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Hyperpolarizabilities for Hartree-Fock Atoms[*]

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A fully coupled Hartree-Fock variational method is used to calculate the hyperpolarizability of the He, Be, Ne, and Ar atoms. In these calculations the hyperpolarizability is inferred from the electric moment induced in the atoms for various finite values of the external static electric field. A formulation of the problem and the justification for the methods used is given. The nonlinear parameters of all the wave functions used in these calculations are presented along with a convergence test for the wave function of the helium atom. The nuclear dipole shielding factor, polarizability, and hyperpolarizability are tabulated for these atoms and the results are discussed and compared with previous theoretical and experimental results.

I. INTRODUCTION

The large electric fields introduced by lasers have recently provided an excellent experimental tool for the study of nonlinear distortions in atoms. Experiments with dilute gases are particularly interesting because the measured results can easily be compared with calculations for isolate atoms interacting with the radiation field. Thus, with ordinary light sources, the distortion produced in an atom is adequately characterized by an induced electric moment $\vec{\mu}$ which is proportional to the field $\vec{F}$, that is

$$\vec{\mu} = \underline{\alpha} \cdot \vec{F} \ , \tag{1}$$

where $\underline{\alpha}$ is the polarizability tensor.

On the other hand, for the large fields available from lasers, for example, $|\vec{F}| \sim 10^6$ V/cm, measurable deviations from the linear relation of Eq. (1) exist. For systems with inversion symmetry, the induced moment $\vec{\mu}$ expression can contain only odd powers in the external electric field; thus Eq. (1), when modified to include nonlinear corrections, becomes

$$\vec{\mu} = \underline{\alpha} \cdot \vec{F} + \tfrac{1}{6} \underline{\gamma} \vdots \vec{F}^3 + \cdots \ . \tag{2}$$

Here $\underline{\gamma}$ is the hyperpolarizability tensor[1,2] and is the object of this study.

Four types of laser experiments have been proposed[3-5] for the determination of $\underline{\gamma}$. The most accurate involves measurement of the Kerr effect for which the electrooptical birefringence is proportional to the atomic hyperpolarizability. Less accurate are measurements of $\underline{\gamma}$ from the dc electric-field-induced second-harmonic generation in a focused laser beam. In addition, $\underline{\gamma}$ has been measured from the third-harmonic power generated in a laser beam. Finally, for sufficiently intense light sources the refractive index changes by a term proportional to $\underline{\gamma}$.[6,7]

In this paper the coupled Hartree-Fock calculations of $\underline{\gamma}$ for the He, Be, Ne, and Ar atoms in a static field are presented. Then, following Cohen and Roothaan,[8] the electric field terms are included in the Hamiltonian and the polarizability and hyperpolarizability are inferred from the induced moment without direct recourse to perturbation theory. Although measurements made thus far have customarily been made for optical frequencies, one can nevertheless expect that including frequency dependence would only change the $\underline{\gamma}$ results by a few percent.[2,4]

In Sec. II the formulation of the problem and a justification of the method is presented. Section III contains the numerical results. Finally, Sec. IV presents a short summary and discussion of the results.

II. FORMULATION OF METHOD

The polarizabilities and hyperpolarizabilities are calculated from a fully coupled Hartree-Fock method. Since the systems treated are all spherically symmetric atoms the tensors $\underline{\alpha}$ and $\underline{\gamma}$ are isotropic so that Eq. (2) can be rewritten as

$$\mu = \alpha F + \tfrac{1}{6} \gamma F^3 + \cdots \tag{2$'$}$$

Thus, the coefficients α and γ which characterize these tensors will hereafter be referred to as the polarizability and hyperpolarizability, respectively.

Then proceeding in the usual way the total wave function ψ is expressed as a single Slater determinant consisting of orthonormal spin orbitals

χ_i, $i=1, 2, \cdots, N$, where N is the number of electrons. We will consider only spherically symmetric systems and we choose the electric field F to be in the z direction. Then the total energy is

$$E=\langle \psi | H | \psi \rangle \ , \tag{3}$$

where H is given in atomic units by

$$H=-\sum_{i=1}^{N}\left(\frac{1}{2}\nabla_i^2+\frac{Z_0}{r_i}\right) + \sum_{i=1}^{N}\sum_{j=1}^{N}(i>j)\,\frac{1}{r_{ij}} + \sum_{i=1}^{N} F z_i \ . \tag{4}$$

Z_0 is the atomic number and r_i and z_i are the position of the ith electron and its component along the field, respectively.

