1, J^{\lambda}} = \int_0^{\infty} dr [K_{n\kappa, J^{\lambda}} S_{n\kappa, \kappa_1, J^{\lambda}} + L_{n\kappa, J^{\lambda}} T_{n\kappa, \kappa_1, J^{\lambda}}].$$

The coefficients Λ_{JJ_1} defined in Appendix B, Eq. (B11) are listed in Table I. The factor Π_{lJl_1} is defined by

$$\begin{aligned} \Pi_{lJl_1} &= 1, \quad l+J+l_1 \text{ even} \\ &= 0, \quad l+J+l_1 \text{ odd}. \end{aligned} \quad (3.12)$$

The factor Λ_{JJ_1} which vanishes unless $|j-J| \leq j_1 \leq j+J$ guarantees angular-momentum conservation between the photon multipole, the unexcited electron orbital $|n\kappa m\rangle$, and the perturbed orbital $|n\kappa m\pm\rangle$; the factor Π_{lJl_1} in a similar way takes account of parity conservation.

The functions S and T which are radial components of Eqs. (3.9) satisfy

$$(\epsilon_{n\kappa} + \omega - m - V) S_{n\kappa, \kappa_1, J^{\lambda}} - \left(\frac{d}{dr} - \frac{\kappa_1}{r}\right) T_{n\kappa, \kappa_1, J^{\lambda}} = K_{n\kappa, J^{\lambda}},$$

¹² Similar equations have been considered in connection with the coherent scattering of hard photons by K -shell electrons in heavy atoms by G. E. Brown, R. E. Peierls, and J. B. Woodward, Proc. Roy. Soc. (London) A227, 51 (1954).

¹³ A. Sommerfeld, *Atombau und Spektrallinien* (Friedrich Vieweg und Sohn, Braunschweig, 1951), Vol. II, Part 2, p. 360. A comprehensive account of the nonrelativistic equations is given in the review paper of Dalgarno (Ref. 7), which contains an extensive bibliography on the general subject of atomic polarizabilities.

TABLE I. Angular-momentum coupling parameters $\Lambda(jJj_1)$ for the j - j coupling scheme. Symmetry relation: $\Lambda(jJj_1) = \Lambda(j_1Jj)$.

j	j_1/J	1	2	3	4	5	6	7	8	
$\frac{1}{2}$	$\frac{1}{2}$	1/6								
		1/6	1/10							
$\frac{3}{2}$	$\frac{3}{2}$		1/10	1/14						
			1/10	1/14	1/18					
					1/18	1/22				
$\frac{5}{2}$	$\frac{5}{2}$	1/60	1/20	9/140						
		1/10	1/70	1/35	1/21					
			9/140	1/84	5/252	5/132				
				1/21	1/99	1/66	9/286			
$\frac{7}{2}$	$\frac{7}{2}$	1/210	4/105	4/315	1/63	25/693				
		1/14	1/210	1/42	5/462	5/462	25/858			
			1/21	1/231	4/231	4/429	7/858	7/286		
$\frac{9}{2}$	$\frac{9}{2}$	1/504	5/168	3/616	9/616	75/8008	25/3432	245/10296		
		1/18	1/462	3/154	9/2002	3/286	7/858	7/1287	49/243	
$\frac{9}{2}$	$\frac{9}{2}$	1/990	4/165	12/5005	9/715	3/715	16/2145	784/109395	49/121	

$$\left(\frac{d}{dr} + \frac{\kappa_1}{r}\right) S_{n\kappa, \kappa_1, J^\lambda} + (\epsilon_{n\kappa} + \omega + m - V) T_{n\kappa, \kappa_1, J^\lambda} = L_{n\kappa, J^\lambda}, \quad (3.13)$$

with

$$\begin{pmatrix} K_{n\kappa, J^0} \\ L_{n\kappa, J^0} \end{pmatrix} = r^J \begin{pmatrix} F_{n\kappa} \\ G_{n\kappa} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} K_{n\kappa, J^1} \\ L_{n\kappa, J^1} \end{pmatrix} = r^J \begin{pmatrix} G_{n\kappa} \\ F_{n\kappa} \end{pmatrix}. \quad (3.14)$$

Solutions to Eqs. (3.13) which are physically admissible must vanish at both $r=0$ and $r=\infty$, for frequencies below the lowest photoelectric threshold.

From Eqs. (3.10) and (1.15) we obtain a general expression for the susceptibilities

$$\chi_{2J^\lambda}(\omega) = -\frac{\alpha}{2J+1} \sum_{n\kappa} (2j+1) \times \sum_{\kappa_1} (2j_1+1) R_{n\kappa, \kappa_1, J^\lambda}(\omega). \quad (3.15)$$

The degeneracy $(2j+1)$ should of course be replaced by the actual number of electrons in any incomplete atomic subshell.

