PHYSICAL REVIEW A VOLUME 26, NUMBER 1 JULY 1982

Electric and magnetic susceptibilities and shielding factors for closed-shell atoms and ions of high nuclear charge

Dietmar Kolb* and W. R. Johnson
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

Philip Shorer
Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

(Received 8 February 1982)

Theoretical expressions for the electric and magnetic susceptibilities and shielding factors of closed-shell atoms and ions are derived from the point of view of the relativistic random-phase approximation. These expressions are evaluated to determine electric-dipole, electric-quadrupole, and magnetic-dipole susceptibilities, and shielding factors for ions of the noble-gas isoelectronic sequences, as well as for selected ions having closed *s*, *d*, and *f* shells. Comparisons are given with previous theoretical work and with experiment.

I. INTRODUCTION

A widely used approximation for determining the susceptibilities and shielding factors of closed-shell atoms and ions is the coupled Hartree-Fock (CHF) theory.[1-4]. In this approach, atomic electrons moving in an external field are described by nonspherical Hartree-Fock (HF) orbitals which satisfy one-electron equations determined from a variational principle. Linearizing the orbital equations in the strength of the external field leads to expressions for susceptibilities and shielding factors which include not only the direct effects of the field on the unperturbed HF orbitals, but also those indirect effects due to modifications of the HF central potential resulting in correlation corrections. In the sense of many-body perturbation theory[5] the CHF theory accounts for all of the lowest-order effects of electron-electron correlation as well as those effects of higher order that arise from iteration of the lowest-order terms; it does not, however, account for all second- and higher-order effects. In systems such as the noble gases the second- and higher-order correlation corrections are small and the CHF calculations are remarkably precise[6]; whereas in systems such as the alkaline-earth atoms, higher-order correlations lead to substantial modifications of the CHF predictions.[7]

In the present paper we seek to generalize the CHF technique to treat atoms and ions of high nuclear charge where relativistic effects as well as correlations are expected to be important. To this end we employ the relativistic random-phase approximation (RRPA)[8] which in the nonrelativistic limit reduces to the random-phase approximation with exchange (RPAE).[9] The RPAE describes the linear response of an atom to a dynamic external field. Since in the static-field limit the RPAE reduces to the CHF theory, our application of the RRPA to the static field case leads directly to a relativistic version of the CHF theory.

In the past few years several relativistic calculations of electric-dipole susceptibilities have appeared. A relativistic core potential was used by Konowalow *et al.*[10] to calculate the susceptibilities of the group-IIb elements. Relativistic calculations of the electric-dipole susceptibilities of the alkaline earths, the group-IIb elements, and the heavy noble gases Kr, Xe, and Rn, have been carried out by Sin Fai Lam[11] using a relativistic version of the Pople-Schofield method. Neither of these calculations account for correlation effects.

Desclaux *et al.*[12] have employed finite-difference methods in conjunction with one-center molecular orbitals to evaluate the electric-dipole susceptibilities of atoms with one or two *s* electrons outside of closed shells. These calculations are relativistic and include the same correlation corrections that we include in the present study. The advantages of the present formulation are first, that the technique can be easily applied to study systems with closed *p*, *d*, or *f* shells; and second, that electric and magnetic susceptibilities of higher multipolarity can be treated with the same facility as the electric-dipole susceptibility.

Although the present calculations go beyond the previous relativistic calculations, they by no means represent the best calculations possible, since correlation effects are treated only in a limited way. Nevertheless, the present calculations do represent a complete treatment of RPA contributions to correlations within a relativistic framework, and therefore, provide a basis for future studies.

In Sec. II, the static RRPA equations are derived and reduced to forms convenient for direct numerical calculations of electric and magnetic susceptibilities and shielding factors. Numerical results obtained from our calculations together with comparisons with other theoretical and experimental values for the susceptibilities and shielding factors are presented in Sec. III.

II. THEORY

Consider a closed-shell atom or ion in a static electric multipole field described by a scalar potential $\phi_J(\vec{r})$ or in a static magnetic multipole field described by a vector potential $\vec{A}_J(\vec{r})$. The multipole potentials have one of the two forms

$$\begin{aligned} &\phi_J(\vec{r})=r^J Y_{J0}(\hat{r}) \ \text{(electric case)}\,,\\ &\vec{A}_J(\vec{r})=r^J \vec{Y}_{JJ0}(\hat{r}) \ \text{(magnetic case)}\,, \end{aligned} \tag{1}$$

where $\vec{Y}_{JJ0}(\vec{r})$ is a vector spherical harmonic. The applied multipole field induces a multipole moment in a closed-shell atom which gives rise to a secondary field described by potentials $\phi_J^{(1)}(\vec{r})$ or $\vec{A}_J^{(1)}(\vec{r})$ with the same symmetry as the applied field. These potentials fall off at large distances as

$$\phi_J^{(1)}(\vec{r}) \underset{r\to\infty}{\longrightarrow} -\alpha_J Y_{J0}(\hat{r})/r^{J+1}$$

or (2)

$$\vec{A}_J^{(1)}(\vec{r}) \underset{r\to\infty}{\longrightarrow} \frac{J+1}{J}\chi_J \vec{Y}_{JJ0}(\hat{r})/r^{J+1}\,.$$

The proportionality constants α_J and χ_J are the electric and magnetic susceptibilities, respectively. Near the nucleus the secondary potentials reduce to

$$\phi_J^{(1)}(\vec{r}) \underset{r\to\infty}{\longrightarrow} -\gamma_J \phi_J(\vec{r})$$

or (3)

$$\vec{A}_J^{(1)}(\vec{r}) \underset{r\to\infty}{\longrightarrow} -\sigma_J \vec{A}_J(\vec{r})\,.$$

The dimensionless parameters γ_J and σ_J are electric or magnetic shielding factors. On general grounds the electric-dipole shielding factor γ_1 has the value $\gamma_1=N/Z$, where N is the number of electrons and Z the nuclear charge. The quadrupole shielding factor γ_2 commonly referred to as the Sternheimer shielding factor,[13] may take a negative as well as positive value, in which case it is referred to as the Sternheimer antishielding factor.