The usual Hartree-Fock procedure of minimizing the energy leads to the perturbed one-electron Fock equations[9]

$$[h(1)+Fz_1]\,\chi_i(1)=\epsilon_i\,\chi_i(1) \ , \tag{5}$$

where

$$h(1)=-\frac{1}{2}\nabla_1^2-\frac{Z_0}{r_1}+\sum_{j=1}^{N}\langle \chi_j(2)|\,\frac{1}{r_{12}}(1-P_{12})\,|\chi_j(2)\rangle \ , \tag{6}$$

with

$$\begin{aligned}\langle\chi_j(2)|\,(1/r_{12})(1-P_{12})\,|\chi_j(2)\rangle f(1) &= \langle\chi_j(2)|\,(1/r_{12})\,|\chi_j(2)\rangle f(1) \\ &\quad -\langle\chi_j(2)|\,(1/r_{12})\,|f(2)\rangle\,\chi_j(1) \ .\end{aligned}$$

Once Eqs. (5) are solved, α and γ can be determined from the induced moment μ. Thus, we have

$$\mu=-\langle\psi|\sum_{i=1}^{N} z_i|\psi\rangle=-\sum_{i=1}^{N}\langle\chi_i(1)|z_1|\chi_i(1)\rangle \ , \tag{7}$$

$$\mu=\alpha F+\tfrac{1}{6}\gamma F^3+\tfrac{1}{120}\,\delta F^5+\cdots \ . \tag{8}$$

The numerical results of μ obtained from Eq. (7) for different values of the field are used to determine α and γ from Eq. (8).

In this work Eqs. (5) are solved using the analytical expansion technique of Roothaan.[9] Specifically, the Fock orbitals χ_i have the general form

$$\chi_i=s\textstyle\sum_l R_{li}(r)\,Y_{lm}(\theta,\phi) \ , \tag{9}$$

where

$$R_{li}(r)=\textstyle\sum_k C_{ki}N_k r^{n_k}-e^{-\xi_k r} \ . \tag{10}$$

The C_{ki} are variational coefficients which when varied in the expression for the total energy lead to an algebraic eigenvalue problem,[8] and they are determined from its solution. Here $n_k(\geq l)$ and ξ_k are also variational parameters chosen so as to minimize the energy and N_k is a normalizing factor. Further s is an $\underline{\alpha}$ or $\underline{\beta}$ spin function and the required spherical harmonics $Y_{lm}(\theta,\phi)$ are discussed in what follows.

In initial calculations using this method, Cohen[10] obtained quite reasonable results for α but his numerical estimates for γ do not agree very well with approximate perturbation calculations[11] or with the experimental Kerr effect measurements of Buckinham and Dunmur[2] or with the results obtained herein.

This method is clearly equivalent to fully coupled Hartree-Fock perturbation theory. Thus, it is of interest in light of the Cohen results to carefully consider the problems of the radial flexibility [cf. Eq. (10)] and the angular symmetries one should introduce into the spin orbitals χ_i if one wishes to obtain accurate values of the hyperpolarizabilities.

To this end we assume that the field-dependent spin-orbitals must contain terms with those angular symmetries as required in the Hartree-Fock perturbation theory. Then, proceeding as has been previously outlined,[11] the spin orbitals χ_i and the orbital eigenvalues ϵ_i are expanded as functions of the field F according to

$$\chi_i=\chi_i^0+F\chi_i^1+F^2\chi_i^2+\cdots \ , \tag{11}$$

$$\epsilon_i=\epsilon_i^0+F\epsilon_i^1+F^2\epsilon_i^2+\cdots \ . \tag{12}$$

On substituting these expansions into Eqs. (5) we have the following hierarchy of one-electron perturbation equations:

$$[h^0(1)-\epsilon_i^0]\,\chi_i^0(1)=0 \ , \tag{13a}$$

$$[h^0(1)-\epsilon_i^0]\,\chi_i^1(1)+[z_1+v^1(1)-\epsilon_i^1]\,\chi_i^0(1)=0 \ , \tag{13b}$$

and, for $n\geq 2$,

$$[h^0(1)-\epsilon_i^0]\,\chi_i^n(1)+[z_1+v^1(1)-\epsilon_i^1]\,\chi_i^{n-1}(1) + \sum_{p=2}^{\infty}[v^p(1)-\epsilon_i^p]\,\chi_i^{n-p}(1)=0 \ , \tag{13c}$$