Some numerical studies of Eqs. (3.12) will be given in Sec. V; first, however, we will present the nonrelativistic limits of the above equations to facilitate comparison with other theoretical work.

IV. NONRELATIVISTIC LIMITS

A. Electric Equations ($\lambda=1$)

In the nonrelativistic limit, $F_{n\kappa}(L_{n\kappa, \kappa_1, J^1})$ is negligible compared with $G_{n\kappa}(K_{n\kappa, J^1})$, and Eqs. (3.13) reduce to an inhomogeneous radial Schrödinger equation

$$\left[(\epsilon_{n\kappa} + \omega - m - V) + \frac{1}{2m} \left(\frac{d^2}{dr^2} - \frac{\kappa_1(\kappa_1+1)}{r^2} \right) \right] \times S_{n\kappa, \kappa_1, J^1} = K_{n\kappa, J^1}, \quad (4.1)$$

where we have approximated T by

$$T_{n\kappa, \kappa_1, J^1} \approx -\frac{1}{2m} \left(\frac{d}{dr} + \frac{\kappa_1}{r} \right) S_{n\kappa, \kappa_1, J^1}. \quad (4.2)$$

Since T and L are small compared to S and K , we may write

$$J_{n\kappa, \kappa_1, J^1} \approx \int_0^\infty dr K_{n\kappa, J^1} S_{n\kappa, \kappa_1, J^1}. \quad (4.3)$$

For the sake of simplicity let us consider only the dipole term $J=1$. Six cases then arise for fixed n and l , corresponding to the two values of $\kappa(l, -l-1)$ associated with $j=l\pm\frac{1}{2}$, and the three values of $\kappa_1 = -\kappa, \kappa\pm 1$ allowed by the dipole selection rules for a fixed κ . The differential equation (4.1) depends only on l and $l_1 = l\pm 1$; therefore in the nonrelativistic limit only two distinct values of the radial integrals (4.3) occur:

$$\begin{aligned} I_{nl, l+1}(\omega) &= J_{nl, l+1, 1^1}(\omega) \\ &= J_{n, -l-1, -l-2, 1^1}(\omega) = J_{n, -l-1, l+1, 1^1}(\omega), \\ I_{nl, l-1}(\omega) &= J_{nl, l-1, 1^1}(\omega) \\ &= J_{n, -l-1, -l, 1^1}(\omega) = J_{n, l, -l-1, 1^1}(\omega). \end{aligned} \quad (4.4)$$

If we make use of the analytic expressions for $\Lambda_{j_1 j}$,

$$\begin{aligned} \Lambda_{j-1, j+1} &= \frac{1}{4(j+1)}, \\ \Lambda_{j_1 j} &= \frac{1}{4(j+1)(2j+1)j}, \end{aligned} \quad (4.5)$$

and sum Eq. (3.13) over the six possibilities mentioned above, we find

$$\begin{aligned} \chi_2^1(\omega) &= \sum_{nl} \alpha_{nl}(\omega), \\ \alpha_{nl}(\omega) &= -\frac{2}{3}\alpha [(l+1)(I_{nl, l+1}(\omega) + I_{nl, l+1}(-\omega)) \\ &\quad + l(I_{nl, l-1}(\omega) + I_{nl, l-1}(-\omega))]. \end{aligned} \quad (4.6)$$

As $\omega \rightarrow 0$, Eqs. (4.1)-(4.6) reduce to the equations

for the static polarizability discussed, for example, in Ref. 7. One implicit difference between the above results and the corresponding results of Ref. 7 is our use of the HFS potential and wave functions which include exchange effects in a simple and consistent fashion.

B. Magnetic Equations ($\lambda=0$)

Since the roles of $F_{n\kappa}$ and $G_{n\kappa}$ in the inhomogeneous terms of (3.13) are now reversed, we must proceed in a slightly different manner. Let us again consider $J=1$ and approximate T by

$$T_{n\kappa, \kappa_1, 1}^0 \approx -\frac{1}{2m} \left(\frac{d}{dr} + \frac{\kappa_1}{r} \right) S_{n\kappa, \kappa_1, 1}^0 + r G_{n\kappa}. \quad (4.7)$$

Making use of the nonrelativistic limit of Eqs. (3.4) for $F_{n\kappa}$ and $G_{n\kappa}$, we find

$$\left[(\epsilon_{n\kappa} + \omega - m - V) + \frac{1}{2m} \left(\frac{d^2}{dr^2} - \frac{\kappa_1(\kappa_1+1)}{r^2} \right) \right] \times S_{n\kappa, \kappa_1, 1}^0 = \frac{(1-\kappa-\kappa_1)}{2m} G_{n\kappa}. \quad (4.8)$$