We describe the unperturbed closed-shell atom or ion by Dirac-Fock (DF) wave functions. The individual DF orbitals $u_i(\vec{r})$ satisfy one-electron Dirac equations

$$(h_0+V)u_i=\epsilon_i u_i\,,\quad i=1,\ldots,N \tag{4}$$

where $h_0=\vec{\alpha}\cdot\vec{p}+\beta m-e^2Z/r$ is the Dirac Hamiltonian. The DF potential V in Eq. (4) is given by

$$Vu_i=\sum_j e^2\int\frac{d^3r'}{|\vec{r}-\vec{r}\,'|}\times[(u_j^\dagger u_j)'u_i-(u_j^\dagger u_i)'u_j]\,, \tag{5}$$

while the parameter ϵ_i is the energy eigenvalue for the ith orbital. In the expression for h_0, $\vec{p}$ is momentum operator, $\vec{\alpha}$ and β are Dirac matrices, and m is the electron mass.

The interaction between the atomic electrons and the external field is described by the Hamiltonian

$$H_I=\sum_{i=1}^{N} v(\vec{r}_i)\,,$$

with

$$v(\vec{r})=\begin{cases} e\phi_J(\vec{r}), & \text{electric,}\\ -e\vec{\alpha}\cdot\vec{A}_J(\vec{r}), & \text{magnetic.}\end{cases} \tag{6}$$

The individual electron orbitals u_i are perturbed by the external potential v. To first order in the external field we have

$$u_i\rightarrow u_i+w_i\,, \tag{7}$$

where the perturbed orbitals w_i satisfy the linearized DF equations

$$(h_0+V-\epsilon_i)w_i=-(v+V^{(1)})u_i+\sum_j \lambda_{ji}u_j\,. \tag{8}$$

In Eq. (8) V is the DF potential and $V^{(1)}$ is the first-order correction to V induced by the external field. This first-order potential $V^{(1)}$ which correlates the various electrons u_i is given by

$$V^{(1)}u_i=\sum_j e^2\int\frac{d^3r'}{|\vec{r}-\vec{r}\,'|}[(w_j^\dagger u_j)'u_i+(u_j^\dagger w_j)'u_i-(w_j^\dagger u_i)'u_j-(u_j^\dagger u_i)'w_j]\,. \tag{9}$$

The parameters λ_{ji} are Lagrange multipliers which ensure that the perturbed orbitals w_i are orthogonal to the ground-state DF orbitals

$$\langle w_i \mid u_j \rangle = 0, \quad i,j = 1, \ldots, N \; . \tag{10}$$

One finds from Eqs. (4) and (8) that

$$\lambda_{ji} = \langle j \mid v + V^{(1)} \mid i \rangle \; . \tag{11}$$

Equations (8) are the RRPA equations for the case of a static perturbation $v(\vec{r})$; in the present form they provide a relativistic version of the CHF equations.

The first-order corrections to the charge and current densities of the atom are

$$\begin{aligned} \rho^{(1)}(\vec{r}) &= e \sum_j (w_j^\dagger u_j) + \text{c.c.} \; , \\ \vec{j}^{\,(1)}(\vec{r}) &= e \sum_j (w_j^\dagger \vec{\alpha} u_j) + \text{c.c.} \end{aligned} \tag{12}$$

These induced charge-current densities are the sources of the secondary fields $\phi_J^{(1)}$ and $\vec{A}_J^{(1)}$.

In the Appendix we reduce the RRPA equations (8) to coupled differential equations describing the radial wave functions for the perturbed orbitals. The induced charge and current densities may then be expressed in terms of the radial wave functions. The secondary field due to $\rho^{(1)}(\vec{r})$ is found to be

$$\phi_J^{(1)}(\vec{r}) = \left[\frac{1}{r^{J+1}} \int_0^r r^J R_J^{(1)}(r) dr + r^J \int_r^\infty \frac{1}{r^{J+1}} R_J^{(1)}(r) dr \right] Y_{J0}(\hat{r}) \; , \tag{13}$$

where $R_J^{(1)}(r)$ is defined in Eq. (A19). The secondary field due to $\vec{j}^{\,(1)}(\vec{r})$ may be written similarly as

$$\vec{A}_J^{(1)}(\vec{r}) = \left[\frac{1}{r^{J+1}} \int_0^r r^J S_J^{(1)}(r) dr + r^J \int_r^\infty \frac{1}{r^{J+1}} S_J^{(1)}(r) dr \right] \vec{Y}_{JJ0}(\hat{r}) \; , \tag{14}$$

where $S_J^{(1)}(\vec{r})$ is given in Eq. (A22). From the large-r behavior of Eqs. (13) and (14) one finds on comparing with Eq. (2) the expressions for susceptibilities:

$$\begin{aligned} \alpha_J &= -\int_0^\infty dr\, r^J R_J^{(1)}(r) \; , \\ \chi_J &= \frac{J}{J+1} \int_0^\infty dr\, r^J S_J^{(1)}(r) \; . \end{aligned} \tag{15}$$

From the small-r behavior of the induced fields one finds on comparing with Eq. (3):

$$\begin{aligned} \gamma_J &= -\int_0^\infty \frac{dr}{r^{J+1}} R_J^{(1)}(r) \; , \\ \sigma_J &= -\int_0^\infty \frac{dr}{r^{J+1}} S_J^{(1)}(r) \; . \end{aligned} \tag{16}$$

III. NUMERICAL RESULTS AND COMPARISONS

Values of the electric-dipole susceptibilities α_1 and of the electric-dipole shielding factors γ_1 from the present calculation are given in Table I. Susceptibilities for ions of the He, Ne, Ar, Cu^+, Kr, Pd, and Xe sequences are shown in the lower triangular portion of the table and corresponding shielding factors are given in the upper triangular part.