where h^0 is the usual one-electron Fock operator

$$h^0(1)=-\frac{1}{2}\nabla_1^2-\frac{Z_0}{r_1}+\sum_{j=1}^{N}\langle\chi_j^0(2)|\,\frac{1}{r_{12}}(1-P_{12})\,|\chi_j^0(2)\rangle \tag{14}$$

and

$$v^p(1)=\sum_{s=0}^{p}\ \sum_{j=1}^{N}\langle\chi_j^s(2)|\,\frac{1}{r_{12}}(1-P_{12})\,|\chi_j^{p-s}(2)\rangle \ . \tag{15}$$

We now consider the angular symmetries required in the spin orbitals χ_i given in Eq. (9). A consideration of Eqs. (13) shows that the angular symmetries of the pth orbital are obtained by the operation of z on the $(p-1)$th orbital.[11] Thus, if χ_i^0 contains the spherical harmonic Y_{lm}, then successive operations $[Y_{10}=(3/4\pi)(z/r)]$ of Y_{10} on Y_{lm} will give the symmetries of χ_i^p. If we use the coupling rule for spherical harmonics[12] we can deduce the symmetries of the pth orbital. The coupling rule is

$$Y_{l_1m_1}Y_{l_2m_2}=\sum_{l=|l_1-l_2|}^{l_1+l_2}\left(\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}\right)^{1/2}$$

$$\times C(l_1l_2l;m_1m_2)\,C(l_1l_2l;00)\,Y_{lm_1+m_2}\ , \tag{16}$$

where $C(l_1l_2l;m_1m_2)$ is the Clebsch-Gordan coefficient which vanishes unless l_1+l_2+l is even. From the above we see that the maximum azimuthal quantum number occurring in χ_i^p is $l+p$.

On substitution of Eq. (11) into the expression for the induced moment Eq. (7) one finds that μ is given by a power series in the field F:

$$\mu(F)=\sum_{i=1}^{N}\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\langle\chi_i^p|z|\chi_i^q\rangle F^{p+q}\,. \tag{17}$$

We are now in a position to determine the angular symmetries necessary to calculate the dipole moment $\mu(F)$ accurately to the nth power in the field. Cutting off the series in Eq. (17) at the nth term we have

$$\mu(F^n)=\frac{1}{2}\sum_{r=0}^{n}\left(\sum_{p=0}^{r}\sum_{i=1}^{N}(\langle\chi_i^p|z|\chi_i^{r-p}\rangle+\langle\chi_i^{r-p}|z|\chi_i^p\rangle)\right)F^r. \tag{18}$$

The actual number of spherical harmonics required in χ_i is much fewer than one would suppose from inspection of Eq. (18). This is because many angular factors in Eq. (18) integrate to zero[13] due to the selection rules for the angular integration; that is

$$\langle Y_{lm}|Y_{10}|Y_{l'm'}\rangle=0 \tag{19}$$

unless

TABLE I. Convergence of helium calculations as size of SCF basis is increased.[a–c]