Substituting the approximation (4.7) into the expression for $J_{n\kappa, \kappa_1, 1}^0$, we obtain

$$J_{n\kappa, \kappa_1, 1}^0 = \frac{1}{2m} \int_0^\infty dr [r^2 G_{n\kappa}^2 + (1-\kappa-\kappa_1) S_{n\kappa, \kappa_1, 1}^0 G_{n\kappa}]. \quad (4.9)$$

Three possibilities arise in Eqs. (4.8) and (4.9) corresponding to the magnetic-dipole selection rules $\kappa_1 = \kappa, -\kappa \pm 1$:

(i) $\kappa_1 = \kappa$: It is trivial to verify that the desired solution to Eq. (4.8) is

$$S_{n\kappa, \kappa, 1}^0 = \frac{(1-2\kappa)}{2m\omega} G_{n\kappa}, \quad (4.10)$$

from which it follows that

$$J_{n\kappa, \kappa, 1}^0 = \frac{1}{2m} \langle r^2 \rangle_{n\kappa} + \frac{(1-2\kappa)^2}{4m^2\omega}, \quad (4.11)$$

where $\langle \rangle_{n\kappa}$ represents the expectation value computed in the one-electron state, n, κ . The second term in (4.11) has no effect on the magnetic susceptibility since it cancels on summing over ω and $-\omega$.

(ii) $\kappa_1 = -\kappa + 1$: In this case the differential equation (4.8) becomes homogeneous and has only the solution $S_{n\kappa, -\kappa+1, 1}^0 = 0$, so that

$$J_{n\kappa, -\kappa+1, 1}^0 = \frac{1}{2m} \langle r^2 \rangle_{n\kappa}. \quad (4.12)$$

(iii) $\kappa_1 = -\kappa - 1$: Equation (4.8) now has as its solution

$$S_{n\kappa, -\kappa-1, 1}^0 = \frac{1}{m(\Delta\epsilon_{n\kappa} + \omega)} G_{n\kappa}, \quad (4.13)$$

where $\Delta\epsilon_{n\kappa} = \epsilon_{n\kappa} - \epsilon_{n-\kappa-1}$ is the fine structure separation between the levels n, κ and $n, -\kappa-1$. (Both of these levels belong to the same value of l but have j values differing by one unit.) In a completely nonrelativistic theory $\Delta\epsilon_{n\kappa}$ would vanish, but it is instructive to use the slightly more general expression (4.13). Substituting in Eq. (4.8), we find

$$J_{n\kappa, -\kappa-1, 1}^0 = \frac{1}{2m} \langle r^2 \rangle_{n\kappa} + \frac{1}{m^2(\Delta\epsilon_{n\kappa} + \omega)}. \quad (4.14)$$

If $\Delta\epsilon_{n\kappa} = 0$, the second term in (4.14) would again cancel on summing over $\pm\omega$.

Using the easily derived identity

$$\sum_{\kappa_1} (2j_1+1)^{\frac{1}{2}} (\kappa_1 + \kappa)^2 \Lambda_{j_1 j_1} = 1, \quad (4.15)$$

where the summation is over $\kappa_1 = \kappa, -\kappa \pm 1$, one may sum the first term in each of the expressions (4.11), (4.12), and (4.14) to give

$$\chi_2^0 = -\frac{\alpha}{6m} \sum_{n\kappa} (2j+1) \langle r^2 \rangle_{n\kappa}. \quad (4.16)$$

This is the well-known Van Vleck equation for the diamagnetic susceptibility of an atom.¹⁴

There is, of course, a frequency-dependent addition to (4.16) which arises from the second term of Eq. (4.14). Making use of the analytic expression for $\Lambda_{j_1 j_1}$ given in (4.5) one shows

$$\chi_2^0(\omega) = \frac{\alpha}{6m^2} \sum_{n\kappa} \frac{\Delta_{n\kappa}}{(\Delta_{n\kappa})^2 - \omega^2} \left[\frac{(l+1)d_{n\kappa} - l d_{n, -l-1}}{2l+1} \right], \quad (4.17)$$

where $\Delta_{n\kappa} = \epsilon_{n, -l-1} - \epsilon_{n, \kappa}$ represents the (positive) fine structure separation, and $d_{n, \kappa}$ represents the number of electrons in the subshell $n, \kappa = l, -l-1$. For a closed (n, l) shell, the numerator of Eq. (4.17) vanishes; only unfilled shells therefore contribute to the sum. As $\omega \rightarrow 0$, the expression (4.17) reduces to an already known result of nonrelativistic quantum mechanics.¹⁵

V. EVALUATION OF THE DIPOLE SUSCEPTIBILITIES FOR THE NOBLE GASES

To demonstrate the utility of the technique outlined in Sec. III, we present some numerical results for the electric- and magnetic-dipole susceptibilities of the noble gases He, Ne, Ar, Kr, and Xe.

The radial RHFS wave functions $G_{n\kappa}$ and $F_{n\kappa}$ of the various atomic subshells are generated by solving Eqs. (3.4) numerically, using the methods outlined in Ref. 6. Some measure of the validity of the RHFS wave functions for describing atomic properties is provided

¹⁴ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932), p. 275.