As in the nonrelativistic CHF theory, the dipole shielding factor $\gamma_1 = N/Z$, where N is the number of electrons and Z is the nuclear charge. The deviation of the values of γ_1 from N/Z in Table I serves as a measure of the numerical accuracy of the present calculations. The sequences considered are those with closed $1s^2$, $2p^6$, $3p^6$, $3d^{10}$, $4p^6$, $4d^{10}$, and $5p^6$ subshells. Read horizontally, the entries show how the susceptibility varies at different stages of ionization; read vertically, the variation of α_1 or γ_1 with Z along an isoelectronic sequence is shown. All of the values presented in Table I are from "fully coupled" RRPA calculations in which all of the possible dipole excitations are included. In the case of ions of the He sequence there are two coupled channels ($1s \to p_{1/2}$, $1s \to p_{3/2}$) in Eqs. (A14) while for Xe there are 42 coupled channels.

In Tables II and III the electric-quadrupole and magnetic-dipole susceptibilities and shielding factors are given in the format of Table I. In these calculations we have attempted to maintain the numerical accuracy at one part in 10^4. A more detailed study of the Ne sequences is given in Table IV, where we present values of the susceptibilities and shielding factors for ions from Ne^0 to U^{82+}. The electric-dipole susceptibilities and shielding factors α_1 and γ_1 listed in columns 4 and 5 are from nine-channel calculations. In column 6 we tabulate N/Z which can be compared with γ_1 to check the accuracy of our numerical methods. The quadrupole susceptibilities α_2 and the Sternheimer antishielding factor γ_2 are given in columns 7 and 8. These quadrupole calculations involve 13 coupled channels. Results for the magnetic susceptibility are presented in column 9. In the Pauli approximation Eqs. (A15) and (15) reduce to the van Vleck relation[14]

TABLE I. Electric-dipole susceptibilities and shielding factors for closed-shell ions. Susceptibilities are given in lower triangle in units of a_0^3. Shielding factors are given in upper triangle.

Dipole shielding factor (γ_1)

Xe seq $N=54$	Pd seq $N=46$	Kr seq $N=36$	Cu$^+$ seq $N=28$	Ar seq $N=18$	Ne seq $N=10$	He seq $N=2$	Z	Element
9.999(−1)	8.519(−1)	6.667(−1)	5.185(−1)	2.333(−1)	1.852(−1)	3.704(−2)	54	Xe
	1.000	7.826(−1)	6.087(−1)	3.913(−1)	2.174(−1)	4.348(−2)	46	Pd
		1.000	7.778(−1)	5.000(−1)	2.778(−1)	5.556(−2)	36	Kr
			9.653(−1)	6.207(−1)	3.448(−1)	6.897(−2)	29	Cu
				1.000	5.555(−1)	1.111(−1)	18	Ar
					1.000	2.000(−1)	10	Ne
						1.000	2	He

Element	Z	$N=2$ He seq	$N=10$ Ne seq	$N=18$ Ar seq	$N=28$ Cu$^+$ seq	$N=36$ Kr seq	$N=46$ Pd seq	$N=54$ Xe seq
He	2	1.322						
Ne	10	1.038(−3)	2.380					
Ar	18	9.138(−5)	3.708(−2)	1.077(1)				
Cu	29	1.277(−5)	3.318(−3)	2.688(−1)	5.360			
Kr	36	5.189(−6)	1.203(−3)	9.161(−2)	2.021(−1)	1.647(1)		
Pd	46	1.838(−6)	3.909(−4)	3.040(−2)	3.113(−2)	8.235(−1)	2.117(1)	
Xe	54	9.173(−7)	1.885(−4)	1.520(−2)	1.164(−2)	2.764(−1)	8.345(−1)	2.697(1)

Dipole susceptibility (α_1)

TABLE II. Electric-quadrupole susceptibilities and shielding factors for closed-shell ions. Susceptibilities are given in lower triangle in units a_0^5. Shielding factors are given in upper triangle.

Sternheimer shielding factor (γ_2)

Xe seq $N=54$	Pd seq $N=46$	Kr seq $N=36$	Cu$^+$ seq $N=28$	Ar seq $N=18$	Ne seq $N=10$	He seq $N=2$	Z	Element
−1.685(2)	−1.575(1)	−8.657	−2.067	−1.414	−1.930(−1)	1.156(−2)	54	Xe
	−8.529(1)	−1.380(1)	−2.816	−1.726	−2.293(−1)	1.389(−2)	46	Pd
		−7.998(1)	−5.390	−2.541	−3.123(−1)	1.814(−2)	36	Kr
			−2.131(1)	−3.956	−4.283(−1)	2.281(−2)	29	Cu
				−3.009(1)	−1.040	3.743(−2)	18	Ar
					−9.145	6.866(−2)	10	Ne
						3.962(−1)	2	He

Element	Z	$N=2$ He seq	$N=10$ Ne seq	$N=18$ Ar seq	$N=28$ Cu$^+$ seq	$N=36$ Kr seq	$N=46$ Pd seq	$N=54$ Xe seq
He	2	2.326						
Ne	10	3.934(−5)	6.425					
Ar	18	1.003(−6)	1.077(−2)	5.012(1)				
Cu	29	5.191(−8)	2.749(−4)	1.061(−1)	2.907(1)			
Kr	36	1.342(−8)	5.889(−5)	1.675(−2)	1.329(−1)	9.425(1)		
Pd	46	2.834(−9)	1.068(−5)	2.492(−3)	7.522(−3)	7.037(−1)	2.688(2)	
Xe	54	1.002(−9)	3.523(−6)	7.533(−4)	1.676(−3)	1.153(−1)	8.482(−1)	2.043(2)

Quadrupole susceptibility (a_2)

TABLE III. Magnetic-dipole susceptibilities and shielding factors for closed-shell ions. Magnetic susceptibilities are given in the lower triangle in units a_0^3. Magnetic shielding factors are given in the upper triangle.