6-term basis[d]			9-term basis			12-term basis			15-term basis			20-term basis			24-term basis		
n_k	l	ξ_k	n_k	l	ξ_k	n_k	l	ξ_k	n_k	l	ξ_k	n_k	l	ξ_k	n_k	l	ξ_k
0	0	1.450	0	0	1.450	0	0	1.450	0	0	1.450	0	0	1.4511	0	0	1.4511
1	0	2.640	1	0	2.640	1	0	2.640	1	0	2.640	1	0	2.6314	1	0	2.6314
1	0	1.723	1	0	1.723	1	0	1.723	1	0	1.723	1	0	1.7230	1	0	1.7230
1	1	0.971	1	1	0.971	1	1	0.971	1	1	0.971	1	1	0.9710	1	1	0.9710
3	1	1.100	3	1	1.100	3	1	1.100	3	1	1.100	3	1	1.1000	3	1	1.1000
2	2	1.100	2	2	1.100	2	2	1.100	2	2	1.100	2	2	1.1000	2	2	1.1000
			2	0	2.640	2	0	2.640	2	0	2.640	2	0	2.6400	2	0	2.6400
			2	1	1.100	2	1	1.100	2	1	1.100	2	1	1.4890	2	1	1.4890
			3	2	1.100	3	2	1.100	2	2	1.500	3	2	1.1000	3	2	1.1000
						1	0	5.000	1	0	1.100	1	0	1.1000	1	0	1.1000
						2	1	2.500	2	2	0.900	2	2	0.9710	2	2	0.9710
						2	2	2.500	2	2	1.000	3	2	2.3940	3	2	2.3940
									0	0	1.100	0	0	1.1000	0	0	1.1000
									3	1	0.900	3	1	0.9000	3	1	0.9000
									2	1	0.900	2	1	0.9000	2	1	0.9000
												2	0	1.1000	2	1	1.1000
												1	1	0.4740	1	1	0.4740
												1	1	1.1560	1	1	1.1560
												2	1	2.8060	2	1	1.8060
												2	2	0.7930	2	2	0.7930
															3	3	0.7930
															3	3	0.9710
															3	3	1.1000
															4	3	1.1000
$\alpha=1.32$ a.u. $\frac{1}{6}\gamma=4.0$ a.u. $\beta_\infty=1.029$			$\alpha=1.3218$ a.u. $\frac{1}{6}\gamma=4.4$ a.u. $\beta_\infty=1.011$			$\alpha=1.322$ a.u. $\frac{1}{6}\gamma=5.941$ a.u. $\beta_\infty=0.998$			$\alpha=1.3222$ a.u. $\frac{1}{6}\gamma=5.945$ a.u. $\beta_\infty=0.9935$			$\alpha=1.32224$ a.u. $\frac{1}{6}\gamma=6.003$ a.u. $\beta_\infty=2.00054$			$\alpha=1.32224$ a.u. $\frac{1}{6}\gamma=6.003$ a.u. $\beta_\infty=1.00054$		

[a] Form of orbital is given by Eq. (7).

[b] The ξ_k are the values actually used in the calculations. This is not to imply that these parameters are optimized to that number of significant figures listed. Further, the n_k and ξ values are not to be considered a unique set but are merely a set which by trial and error, using various combinations, has been indicated to give about the lowest total energy.

[c] Here α, $\frac{1}{6}\gamma$, and β_∞ are given to the number of significant figures considered to be numerically reliable.

[d] This 6-term basis was used by Cohen (Ref. 16).

TABLE II. Spin-orbital functions[a,b] for He, Be, Ne, and, Ar in external electric field.[c,d]

Helium			Beryllium			Neon						Argon					
$m=0$			$m=0$			$m=0$			$m=\pm1$			$m=0$			$m=\pm1$		
n_k	l	ξ_k	n_k	l	ξ_k	n_k	l	ξ_k	n_k	l	ξ_k	n_k	l	ξ_k	n_k	l	ξ_k
0	0	1.4511	0	0	5.748	0	0	14.0940	1	1	9.4550	0	0	20.1000	1	1	14.7820
0	0	1.1000	0	0	2.945	0	0	9.0670	1	1	4.4545	0	0	15.6644	1	1	9.4975
1	0	2.6314	1	0	5.748	1	0	9.7570	1	1	2.3717	1	0	15.6838	1	1	5.7870
1	0	1.7230	1	0	2.945	1	0	3.3830	1	1	1.4700	1	0	10.3041	2	1	4.2264
1	0	1.1000	1	0	1.290	1	0	2.3500	2	1	4.4545	1	0	7.2867	2	1	2.6757
2	0	2.6400	1	0	0.845	2	0	9.0670	2	1	2.3717	2	0	6.8971	2	1	1.9232
2	0	1.1000	2	0	5.748	2	0	3.8310	2	1	1.4700	2	0	3.7052	2	1	0.9649
1	1	1.1560	2	0	3.630	2	0	2.3500	2	2	9.4550	2	0	2.5450	3	1	9.4975
1	1	0.9710	2	0	2.945	3	0	2.3500	2	2	4.4545	2	0	1.5878	3	1	5.7870
1	1	0.4740	2	0	1.290	3	0	1.4700	2	2	2.3717	2	0	0.9649	3	1	2.6757
2	1	0.9000	1	1	3.360	1	1	14.0940	2	2	1.4700	1	1	14.7820	2	2	9.4975
2	1	1.4890	1	1	2.945	1	1	9.4550	3	2	2.3717	1	1	9.4975	2	2	5.7870
2	1	2.8060	1	1	2.216	1	1	4.4545	3	3	9.4550	1	1	5.787	2	2	2.6757
3	1	0.9000	1	1	0.991	1	1	2.3717	3	3	4.4545	2	1	4.2264	2	2	0.9649
3	1	1.1000	1	1	0.620	1	1	1.4700	3	3	2.3717	2	1	2.6757	3	2	2.6757
2	2	0.7930	2	1	3.630	2	1	14.0940	3	3	1.4700	2	1	1.9232	3	2	0.9649
2	2	0.9710	2	1	2.216	3	1	9.7570				2	1	0.9649	3	3	9.4975
2	2	1.1000	2	1	1.500	2	2	9.4550				3	1	9.4975	3	3	5.7870
3	2	1.1000	2	1	0.991	2	2	4.4545				3	1	5.7870	3	3	2.6757
3	2	2.3940	2	2	2.216	2	2	2.3717				3	1	2.6757	3	3	0.9649
			2	2	1.500	2	2	1.4700				2	2	9.4975			
			2	2	1.300	3	3	9.4550				2	2	5.7870			
			2	2	1.100	3	3	4.4545				2	2	2.6757			
			2	2	0.900	3	3	2.3717				2	2	0.9649			
			2	2	0.620	3	3	1.4700				3	2	2.6757			
												3	2	0.9649			
												3	3	9.4975			
												3	3	5.7870			
												3	3	2.6757			
												3	3	0.9649			