¹⁵ R. Becker, *Quantum Theory of Atoms and Radiation* (Blaisdell Publishing Co., New York, 1965), Vol. II, p. 224.

TABLE II. Magnetic susceptibilities χ_2^0 of the noble gases at $\omega=0$ (10^{-6} cm³/mole).

	Theory	Semirel. ^a	Nonrelativistic theory ^b	Experiment ^c
He	1.88	1.88	1.95	2.02±0.08
Ne	7.02	7.10	7.09	6.96±0.14
Ar	19.12	19.17	19.17	19.32
Kr	28.82	28.83	29.06	29.00±0.40
Xe	45.28	45.05	43.93	45.5 ±0.7

^a Computed using the nonrelativistic formula (4.16) of the text with $\langle r^2 \rangle_{n\kappa}$ evaluated using the RHFS wave functions.

^b K. M. S. Saxena and P. T. Narasimhan, *J. Chem. Phys.* **42**, 4304 (1965). Calculated using the Van Vleck formula with $\langle r^2 \rangle$ taken from F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

^c C. Barter, R. G. Meisenheimer, and D. P. Stevenson, *J. Phys. Chem.* **64**, 1312 (1960).

by the close comparison of the calculated one-electron binding energies with their experimental values. Inspection of the tables of Ref. 6 shows that the outer subshells, which contribute most importantly to the present calculation, have the least accurately determined energy values. This fact, of course, has a reflection in the evaluation of atomic susceptibilities.

For the special case of He, a RH, rather than a RHFS, ground state is used since the Slater average exchange term seriously underestimates the He binding energy.

The numerical methods used to solve the inhomogeneous equation (3.13) are similar to those used in Ref. 16, to which the reader is referred for greater detail.

One theoretical difficulty should be mentioned before passing on to the results of the calculations. In the special case $\kappa=\kappa_1$, which is allowed for example by the magnetic-dipole selection rules, the desired solutions to Eqs. (3.13) are singular in the $\omega=0$ limit. To remedy this difficulty we set

$$\begin{aligned}\tilde{S}_{n,\kappa,\kappa_1,J^\lambda} &= S_{n,\kappa,\kappa_1,J^\lambda} - C_{n\kappa,J^\lambda} G_{n\kappa}/\omega, \\ \tilde{T}_{n\kappa,\kappa_1,J^\lambda} &= T_{n\kappa,\kappa_1,J^\lambda} - C_{n\kappa,J^\lambda} F_{n\kappa}/\omega,\end{aligned}\quad (5.1)$$

where

$$C_{n\kappa,J^\lambda} = \int_0^\infty dr [K_{n\kappa,J^\lambda} G_{n\kappa} + L_{n\kappa,J^\lambda} F_{n\kappa}].$$

The functions \tilde{S} and \tilde{T} satisfy Eqs. (3.13) with

$$\begin{aligned}K_{n\kappa,J^\lambda} &\rightarrow K_{n\kappa,J^\lambda} - C_{n\kappa,J^\lambda} G_{n\kappa}, \\ L_{n\kappa,J^\lambda} &\rightarrow L_{n\kappa,J^\lambda} - C_{n\kappa,J^\lambda} F_{n\kappa},\end{aligned}\quad (5.2)$$

and one easily verifies that \tilde{S} and \tilde{T} are regular as $\omega \rightarrow 0$. Since the added terms behave as $1/\omega$, they cancel identically on summing over $\pm\omega$: it is therefore sufficient to replace S and T by \tilde{S} and \tilde{T} in the radial integrals of (3.11).

We present the results of our evaluation of the static magnetic-dipole susceptibilities of the various noble gases in Table II. It can be seen that the numerical results of the present calculation agree well with experi-

¹⁶ F. C. Smith and W. R. Johnson, *Phys. Rev.* **160**, 136 (1967).

TABLE III. Electric susceptibilities of the noble gases at $\omega=0$. (HF=Hartree-Fock.)

	Theory	Nonrelativistic theory		Experiment ^d
		Uncoupled H-F ^a	Coupled H-F	
He	1.486	1.485	1.323 ^b	1.383
Ne	2.801	2.760	2.366 ^c	2.667
Ar	15.09	15.66	...	11.08
Kr	23.43	16.73
Xe	40.45	27.25

^a M. Yoshimine and R. P. Hurst, *Phys. Rev.* **135**, A612 (1964).

^b A. Dalgarno and J. M. McNamee, *Proc. Roy. Soc. (London)* **77**, 673 (1961).

^c H. D. Cohen, *J. Chem. Phys.* **45**, 10 (1966).