Magnetic-dipole shielding factor ($10^2\sigma_1$)								
Xe seq $N=54$	Pd seq $N=46$	Kr seq $N=36$	Cu$^+$ seq $N=28$	Ar seq $N=18$	Ne seq $N=10$	He seq $N=2$	Z	Element
7.040(−1)	6.953(−1)	6.714(−1)	6.434(−1)	5.709(−1)	4.947(−1)	2.921(−1)	54	Xe
	5.339(−1)	5.201(−1)	5.004(−1)	4.443(−1)	3.841(−1)	2.209(−1)	46	Pd
		3.598(−1)	3.503(−1)	3.149(−1)	2.727(−1)	1.531(−1)	36	Kr
			2.575(−1)	2.368(−1)	2.067(−1)	1.152(−1)	29	Cu
				1.276(−1)	1.159(−1)	6.588(−2)	18	Ar
					5.586(−2)	3.492(−2)	10	Ne
						5.995(−3)	2	He
He	2	−2.103(1)						
Ne	10	−5.740(−1)	−8.310(1)					
Ar	18	−1.681(−1)	−1.258(1)	−2.305(2)				
Cu	29	−6.133(−2)	−3.794	−3.721(1)	−1.650(2)			
Kr	36	−3.826(−2)	−2.274	−2.015(1)	−5.701(1)	−3.469(2)		
Pd	46	−2.188(−2)	−1.282	−1.058(1)	−2.525(1)	−9.472(1)	−3.813(2)	
Xe	54	−1.483(−2)	−8.801(−1)	−7.055	−1.581(1)	−5.355(1)	−1.358(2)	−5.428(2)
Element	Z	$N=2$ He seq	$N=10$ Ne seq	$N=18$ Ar seq	$N=28$ Cu$^+$ seq	$N=36$ Kr seq	$N=46$ Pd seq	$N=54$ Xe seq
Magnetic-dipole susceptibility ($10^6\chi_1$)								

TABLE IV. Susceptibilities and shielding factors for ions of the Ne isoelectronic sequence. Z is nuclear charge, Z_i is the ionic charge. α_1, χ_1, and χ_{NR} are in units a_0^3. α_2 is in units a_0^5. γ_1, γ_2, σ_1, and σ_{NR} are dimensionless.

Ion	Z	Z_i	α_1	γ_1	N/Z	α_2	γ_2	$10^6\chi_1$	$10^6\chi_{\mathrm{NR}}$	$10^2\sigma_1$	$10^2\sigma_{\mathrm{NR}}$
Ne	10	0	2.38	1	1	6.425	−9.145	−83.1	−83.11	0.05586	0.05534
Na	11	1	0.9457	0.9091	0.9091	1.521	−5.097	−56.83	−56.85	0.06322	0.06253
Mg	12	2	0.4698	0.8333	0.8333	0.5183	−3.432	−41.79	−41.8	0.0706	0.06972
Al	13	3	0.2649	0.7692	0.7692	0.2156	−2.544	−32.17	−32.19	0.07802	0.07691
Si	14	4	0.1624	0.7143	0.7143	0.1021	−2	−25.6	−25.61	0.08548	0.0841
P	15	5	0.1057	0.6667	0.6667	0.05308	−1.637	−20.88	−20.9	0.093	0.09129
S	16	6	0.07205	0.625	0.625	0.0296	−1.379	−17.37	−17.39	0.1006	0.0985
Cl	17	7	0.05093	0.5882	0.5882	0.01746	−1.187	−14.68	−14.7	0.1082	0.1057
Ar	18	8	0.03708	0.5555	0.5556	0.01077	−1.04	−12.58	−12.59	0.1159	0.113
K	19	9	0.02767	0.5263	0.5263	0.006899	−0.9239	−10.9	−10.91	0.1237	0.1202
Ca	20	10	0.02108	0.5	0.5	0.004563	−0.83	−9.531	−9.548	0.1316	0.1275
Sc	21	11	0.01636	0.4762	0.4762	0.003101	−0.7527	−8.407	−8.425	0.1395	0.1348
Ti	22	12	0.01289	0.4545	0.4545	0.002159	−0.6882	−7.471	−7.489	0.1475	0.1421
V	23	13	0.0103	0.4348	0.4348	0.001535	−0.6336	−6.683	−6.7	0.1557	0.1494
Cr	24	14	0.008325	0.4167	0.4167	0.001111	−0.5868	−6.012	−6.029	0.1639	0.1568
Mn	25	15	0.006803	0.4	0.4	8.18(−4)	−0.5464	−5.437	−5.454	0.1722	0.1641
Fe	26	16	0.005615	0.3846	0.3846	6.112(−4)	−0.5111	−4.94	−4.957	0.1807	0.1715
Co	27	17	0.004676	0.3704	0.3704	4.628(−4)	−0.4802	−4.507	−4.524	0.1892	0.179
Ni	28	18	0.003924	0.3571	0.3571	3.547(−4)	−0.4527	−4.128	−4.146	0.1979	0.1864
Cu	29	19	0.003318	0.3448	0.3448	2.749(−4)	−0.4283	−3.794	−3.812	0.2067	0.1939
Zn	30	20	0.002824	0.3333	0.3333	2.152(−4)	−0.4064	−3.499	−3.517	0.2157	0.2014
Br	35	25	0.001371	0.2857	0.2857	7.181(−5)	−0.3246	−2.43	−2.447	0.2628	0.2395
Kr	36	26	0.001203	0.2778	0.2778	5.889(−5)	−0.3123	−2.274	−2.292	0.2727	0.2472
Rb	37	27	0.00106	0.2703	0.2703	4.859(−5)	−0.3009	−2.133	−2.15	0.2828	0.255
Nb	41	31	6.61(−4)	0.2439	0.2439	2.373(−5)	−0.2634	−1.678	−1.695	0.3255	0.2865
Mo	42	32	5.92(−4)	0.2381	0.2381	2.007(−5)	−0.2556	−1.586	−1.603	0.3366	0.2945
Ag	47	37	3.545(−4)	0.2128	0.2128	9.206(−6)	−0.2237	−1.22	−1.237	0.3967	0.3352
Cd	48	38	3.221(−4)	0.2083	0.2083	7.959(−6)	−0.2185	−1.161	−1.178	0.4096	0.3436
I	53	43	2.053(−4)	0.1887	0.1887	4.01(−6)	−0.1966	−0.9198	−0.9373	0.4795	0.3862
Xe	54	44	1.885(−4)	0.1852	0.1852	3.523(−6)	−0.193	−0.8801	−0.8976	0.4947	0.3949
Cs	55	45	1.734(−4)	0.1818	0.1818	3.103(−6)	−0.1895	−0.8427	−0.8602	0.5103	0.4037
Ba	56	46	1.598(−4)	0.1786	0.1786	2.738(−6)	−0.1862	−0.8074	−0.8249	0.5263	0.4126
Tb	65	55	8.094(−5)	0.1539	0.1538	9.694(−7)	−0.1637	−0.5643	−0.5818	0.6943	0.4967
W	74	64	4.453(−5)	0.1352	0.1351	3.878(−7)	−0.1503	−0.409	−0.4264	0.9243	0.5902
Pt	78	68	3.485(−5)	0.1282	0.1282	2.66(−7)	−0.1465	−0.3574	−0.3748	1.055	0.6356
Au	79	69	3.284(−5)	0.1266	0.1266	2.426(−7)	−0.1458	−0.3458	−0.3632	1.091	0.6474
Hg	80	70	3.097(−5)	0.125	0.125	2.216(−7)	−0.1451	−0.3347	−0.3521	1.129	0.6595
Pb	82	72	2.758(−5)	0.122	0.122	1.853(−7)	−0.144	−0.3136	−0.331	1.21	0.6841
Rn	86	76	2.204(−5)	0.1163	0.1163	1.309−7)	−0.1425	−0.2761	−0.2934	1.394	0.7362
U	92	82	1.6(−5)	0.1088	0.1087	7.948(−8)	−0.1424	−0.229	−0.2464	1.744	0.8225