[a] Total wave function is the closed-shell single Slater determinant corresponding to orbital parameters listed in this table.

[b] Form of orbitals is given by Eq. (10).

[c] The linear SCF coefficients C_{ki} [see Eq. (10)] for various values of the external field are given by Richard E. Sitter, Jr., Ph.D. dissertation (State University of New York at Buffalo, 1969) (unpublished).

[d] The wave functions were constructed using the zero-field functions of E. Clementi, IBM J. Res. Develop. 9, 2 (1965).

$$m=m', \quad l=l'\pm1 . \tag{20}$$

Then if χ_i^0 corresponds to azimuthal quantum number l and since χ_i^p contains spherical harmonics with a maximum azimuthal quantum number $l+p$, then for the last terms in Eq. (18), Eqs. (20) gives

$$p+l=n-p+l\pm1 . \tag{21}$$

This puts the maximum value of p at

$$p_{\max}=\tfrac{1}{2}(n+1) \quad (n \text{ is odd}) . \tag{22}$$

Thus we conclude that if our orbitals Eq. (9) are to contain all spherical harmonics which would be required for μ to be accurate to the nth order, then they must contain the spherical harmonics that appear in all the perturbation functions up to $\chi_i^{(n+1)/2}$. Hence to calculate $\mu(F^3)$ we need the spherical harmonics which appear in χ_i^0, χ_i^1, and χ_i^2.

To illustrate this result, if χ_i^0 is an S function, one must include S, P, and D terms in χ_i to obtain the electric moment to the third power in F. Similarly, if χ_i^0 is a P function, one must include S, P, D, and F terms in χ_i. It is of interest to note that this result concerning the required spherical harmonics in χ_i is equivalent to the results previously obtained for the energies in Hartree-Fock perturbation theory.[11,14] That is, if the perturbation functions χ_i^p are known up to the nth order, the energy can be determined up to the $2n+1$ order. The corresponding result obtained here, i.e., $2n-1$, is only apparently different, as here our result involved the moment and hence the coefficients to the even powers in F are zero. It is also well to note that the flexibility of the radial function [see

TABLE III. Calculated polarizabilities, hyperpolarizabilities, and shielding factors for He, Be, Ne, and Ar.

Atom	α (a.u.)[a]	γ (a.u.)[a]	β_∞[b,c]
He	1.322	3.6×10^1	1.000 544
Be	45.62	3.68×10^4	1.004 2
Ne	2.374	4.2×10^1	1.004 6
Ar	10.774	1.01×10^3	1.011 1

[a] Determined from polynomial fit of induced moment:

$$\mu = \alpha F + \tfrac{1}{6}\gamma F^3 + \cdots$$

[see Eq. (8)].

[b] Computed from

$$\beta_\infty = \langle \psi | \sum_{i=1}^{N} \frac{z_i}{r_i^3} | \psi \rangle \frac{1}{F},$$

where ψ is the total wave function for atom in the external field and N is the number of electrons.

[c] Hartree-Fock limit for shielding factor is unity (see Ref. 15).