^d These values were determined from the zero-frequency limits of the dispersion formulas for the index of refraction given in Ref. 10.

mental values for all of the noble gases He to Xe. In the second column of Table II, we list the results of a corresponding calculation of the susceptibilities using the Van Vleck equations. The required values of $\langle r^2 \rangle_{n\kappa}$ are computed, using the RHFS wave functions. The close agreement between the two determinations serves as a measure of the smallness of relativistic effects in the outer atomic subshells.

The extent to which inner shells are important in magnetic susceptibility calculations is illustrated by the Kr results, where we have the following partial contributions:

$$\begin{aligned}\chi_2^0/a_0^3 &= -0.38 \times 10^{-7}, & K \text{ shell} \\ &= -0.23 \times 10^{-5}, & L \text{ shell} \\ &= -0.55 \times 10^{-4}, & M \text{ shell} \\ &= -2.64 \times 10^{-4}, & N \text{ shell} \\ &= -3.22 \times 10^{-4}, & \text{Kr atom.}\end{aligned}\quad (5.3)$$

It can be seen that 82% of the susceptibility is contributed by the outer N shell, while a completely negligible fraction (0.012%) is due to the innermost K shell. Similar results are, of course, obtained for Ar and Xe.

In Table III static electric susceptibilities for the noble gases are given. These results are compared with calculations carried out using the nonrelativistic uncoupled Hartree-Fock approximation. For He and Ne the present results agree well with nonrelativistic calculations; our value for Ar is somewhat smaller than the corresponding nonrelativistic result.

The tendency of Hartree-Fock calculations to overestimate seriously the electric susceptibilities of heavy atoms is seen to persist even in a relativistic theory. In view of the known sensitivity of the electric calculations to the choice of atomic wave functions, the numerical results could perhaps be improved by employing the more general coupled RHF equations¹⁶ in the calculation, rather than the RHFS equations used here.

The relative contributions of the inner shells to the static electric susceptibility of Kr are given in the

TABLE IV. Dispersion (in units of a_0^3) of the electric susceptibilities of the noble gases.

ω (eV)	He		Ne		Ar		Kr		Xe	
	Theor.	Expt. ^a	Theor.	Expt. ^a	Theor.	Expt. ^a	Theor.	Expt. ^a	Theor.	Expt. ^a
0	1.49	1.38	2.80	2.67	15.09	11.08	23.43	16.73	40.45	27.25
1	1.49	1.39	2.81	2.67	15.15	11.12	23.56	16.81	40.78	27.43
2	1.50	1.39	2.82	2.68	15.35	11.24	23.96	17.04	41.81	27.98
3	1.51	1.40	2.84	2.70						
4	1.52	1.42	2.87	2.73						
5	1.55	1.44	2.92	2.77						
6	1.57	1.46	2.97	2.82						
7	1.61	1.50	3.05	2.88						
8	1.65	1.53	3.14	2.95						
9	1.70	1.58	3.26	3.03						
10	1.76	1.63	3.41	3.14						

^a Computed from the dispersion formulas for the index of refraction given in Ref. 10.

following list:

$$\begin{aligned}
 \chi_2^1/a_0^3 &= +0.50 \times 10^{-5}, & K \text{ shell} \\
 &= +0.13 \times 10^{-2}, & L \text{ shell} \\
 &= +0.26, & M \text{ shell} \\
 &= +23.70, & N \text{ shell} \\
 &= 23.96, & \text{Kr atom.}
 \end{aligned} \tag{5.4}$$

Here, it is clear that all of the inner subshells are unimportant; 98.9% of the susceptibility is due to the N shell alone.

Table IV compares values of the frequency-dependent electric susceptibilities with values derived from the experimentally determined dispersion formulas of Cuthbertson and Cuthbertson.¹⁰ For He and Ne, one sees that the relative error stays approximately constant in the range $\omega=0-10$ eV. It follows that the "oscillator frequency" in a two-parameter dispersion formula is considerably more accurately determined than the corresponding "oscillator strength." For Ar, Kr, and Xe only the values of $\chi_2^1(\omega)$ at $\omega=0, 1$, and 2 eV are given.

TABLE V. Dispersion of the index of refraction H .

$\lambda(A)$	Present calculation $10^4(n^2-1)$	Nonrelativistic calculation ^a
∞	2.2514	2.2515
9000	2.2861	2.2862
6000	2.3311	2.3312
4000	2.4399	2.4400
3000	2.6125	2.6127
2500	2.8158	2.8161
2000	3.3006	3.3009
1750	3.8910	3.8914
1500	5.4946	5.4953
1250	28.4601	28.4741
1240	38.7761	38.8054
1220	182.923	183.564
1210	-176.858	-176.244
1200	-56.9915	-56.9245
1180	-22.6194	-22.6059
1140	-8.5757	-8.5721
1100	-3.7661	-3.7645
1080	-1.9962	-1.9913
1060	0.0946	0.0976
1040	4.9555	4.9600

^a M. Karplus and H. J. Kolker, J. Chem. Phys. 39, 1493 (1963).