$$\chi_{\mathrm{NR}} = -\frac{1}{6}\frac{e^2}{mc^2}\sum_a (2j_a+1)\langle r^2\rangle_a \, , \tag{17}$$

where the summation is over all atomic subshells a. In column 10 we give values of χ_{NR} determined from the van Vleck formula using DF wave functions to evaluate the expectation values $\langle r^2\rangle_a$. The differences between the values in columns 9 and 10 at high Z are due to the failure of the Pauli approximation. In column 11 we give values of the magnetic shielding factor σ_1. The values of σ_{NR} tabulated in column 12 are determined from the Lamb formula[15]

$$\sigma_{\mathrm{NR}}=\frac{1}{3}\frac{e^2}{mc^2}\sum_a(2j_a+1)\left\langle\frac{1}{r}\right\rangle_a \tag{18}$$

which follows from Eqs. (A15) and (16) in the Pauli approximation. Again, in Eq. (18) the expectation values are evaluated using DF wave functions. It is interesting to note that the value of σ_{NR} for U^{82+} is in error by more than a factor of 2.

Two miscellaneous examples are given in Table V: Yb^{2+}, which has a closed $4f^{14}$ valence shell and Hg, which has a closed $6s^2$ valence shell. As a result of the large number of channels involved, we reduced our accuracy criterion for these particular calculations to one part in 10^3.

In Table VI we compare the present electric-dipole susceptibilities with those obtained from other relativistic calculations. The values of Desclaux *et al.*[12] listed in column 4 were obtained using one-center DF molecular orbitals; they are expected to be in good agreement with the RRPA values. The differences between the RRPA and Desclaux results in Table VI are in part due to the fact that Desclaux *et al.* omit contributions from the atomic core, and are in part due to differences in numerical technique. The results of Sin Fai Lam[11] shown in column 5 were determined using a relativistic version of the Pople-Schofield approximation. These values illustrate characteristic features of relativistic calculations such as the decrease in value of α_1 from Cd to Hg which are *not* obtained in nonrelativistic calculations. In column 6 we list values of α_1 from Konowalow *et al.*,[10] who use an empirically determined core potential and solve the equations for the valence electron perturbations using a relativistic MCSCF method. This semiempirical procedure leads to values of α_1 within 10% of the values recommended by Miller and Bederson.[6]

TABLE V. Susceptibilities and shielding factors for Yb^{2+} and Hg. α_1, χ_1, χ_{NR} are in units a_0^3. α_2 is in units a_0^5.

Atomic property	$Yb^{2+}4f^{14}$	Hg $6s^2$
α_1	6.39	44.9
γ_1	0.972	0.997
N/Z	0.971	1.00
α_2	13.9	337.0
γ_2	−89.5	−47.0
$10^6\chi_1$	−314.0	−551.0
$10^6\chi_{\mathrm{NR}}$	−314.0	−552.0
$10^2\sigma_1$	1.18	1.61
$10^2\sigma_{\mathrm{NR}}$	0.885	1.10

The influence of relativistic effects on the electric-dipole and -quadrupole susceptibilities and shielding factors is illustrated in Fig. 1, where we compare the results obtained in the present calculation for ions of the Ar sequence with accurate nonrelativistic CHF calculations by McEachran *et al.*[16] One finds small but systematic changes in the electric-dipole susceptibilities and in the electric-quadrupole susceptibilities and shielding factors which remain below 5% for $Z \le 30$. For heavier

TABLE VI. Comparison of RRPA dipole susceptibilities with other relativistic calculations (units a_0^3).