Eq. (10)] must be greater as one goes to higher powers in F. Thus, for example, if χ_i^0 corresponds to an S orbital, one should note that in order to obtain γ the radial function must have sufficient flexibility than the $Y_{0,0}$ term can contribute to both χ_i^0 and χ_i^2. Similarly, for a P orbital the radial function corresponding to $Y_{1,0}$ must describe those terms in χ_i^0 and χ_i^2.

In order to determine if the radial functions in χ_i are chosen sufficiently flexible one must show that both the polarizability α and the hyperpolarizability γ are stable with the respect to addition of more terms in the radial functions. This facet of the problem is considered in more detail in the Sec. III in which we present our numerical results.

III. RESULTS

In this work it is essential to carry out arithmetic to high precision as well as use adequate radial functions. The first consideration is not very important here, except if one should use nearly redundant basis functions, as the CDC-6400 computer used for this problem does arithmetic to more than 14 significant decimal digits. On the other hand, there seems to be no adequate test as to whether the radial functions are sufficiently flexible. Thus, studies of three types are made for helium. First, the convergence of α and γ as additional radial terms are included, is studied. In order to test the numerical consistency four "F-type" terms, in addition to the required S, P, and D terms, are added to the helium oribital. In principle, these terms should lower the total energy and change the induced moment but should not effect either α or γ. Thus, this is to serve as a test of the accuracy of the fit of μ to powers in F and as a test of the accuracy of the solution to the eigenvalue problem. Finally, to test the accuracy of the wave functions near the nucleus, calculations of the dipole shielding factors β_∞ are made.

In Table I α, γ, and β_∞ are given for helium as additional radial terms are included in χ_i. Also in this table are presented calculations for α, γ, and β_∞ when four "F-type" terms have been included in χ_i. It seems clear for helium at least that our best γ value should equal the Hartree-Fock limit to better than 0.5%. This is because α and γ have both converged and β_∞ is quite near its theoretical Hartree-Fock limit of 1.0.[15]

Further, one has confidence in these results, as the inclusion of "F-type" terms has no significant effect on α, γ, or β_∞ despite the fact the coefficient to the fifth power in the field was markedly altered.

Table II summarizes the He, Be, Ne, and Ar wave functions that were used. In Table III our computed values for α, γ, and β_∞ for these atoms are given. Finally, in Table IV the present results are presented with previous calculations and with the experimental values.

IV. SUMMARY AND DISCUSSION

The polarizabilities and hyperpolarizabilities of the present work are obtained from solving the Hartree-Fock equations in the field directly without recourse to perturbation theory. This procedure requires more computer time than the previous Hartree-Fock perturbation methods.[11] The primary gain over the perturbation methods is a saving in programming effort. Further, one might expect to obtain more relaible results here than from the perturbation method because the linear parameters of the zero-order orbitals are solved to greater accuracy. This greater accuracy in the linear parameters of χ_i^0 of course propagates itself, resulting in greater numerical accuracy in the first- and second-order type terms in the orbitals.

It is amply demonstrated by this work that coupling the Hartree-Fock equations has a rather profound effect on the results for γ. An inspection of Table IV shows that coupling the equations has reduced the size of γ over the corresponding[11] uncoupled Hartree-Fock results by a factor of two or more. The polarizability results are in good agreement with the previous coupled Hartree-Fock calculations.

It is of interest to consider the present hyperpolarizability results for the beryllium atom. Here γ is rather large and positive in sign. This same qualitative result was obtained from the uncoupled theory[11] except there γ is much larger. On the other hand, Cohen[10] states that his γ is negative, but is unable to give its magnitude. Inasmuch as it is well known that the usual Hartree-Fock single Slater determinant function does not give a good

TABLE IV. Comparison of present with previous and experimental results (a.u.).

	Polarizability α					Hyperpolarizability γ				
Atom	Present	CHF[a]	UHF[b]	Other calc.	Expt.[c]	Present	CHF[a]	UHF[d]	Other calc.	Expt.
He	1.332	1.32	1.48	1.384[e]	1.384	36.0	24	51.6	42.8[f] 42.6[g] 43.1[h] 31.2[i] 28.5[j]	52.8 ± 4[k]
Be	45.62	45.55	64.4	46.77[l]	···	3.68×10^4	$\gamma < 0$	7.71×10^4	1.71×10^2[j]	···
Ne	2.374	2.366	2.82	2.48[m]	2.68	42	50	124	···	101 ± 8[n] 118 ± 3[o] 95 ± 16[p]
Ar	10.774	···	16.47	···	11.0	1.01×10^3	···	2.31×10^3	···	1171 ± 79[k] 1339 ± 43[o] 1344 ± 213[p]

[a] Coupled Hartree-Fock. Reference 10.