Table V lists values of $(n^2-1) \times 10^6$ determined for hydrogen, using the present techniques modified to the extent that $V(r)$ is chosen as a Coulomb potential and $G_{n\kappa}, F_{n\kappa}$ are taken to be K -shell Coulomb wave functions. The agreement with a previous nonrelativistic calculation is apparent for large wavelengths. Near the resonant frequency, the present results lie below the nonrelativistic values, a reflection of the fact that the actual resonant frequency is higher than that given in a nonrelativistic calculation.

It is interesting to compare the static electric susceptibility for hydrogenlike ions determined from the present calculation with the corresponding nonrelativistic values which can be determined analytically.⁷ We find, for example,

$$\begin{aligned}
 Z^4 \chi_2^1(0) &= 4.4997 a_0^3, & \text{for } Z=1 \\
 &= 2.9722 a_0^3, & \text{for } Z=80,
 \end{aligned} \tag{5.5}$$

whereas nonrelativistically

$$Z^4 \chi_2^1(0) = \frac{3}{2} a_0^3, \text{ for all } Z,$$

Z being the nuclear charge. The deviations from the nonrelativistic values are seen to be of $O(\alpha Z)^2$, typical of relativistic fine structure effects.

From the numerical results of this section, we may draw the following conclusions:

(a) The calculation of magnetic susceptibilities using the present techniques give reliable values even for the heavier elements. For the lighter elements, there is little reason to choose between the three calculations presented in Table II. The relativistic and semirelativistic calculations for Xe both agree with experiment somewhat better than the nonrelativistic values of Saxena and Narasimhan. It is therefore sufficient to use the semirelativistic formulation (Van Vleck formula with $\langle r^2 \rangle_{n\kappa}$ evaluated relativistically) to obtain reliable magnetic susceptibilities for the entire range of elements considered.

(b) Electric susceptibilities calculated using the present relativistic techniques agree with the available nonrelativistic uncoupled Hartree-Fock calculations and both seriously overestimate χ_2^1 for heavier ele-

ments. While the tendency to overestimate the susceptibilities is removed in the nonrelativistic coupled Hartree-Fock calculations, the relative agreement with experiment is only slightly improved for He and somewhat worsened for Ne. As mentioned in the text, precision values of the electric susceptibility for He have been obtained using nonrelativistic wave functions including correlation. It is clear that substantial improvement of the electric-susceptibility calculations can be accomplished by modifying the existing nonrelativistic theory rather than including relativistic effects.

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APPENDIX A

We will show that it is possible to replace $\alpha \cdot \mathbf{a}_{JM^1}$ by $b_{JM^1} = [(J+1)/J]^{1/2} \phi_{JM}$ in the one-electron matrix elements of Eq. (3.5). Using the approximation (1.7) it follows that

$$(q | \alpha \cdot \mathbf{a}_{JM^1} | n\kappa m) = i \frac{(\epsilon_q - \epsilon_{n\kappa})}{\omega} ((J+1)/J)^{1/2} \times (q | \phi_{JM} | n\kappa m), \quad (\text{A1})$$

where we have used the commutation relation

$$[H, \phi_{JM}] = \frac{1}{i} \alpha \cdot \nabla \phi_{JM}, \quad (\text{A2})$$

which is valid for a one-electron central field Dirac Hamiltonian H .

Substituting (A1) into the expression (3.5) for X_{J^1} we find

$$X_{J^1} = \frac{1}{4\pi} \sum_{n\kappa m} \left\{ \sum_q \left[\frac{(n\kappa m | b_{JM^1} | q)(q | b_{JM^1} | n\kappa m)}{\epsilon_{n\kappa} + \omega - \epsilon} + \frac{(n\kappa m | b_{JM^1} | q)(q | b_{JM^1} | n\kappa m)}{\epsilon_{n\kappa} - \omega - \epsilon} \right] + R_{n\kappa m, J} \right\}, \quad (\text{A3})$$

where b_{JM^1} is defined above and where

$$R_{n\kappa m, J} = \sum_q [(\epsilon_{n\kappa} - \epsilon_q - \omega)(n\kappa m | \phi_{JM^1}^* | q)(q | \phi_{JM} | n\kappa m) + (\epsilon_{n\kappa} - \epsilon_q + \omega)(n\kappa m | \phi_{JM} | q)(q | \phi_{JM^1}^* | n\kappa m)]. \quad (\text{A4})$$

We can now show that $R_{n\kappa m, J} = 0$. This follows directly by using the completeness of the set of intermediate

states q to give

$$R_{n\kappa m, J} = \frac{1}{\omega} (n\kappa m | [b_{JM^1}, b_{JM^1}^*] | n\kappa m) + \frac{1}{\omega^2} (n\kappa m | [[H, b_{JM^1}^*], b_{JM^1}] | n\kappa m). \quad (\text{A5})$$

The first commutator vanishes trivially, while the second commutator can be shown to vanish by using Eq. (A2) to evaluate $[H, b_{JM^1}^*]$.