Element	Z	α_1	Desclaux[a]	Sin Fai Lam[b]	Konowalow[c]
He	2	1.322	1.327		
Be	4	45.6	45.6		
Mg	12	81.2	81.0		
Ca	20	182.8	180.0	223.5	
Zn	30	50.8	50.3	52.1	35.1
Kr	36	16.5		21.1	
Sr	38	232.6	228.0	286.1	
Cd	48	63.7	62.0	66.0	42.5
Xe	52	27.0		36.4	
Ba	54	324.0	316.0	400.3	
Hg	80	44.9	43.0	51.8	31.8

[a] Desclaux *et al.*, Ref. 12.
[b] Sin Fai Lam, Ref. 11.
[c] Konowalow *et al.*, Ref. 10.

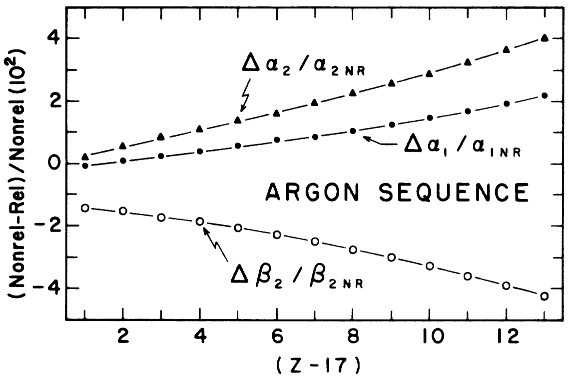

FIG. 1. Percentage difference between the RRPA calculations and the CHF calculations of McEachran *et al.* (Ref. 16) are shown for members of the argon isoelectronic sequence. Quantities α_1 and α_2 are dipole and quadrupole susceptibilities and β_2 is the Sternheimer shielding factor $\beta_2 = \gamma_2$.

elements the modifications due to relativity are expected to be more substantial. An extrapolation based on Fig. 1 leads one to expect 40% changes in $\alpha_{1\mathrm{NR}}$ and $\alpha_{2\mathrm{NR}}$ and a 60% change in $\beta_{2\mathrm{NR}}$ at $Z = 92$. As a further illustration of the influence of relativity on the dipole susceptibilities, in Table VII we compare the present RRPA calculations for various neutral atoms with nonrelativistic CHF (or equivalent) calculations. One sees that for the lighter elements through Ar and for the heavier noble gases Kr and Xe the effects of relativity are small. On the other hand, for the heavier alkaline earths and for the group-IIb elements, where the outer ns^2 valence shell gives the most important contributions, the effects of relativity are substantial. The most striking example is mercury where relativistic effects reduce the susceptibilities by roughly a factor of 2. It is clear that for such systems nonrelativistic calculations are completely inadequate. We also list in Table VII the recommended values of the susceptibilities given by Miller and Bederson.[6] For the noble gases the RRPA (and the CHF) values are in good agreement with the recommended values, while for the remaining elements where correlations play a more important role the agreement is not satisfactory.

The principal limitation of the present calculations is the failure to include all of the effects of electron-electron correlation to second order in the sense of perturbation theory. The second-order effects are most pronounced in atoms such as the alkaline earths and are less significant in the noble gases. The importance of these correlation effects is illustrated in Table VIII where we compare α_1, α_2, and χ_1 with more sophisticated nonrelativistic calculations.[7]

The problem of determining accurate values of the susceptibilities of an atom such as Hg is clearly

TABLE VII. Comparison of RRPA dipole susceptibilities with nonrelativistic CHF calculations and with recommended values (and error estimate) of Miller and Bederson (units a_0^3).

Element	Z	α_1	$\alpha_{1\mathrm{NR}}$	Recom.[e]	Error[e] (%)
He	2	1.322	1.322[a]	1.383	
Be	4	45.6	45.6[b]	37.8	2
Ne	10	2.38	2.38[a]	2.67	2
Mg	12	81.2	81.2[d]	71.5	2
Ar	18	10.8	10.8[a]	11.1	0.5
Ca	20	182.8	182[c]	169	8
Zn	30	50.8	53.4[c]	47.8	2
Kr	36	16.5	16.5[a]	16.7	0.5
Sr	38	232.6	241[c]	186	8
Cd	48	63.7	75[c]	40.5	50
Xe	54	27.0	27.1[a]	27.3	0.5
Ba	56	324.0	359[c]	268	8
Hg	80	44.9	80[c]	34	50

[a] McEachran *et al.*, Ref. 16.
[b] Lahiri and Mukerji, Ref. 4.
[c] Desclaux *et al.*, Ref. 12.
[d] S. Kaneko and S. Arai, J. Phys. Soc. Jpn. 26, 170 (1961).
[e] Miller and Bederson, Ref. 6.

TABLE VIII. Comparison of RRPA susceptibilities with nonrelativistic calculations which include correlation beyond the CHF theory. Units : (α_1, χ_1) in a_0^3, α_2 in a_0^5.

Element	α_1	$\alpha_{1\,\mathrm{corr}}$	$10^6\chi_1$	$10^6\chi_{1\,\mathrm{corr}}$	α_2	$\alpha_{2\,\mathrm{corr}}$
He	1.322	1.383[a]	−21.0	−21.2[d]	2.33	2.27[e]
Be	45.6	37.8[b]	−154.0	−145	342.	302[f]
Ne	2.38	2.68[c]	−83.1	−85.7	6.43	7.73
Mg	81.2	71.3[d]	−262.0	−250.0		
Ar	10.8	11.1[d]	−231.0	−233.0		
Ca	182.8	153.9[d]	−499.0	−475.0		

[a] "Exact" value, Ref. 6.