[b] Uncoupled Hartree-Fock. P. W. Langhoff and R. P. Hurst, Phys. Rev. 139A, 1415 (1965).

[c] Refractive index data. A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. (London) A259, 424 (1960).

[d] Uncoupled Hartree-Fock. Reference 11.

[e] Ritz variation method. Kwong T. Chung and R. P. Hurst, Phys. Rev. 152, 35 (1966).

[f] Ritz variation method. M. N. Grasso, Kwong T. Chung, and R. P. Hurst, Phys. Rev. 167, 1 (1968).

[g] Accurate perturbation calculation. Sitz and Yaris, J. Chem. Phys. 49, 3546 (1968).

[h] Accurate perturbation calculation. A. D. Buckingham and P. G. Hibbard, in Proceedings of the Faraday Symposium, London, 1968 (unpublished).

[i] Perturbation calculation. L. L. Boyle, A. D. Buckingham, R. L. Disch, and D. A. Dunmur, J. Chem. Phys. 45, 1318 (1966).

[j] Z-expansion method. G. W. F. Drake and M. Cohen, J. Chem. Phys. 48, 1168 (1968).

[k] Reference 2 actually gave 53.6 ± 4 a.u. for a wavelength of 632.8 mm, but they estimate this corresponds to a static $\gamma = 52.8$ a.u.

[l] Perturbation calculation. H. P. Kelley, Phys. Rev. 136, B896 (1964).

[m] Configuration interaction calculation. W. E. Donath, J. Chem. Phys. 39, 2685 (1963).

[n] Kerr-effect measurement. See Ref. i.

[o] Third-harmonic generation. J. F. Ward and G. H. C. New, Phys. Rev. 185, 57 (1969). Their results renormalized to 42.7 a.u. for helium.

[p] Second-harmonic generation. Reference 3. Their results renormalized to 42.7 a.u. for helium.

representation for the field-free wave function of beryllium,[16] one must suspect that even the coupled Hartree-Fock results for the atom could be very much in error. Nevertheless, since the present method is a true variational method, one should expect that it could underestimate γ, so that if our beryllium results err they most probably err by being too small. Then, the most reasonable assumption is that the γ for beryllium which is negative in sign is quite incorrect.

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[1] A. D. Buckingham and J. A. Pople, Proc. Phys. Soc. (London) A68, 905 (1955).

[2] A. D. Buckingham and D. A. Dunmur, Trans. Faraday Soc. 64, 1776 (1968).

[3] G. H. C. New and J. F. Ward, Phys. Rev. Letters 19, 556 (1967); J. W. F. Ward and G. H. C. New, Phys. Rev. 185, 57 (1969); R. S. Finn and J. F. Ward, Phys. Rev. Letters 26, 285 (1971).

[4] A. L. Dana, dissertation (State University of New York at Buffalo, 1969) (unpublished).

[5] A. D. Buckingham and B. J. Orr, Quart. Rev. (London) 21, 195 (1967).

[6] J. F. Ward, Rev. Mod. Phys. 37, 1 (1965).

[7] A. Dalgarno, in *Perturbation Theory and its Application in Quantum Mechanics*, edited by Calvin H. Wilcox (Wiley, New York, 1966), p. 145.

[8] H. D. Cohen and C. C. J. Roothaan, J. Chem. Phys. 43, S34 (1965).

[9] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951); J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. II, p. 1.

[10] H. D. Cohen, J. Chem. Phys. 43, 3558 (1965); 45, 10 (1966).

[11] P. W. Langhoff, J. D. Lyons, and R. P. Hurst, Phys. Rev. 148, 18 (1966).

[12] M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957), p. 61.

[13] See, for example, H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (Wiley, New York, 1954), p. 117.

[14] A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) A238, 269 (1956); H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two-Electron Atoms* (Academic, New York, 1957), p. 123.

[15] V. G. Kaveeshwar, A. Dalgarno, and R. P. Hurst, J. Phys. B 2, 984 (1969); S. T. Epstein and R. E. Johnson, J. Chem. Phys. 51, 188 (1969); E. S. Chang, J. Chem. Phys. 49, 2904 (1968).

[16] D. Layzer, Ann. Phys. (N.Y.) 8, 271 (1959); J. Linderberg and H. Schull, J. Mol. Spectry. 5, 1 (1960).