APPENDIX B

We wish to give further details on the reduction of the matrix element X_{J^1} of Eq. (3.8). To this end let us write

$$|n\kappa m+\rangle = \sum_{\kappa_1 m_1} \frac{1}{r} \begin{pmatrix} i\mathcal{S}_{\kappa_1 m_1}(r)\Omega_{\kappa_1 m_1}(\hat{r}) \\ \mathcal{T}_{\kappa_1 m_1}(r)\Omega_{-\kappa_1 m_1}(\hat{r}) \end{pmatrix}, \quad (\text{B1})$$

and expand

$$b_{JM^1} |n\kappa m\rangle = \sum_{\kappa_1 m_1} \frac{1}{r} \begin{pmatrix} i\mathcal{K}_{\kappa_1 m_1}(r)\Omega_{\kappa_1 m_1}(\hat{r}) \\ \mathcal{L}_{\kappa_1 m_1}(r)\Omega_{-\kappa_1 m_1}(\hat{r}) \end{pmatrix}. \quad (\text{B2})$$

The inhomogeneous Dirac equations (3.9) then reduce to radial differential equations

$$(\epsilon_{n\kappa} - m + \omega - V)\mathcal{S}_{\kappa_1 m_1} - \left(\frac{d}{dr} - \frac{\kappa_1}{r}\right)\mathcal{T}_{\kappa_1 m_1} = \mathcal{K}_{\kappa_1 m_1},$$

$$\left(\frac{d}{dr} + \frac{\kappa_1}{r}\right)\mathcal{S}_{\kappa_1 m_1} + (\epsilon_{n\kappa} + m + \omega - V)\mathcal{T}_{\kappa_1 m_1} = \mathcal{L}_{\kappa_1 m_1}. \quad (\text{B3})$$

In defining \mathcal{S} , \mathcal{T} , \mathcal{K} , and \mathcal{L} we have suppressed the obvious dependence on J , M , λ , n , κ , and m .

By inverting Eq. (B2) we find

$$\begin{pmatrix} \mathcal{K}_{\kappa_1 m_1}^0 \\ \mathcal{L}_{\kappa_1 m_1}^0 \end{pmatrix} = \frac{i(\kappa + \kappa_1)}{((J+1)J)^{1/2}} I_{-\kappa_1 m_1, \kappa m, JM} j_J(\omega r) \begin{pmatrix} F_{n\kappa}(r) \\ G_{n\kappa}(r) \end{pmatrix},$$

$$\begin{pmatrix} \mathcal{K}_{\kappa_1 m_1}^1 \\ \mathcal{L}_{\kappa_1 m_1}^1 \end{pmatrix} = (J+1/J)^{1/2} I_{\kappa_1 m_1, \kappa m, JM} j_J(\omega r) \begin{pmatrix} G_{n\kappa}(r) \\ F_{n\kappa}(r) \end{pmatrix}. \quad (\text{B4})$$

In writing Eqs. (B4) we have made use of the following angular integrals:

$$\int d\Omega \Omega_{\kappa_1 m_1}^\dagger Y_{JM} \Omega_{\kappa m}$$

$$= I_{\kappa_1 m_1, \kappa m, JM}$$

$$= I_{-\kappa_1 m_1, -\kappa m, JM}$$

$$= (-1)^{J+j-j_1} \left(\frac{(2J+1)(2j+1)}{4\pi(2j_1+1)} \right)^{1/2}$$

$$\times C(jJj_1; \frac{1}{2}0) C(jJj_1; mMm_1) \Pi_{JJ_1}, \quad (\text{B5})$$

where Π_{lJl_1} is defined in Eq. (3.12), and

$$\begin{aligned} \int d\Omega \Omega_{-\kappa_1 m_1} \dagger \boldsymbol{\sigma} \cdot \mathbf{Y}_{JM}^{(0)} \Omega_{\kappa m} \\ = \frac{\kappa_1 + \kappa}{(J(J+1))^{1/2}} I_{-\kappa_1 m_1, \kappa m, JM} \\ = -\frac{(\kappa + \kappa_1)}{(J(J+1))^{1/2}} I_{\kappa_1 m_1, -\kappa m, JM}. \end{aligned} \quad (\text{B6})$$