[b] C. Laughlin and G. A. Victor, in *Atomic Physics*, edited by S. J. Smith and G. K. Walters (Plenum, New York, 1973), Vol. 3, p. 247.

[c] Werner and Meyer, Ref. 7.

[d] Reinsch and Meyer, Ref. 7.

[e] A. Dalgarno, W. D. Davison, and A. L. Stewart, Proc. R. Soc. London, Ser. A 257, 115 (1960).

[f] Reinsch and Meyer (1978), Ref. 7.

very difficult. On the basis of the comparison given in Table VII between relativistic and nonrelativistic CHF calculations one finds a 50% change in α_1 because of relativity, while from Table VIII one finds that for Ca, which has a similar ground-state structure, there is a change in α_1 of 20% due to correlation effects. Thus, to make a reliable calculation of α_1 for Hg, one must certainly consider the effects of relativity and of higher-order correlations simultaneously. Since the effects of correlation are less severe for the noble gases we expect our results for these elements and for their ions to be more reliable. The error due to correlation in the results presented in Tables I—IV is estimated to be less than 10% on the basis of comparisons given in Tables VII and VIII.

ACKNOWLEDGMENTS

The research of D. K. and W. R. J. was supported in part by the National Science Foundation under Grant No. PHY-8107382. The research of P. S. was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2314 from the Notre Dame Radiation Laboratory.

APPENDIX

In the paragraphs below we reduce the RRPA equations (8) to coupled radial differential equations using standard angular-momentum analysis. Let us first consider the DF orbitals $u_i(\vec{r})$. We describe the ith orbital as follows: n is the principal quantum number, κ is the angular quantum number [$\kappa = \mp(j+\frac{1}{2})$ for $j = l \pm \frac{1}{2}$, where l is the orbital angular momentum and j is the total angular momentum], and m is the angular-momentum projection quantum number. We write $u_i(\vec{r})$ with $i = (n,\kappa,m)$ as

$$u_i(\vec{r}) = \frac{1}{r}\begin{bmatrix} iG_{n\kappa}(r)\Omega_{\kappa m}(\hat{r}) \\ F_{n\kappa}(r)\Omega_{-\kappa m}(\hat{r}) \end{bmatrix}, \tag{A1}$$

where $G_{n\kappa}$ and $F_{n\kappa}$ are the large- and small-component radial Dirac functions and where $\Omega_{\kappa m}(\hat{r})$ is a spherical spinor. For convenience we introduce a single two-component radial function

$$f_{n\kappa}(r) = \begin{bmatrix} G_{n\kappa}(r) \\ F_{n\kappa}(r) \end{bmatrix}. \tag{A2}$$

Using a single subscript $a = (n,\kappa)$ to refer to the electrons in the subshell (n,κ) the DF potential of Eq. (5) may be written

$$Vf_a = \sum_b (2j_b+1)\left[\frac{e^2}{r} Y_0(b,b,r) f_a - \sum_l \Lambda_l(a,b)\frac{e^2}{r} Y_l(a,b,r) f_b\right]. \tag{A3}$$

The summation index b ranges over occupied subshells while the index l is limited by the selection rules in the angular coefficient $\Lambda_l(a,b)$. The Hartree screening function $Y_l(a,b,r)$ in Eq. (A3) is given by

$$Y_l(a,b,r)=\frac{1}{r^l}\int_0^r r^l f_a f_b dr + r^{l+1}\int_r^\infty \frac{1}{r^{l+1}} f_a f_b dr \ , \tag{A4}$$

and the angular factor $\Lambda_l(a,b)$ is given by

$$\Lambda_l(a,b)=\begin{pmatrix} j_a & j_b & l \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}^2 \pi(\,l_a\,l_b\,l) \ , \tag{A5}$$

where the large parentheses are a 3-j symbol and where

$$\pi(\,l_a\,l_b\,l)=\begin{cases} 1 \text{ for } l_a+l_b+l, & \text{even} \\ 0 \text{ for } l_a+l_b+l, & \text{odd.} \end{cases} \tag{A6}$$

Introducing the radial Hamiltonian

$$H_a=\begin{bmatrix} m-\dfrac{Ze^2}{r}+V & \dfrac{d}{dr}-\dfrac{\kappa_a}{r} \\ -\dfrac{d}{dr}-\dfrac{\kappa_a}{r} & -m-\dfrac{Ze^2}{r}+V \end{bmatrix} \tag{A7}$$

the DF equations (4) may be written

$$(H_a-\epsilon_a)f_a=0 \ , \tag{A8}$$

where the subscript a ranges over the ionic subshells.

Now let us consider the perturbed orbital $w_i(r)$ in Eq. (8). We take advantage of the fact that an electric [or magnetic] multipole $\phi_J(\vec{r})$ [or $\vec{A}_J(\vec{r})$] will induce a perturbation in the even parity $J=0$ closed-shell ion which has angular momentum J, and parity $\pi=(-1)^J$ [or $(-1)^{J+1}$]. Using the j-j coupling scheme we expect $w_{n\kappa m}(\vec{r})$ to have the form

$$w_{n\kappa m}(\vec{r})=\sum_{\kappa'}(-1)^{j-m}\langle j\,-m,j'm\,|\,jj'J0\rangle\pi(\,l\,l'\,J+\lambda-1)y_{n\kappa\kappa' m}(\vec{r}) \ , \tag{A9}$$

where $y_{n\kappa\kappa' m}(\vec{r})$ is a perturbed one-electron orbital with angular-momentum quantum numbers κ' and m. The parameter λ in the parity factor π takes on the value $\lambda=1$ for electric perturbations and $\lambda=0$ for magnetic perturbations. If we designate the large and small components of $y_{n\kappa\kappa' m}(\vec{r})$ by $S_{n\kappa\kappa'}(r)$ and $T_{n\kappa\kappa'}(r)$ then we may write

$$y_{n\kappa\kappa' m}(\vec{r})=\frac{1}{r}\begin{bmatrix} iS_{n\kappa\kappa'}(r)\Omega_{\kappa' m}(\hat{r}) \\ T_{n\kappa\kappa'}(r)\Omega_{-\kappa' m}(\hat{r}) \end{bmatrix} . \tag{A10}$$