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L_2-L_3X Coster-Kronig Transition Probability at $Z = 82$*

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The probability for Coster-Kronig transfer of vacancies from the L_2 to the L_3 subshell of Pb is measured by observing the K x-ray spectrum in coincidence with $L\alpha$ x rays in the electron-capture decay of Bi^{207}. The intensity of the $K\alpha_2$ component of the coincident spectrum is a measure of the L_2-L_3X Coster-Kronig transition probability. A value of 0.156 ± 0.010 is obtained for f_{23}.

I. INTRODUCTION

Most of the recent experimental measurements[1-6] of the L_2-L_3X Coster-Kronig transition probability f_{23} at high Z were based on the method of Rao and Crasemann,[7] who observed Ta and Hg L_2-subshell characteristic x rays emitted in coincidence with $K\alpha_2$ x rays that signal the formation of L_2-subshell vacancies. Chen *et al.*,[8] and McGuire[9] have calculated the radiative, Auger, and Coster-Kronig partial widths of atomic states characterized by a vacancy in the L_2 subshell (i.e., by a $2p_{1/2}$ hole) and obtained values of f_{23} for various atomic numbers from the relation

$$f_{23} = \frac{\text{Coster-Kronig partial width}}{\text{total width}} = \frac{\Gamma_{CK}(L_2L_3)}{\Gamma_R(L_2)+\Gamma_A(L_2)+\Gamma_{CK}(L_2L_3)} , \qquad (1)$$

where $\Gamma_{CK}(L_2L_3)$ is the partial width corresponding to L_2-L_3X Coster-Kronig transitions, $\Gamma_R(L_2)$ is the radiative partial width corresponding to the emission of L_2-subshell characteristic x rays, and $\Gamma_A(L_2)$ is the radiationless partial width corresponding to L_2-Auger-electron emission. The Coster-Kronig partial width can be written as a sum of radiative and nonradiative parts:

$$\Gamma_{CK}(L_2L_3) = \Gamma_R(L_2L_3) + \Gamma_A(L_2L_3) . \qquad (2)$$

Similarly, f_{23} can be expressed as the sum of radiative and nonradiative Coster-Kronig yields:

$$f_{23} = a_{23} + \omega_{23} . \qquad (3)$$

The theoretical estimates[8,9] of f_{23} deviate significantly from the experimental values; the reason for this discrepancy is not obvious. The calculations of f_{23} are based on the assumption that the radiative part ω_{23} [cf. Eq. (3)] is negligible. That the contribution to f_{23} from this radiative magnetic-dipole transition is indeed negligible has been shown both by experimental and theoretical checks.[10] McGeorge *et al.*[11] have corrected the experimental values of f_{23} at $Z < 80$ for the presence of unresolved $L\eta$ (L_2-M_1) x rays in the $L\alpha$ (L_3-$M_{4,5}$) photopeak, but the correction does not remove the discrepancy.

II. EXPERIMENT

A new coincidence experiment to measure f_{23} is reported here. In principle, this measurement is based upon the following considerations: A source is chosen in which K and L vacancies are formed during radioactive decay. The radiative filling of L_3-subshell vacancies results in the emission L_3-subshell characteristic x rays (mostly $L\alpha$ x rays). The K x-ray spectrum coincident with these $L\alpha$ x rays should contain (a) $K\alpha_1$ x rays, because some of the L_3 vacancies are formed originally as a result of $K\alpha_1$ x-ray emission, and also (b) $K\alpha_2$ x rays, because some of the L_3 vacancies are the result of Coster-Kronig transfers from the L_2 subshell of vacancies originally formed during $K\alpha_2$ x-ray emission. The ratio of the coincidence counting rates of $K\alpha_2$ and $K\alpha_1$ x rays ($C_{K\alpha_2(L\alpha)}$ and $C_{K\alpha_1(L\alpha)}$) is related to the L_2-L_3X Coster-Kronig transition probability as follows:

$$\frac{C_{K\alpha_2(L\alpha)}}{C_{K\alpha_1(L\alpha)}} = \frac{C_{K\alpha_2}}{C_{K\alpha_1}} f_{23} . \qquad (4)$$

Here, $C_{K\alpha_2}/C_{K\alpha_1}$ is the ratio of singles $K\alpha_2$ and $K\alpha_1$ x-ray counting rates. The rate $C_{K\alpha_1(L\alpha)}$ must