We can factor the m -dependent constants from each side of the differential equations (B3) by setting

$$\begin{aligned} \begin{pmatrix} S_{\kappa_1 m_1}^0 \\ T_{\kappa_1 m_1}^0 \end{pmatrix} &= i \frac{\kappa_1 + \kappa}{(J(J+1))^{1/2}} I_{-\kappa_1 m_1, \kappa m, JM} \begin{pmatrix} \bar{S}_{\kappa, \kappa_1, J^0} \\ \bar{T}_{\kappa, \kappa_1, J^0} \end{pmatrix}, \\ \begin{pmatrix} S_{\kappa_1 m_1}^1 \\ T_{\kappa_1 m_1}^1 \end{pmatrix} &= \left(\frac{J+1}{J}\right)^{1/2} I_{\kappa_1 m_1, \kappa m, JM} \begin{pmatrix} \bar{S}_{\kappa, \kappa_1, J^1} \\ \bar{T}_{\kappa, \kappa_1, J^1} \end{pmatrix}. \end{aligned} \quad (\text{B7})$$

If we define

$$\begin{aligned} \begin{pmatrix} \bar{K}_{\kappa, \kappa_1, J^0} \\ \bar{L}_{\kappa, \kappa_1, J^0} \end{pmatrix} &= j_J(\omega r) \begin{pmatrix} F_{\kappa\kappa}(r) \\ G_{\kappa\kappa}(r) \end{pmatrix}, \\ \begin{pmatrix} \bar{K}_{\kappa, \kappa_1, J^1} \\ \bar{L}_{\kappa, \kappa_1, J^1} \end{pmatrix} &= j_J(\omega r) \begin{pmatrix} G_{\kappa\kappa}(r) \\ F_{\kappa\kappa}(r) \end{pmatrix}, \end{aligned} \quad (\text{B8})$$

the functions \bar{S} and \bar{T} will satisfy Eqs. (3.13), with K and L replaced by \bar{K} and \bar{L} .

With the aid of the integrals (B5) and (B6) we find

$$\begin{aligned} \langle n\kappa m | b_{JM}^{0*} | n\kappa m + \rangle &= \sum_{\kappa_1 m_1} \frac{(\kappa_1 + \kappa)^2}{J(J+1)} \\ &\quad \times (I_{-\kappa_1 m_1, \kappa m, JM})^2 \bar{J}_{\kappa, \kappa_1, J^0}, \\ \langle n\kappa m | b_{JM}^{1*} | n\kappa m + \rangle &= \sum_{\kappa_1 m_1} \frac{J+1}{J} \\ &\quad \times (I_{\kappa_1 m_1, \kappa m, JM})^2 \bar{J}_{\kappa, \kappa_1, J^1}, \end{aligned} \quad (\text{B9})$$

with

$$J_{n\kappa, \kappa_1, J^\lambda} = \int_0^\infty dr [\bar{K}_{n\kappa, J^\lambda} \bar{S}_{n\kappa, \kappa_1, J^\lambda} + \bar{L}_{n\kappa, J^\lambda} \bar{T}_{n\kappa, \kappa_1, J^\lambda}]. \quad (\text{B10})$$

We may now sum over m and m_1 using

$$\begin{aligned} \sum_{m, m_1} (I_{\pm \kappa_1 m_1, \kappa m, JM})^2 &= \frac{(2j+1)(2j_1+1)}{4\pi} \\ &\quad \times \Lambda_{jJj_1} \Pi_{l, J+\lambda-1, l_1}, \end{aligned} \quad (\text{B11})$$

where

$$\Lambda_{jJj_1} = \Lambda_{j_1 J j} = \frac{C^2(jJj_1; \frac{1}{2}0)}{2j_1+1}. \quad (\text{B12})$$

It is possible to replace $j_J(\omega r)$ by $(\omega r)^J / (2J+1)!!$ with the neglect of terms of order $(\omega r)^2$. With this in mind we set

$$\begin{aligned} \begin{pmatrix} \bar{S}_{\kappa, \kappa_1, J^\lambda} \\ \bar{T}_{\kappa, \kappa_1, J^\lambda} \end{pmatrix} &= \frac{\omega^J}{(2J+1)!!} \begin{pmatrix} S_{\kappa, \kappa_1, J^\lambda} \\ T_{\kappa, \kappa_1, J^\lambda} \end{pmatrix}, \\ \begin{pmatrix} \bar{K}_{\kappa, \kappa_1, J^\lambda} \\ \bar{L}_{\kappa, \kappa_1, J^\lambda} \end{pmatrix} &= \frac{\omega^J}{(2J+1)!!} \begin{pmatrix} K_{\kappa, \kappa_1, J^\lambda} \\ L_{\kappa, \kappa_1, J^\lambda} \end{pmatrix}, \end{aligned} \quad (\text{B13})$$

$$\bar{J}_{n\kappa, \kappa_1, J^\lambda} = \frac{\omega^{2J}}{[(2J+1)!!]^2} J_{n\kappa, \kappa_1, J^\lambda},$$

and obtain the relations (3.10)–(3.14) of the text.

It should be mentioned that the analysis of the second term in Eq. (3.8) goes through in a parallel way. The entire effect of the second term is to give an additive contribution to the first term with $\omega \rightarrow -\omega$ in the radial differential equations.