To simplify our discussion we introduce the symbol a' to represent the perturbed orbital quantum numbers $n\kappa\kappa'$ and introduce the two-component radial function

$$y_{a'}(r)=\begin{bmatrix} S_{a'}(r) \\ T_{a'}(r) \end{bmatrix} . \tag{A11}$$

The perturbations $y_{a'}(r)$ satisfy a family of coupled radial Dirac equations to be written below.

For convenience we introduce two angular functions

$$C_J(a,b)=(-1)^{j_a+1/2}[j_a][j_b]\begin{pmatrix} j_a & j_b & J \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}\pi(\,l_a\,l_b\,J) \tag{A12a}$$

and

$$A(a,b,c,d,l,J)=(-1)^{l+J-j_c-j_b}C_l(a,b)C_l(c,d)\begin{Bmatrix} j_a\,j_b\,l \\ j_d\,j_c\,J \end{Bmatrix}\pi(\,l_a\,l_c\,J)\pi(\,l_b\,l_d\,J) \ , \tag{A12b}$$

where $[j]=\sqrt{2j+1}$, and where the large curly brackets designate a 6-j symbol. Later, we use the notation $a\rightarrow -a$ to represent the replacement $\kappa_a \rightarrow -\kappa_a$ in Eqs. (A12).

Let the radial Hamiltonian be defined as in Eq. (A7) with V the unperturbed DF potential. We introduce the first-order "direct" potential which is obtained from the first line of Eq. (9) as

$$V_J^{(1)}(r)=2\sum_{b,b'}\frac{C_J(b,b')}{2J+1}\frac{e^2}{r}Y_J(b,b',r)\,, \tag{A13}$$

where the sum is over each perturbed orbital b' of each subshell b of the ion. With the above notation the relativistic coupled Hartree-Fock equations become the following.

(i) *Electric case:*

$$\begin{aligned}(H_{a'}-\epsilon_a)y_{a'}&+C_J(a,a')V_J^{(1)}(r)f_a\\ &-\sum_{bb'l}\left[A(a,b,a',b',l,J)\frac{e^2}{r}Y_l(a,b,r)y_{b'}+(-1)^{j_b-j_{b'}}A(a,b',a',b,l,J)\frac{e^2}{r}Y_l(a,b',r)f_b\right]\\ &=-C_J(a,a')r^Jf_a+\sum_b\lambda_{a'b}f_b\,;\end{aligned} \tag{A14}$$

(ii) *magnetic case:*

$$\begin{aligned}(H_{a'}-\epsilon_a)y_{a'}&\\ &-\sum_{bb'l}\left[A(-a,-b,a',b',l,J)\frac{e^2}{r}Y_l(a,b,r)y_{b'}+(-1)^{j_b-j_{b'}}A(-a,-b',a',b,l,J)\frac{e^2}{r}Y_l(a,b',r)f_b\right]\\ &=(\kappa_a+\kappa_{a'})C_J(-a,a')r^Jg_a+\sum_b\lambda_{a'b}f_b\,.\end{aligned} \tag{A 15}$$

In the magnetic equations (A15) we have introduced the notation

$$g_a(r)=\begin{bmatrix}F_a(r)\\ G_a(r)\end{bmatrix} \tag{A16}$$

in the driving term.

To obtain the electric susceptibilities and shielding factors in terms of the solutions to Eq. (A14) it is only necessary to note that the induced charge density

$$\rho^{(1)}(\vec{r})=e\sum_{n\kappa m}(w_{n\kappa m}^{\dagger}u_{n\kappa m})+\text{c.c.} \tag{A17}$$

may be written

$$\rho^{(1)}(\vec{r})=\frac{2J+1}{4\pi}\frac{1}{r^2}R_J^{(1)}(r)Y_{J0}(\hat{r})\,, \tag{A18}$$

where the radial charge density $R^{(1)}$ is given by

$$R_J^{(1)}(r)=\frac{2e^2}{2J+1}\sum_{aa'}C_J(a,a')(S_{a'}G_a+T_{a'}F_a) \tag{A19}$$

with the sum over all perturbations of all ionic subshells. In a similar way we find that the induced current density

$$\vec{j}^{\,(1)}(\vec{r})=e\sum_{n\kappa m}(w_{n\kappa m}^{\dagger}\vec{\alpha}u_{n\kappa m})+\text{c.c.} \tag{A20}$$

may be written

$$\vec{j}^{\,(1)}(\vec{r})=\frac{2J+1}{4\pi}\frac{1}{r^2}S_J^{(1)}(r)\vec{Y}_{JJ0}(\hat{r})\,, \tag{A21}$$

where the radial current density $S_J^{(1)}(r)$ is

$$S_J^{(1)}(r)=\frac{2e^2}{2J+1}\sum_{a,a'}\frac{\kappa_a+\kappa_{a'}}{J(J+1)}C_J(-a,a')\times(S_{a'}F_a+T_{a'}G_a)\,. \tag{A22}$$

The perturbed potentials $\phi_J^{(1)}(r)$ and $\vec{A}_J^{(1)}(\vec{r})$ can now be easily worked out from Eqs. (A18) and (A22) for the perturbed charge and current densities. Expressions for these potentials are given in Eqs. (13) and (14) in the main body of the text.

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*Permanent address: Fachbereich Physik, Universität Kassel, Kassel, Federal Republic of Germany.

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