If D_m is comparable with $|V_{E,m}|^2$, the following occurs. Those parts of the transition probability which would be within the interval D_m in the case of no configuration interaction will be partially shifted out of the region of integration if the interaction is effective. These parts of the transition probability might be replaced, however, by comparable amounts stemming from adjacent terms. The average cross section is also in this case approximately given by the mean value represented by Eq. (42).

The previously considered absorption measurements in xenon are used for a check of the approximation (42) as follows: As the hitherto undetermined part of σ_0 in Eqs. (42) and (43) is only dependent on Q, but not on $|\bar{V}_E|^2$, and the value of $\bar{\sigma}$ is included in the measurements, it is possible to calculate Q as a function of $|\bar{V}_E|^2$ from each of the two equations. These functions are also shown in Fig. 3. The designated limits of error contain the uncertainty in the evaluation of $\bar{\sigma}$ and σ_0. The curve having the larger Q values represents Eq. (42). As is to be expected, only this equation is consistent within the limits of error with the results previously obtained.

Measurements of the energy of the electrons ejected by photo-ionization in the heavier rare gases at energies lying above the second ionization limit $P_{1/2}$ show two groups of electrons having different kinetic energies. The intensity ratio of the two groups was measured earlier.[8] This ratio also allows the value of the parameter Q to be determined. In accordance with the calculations carried out before, we get $Q=1.88$ which is drawn as a dashed line in Fig. 3. The excellent agreement with the results taken from (38) points out that the inclusion of an additional configuration interaction between the continuous states above the $P_{1/2}$ limit is either very small or nonexistent.

This research was sponsored in part by the Deutsche Forschungsgemeinschaft. The computations were carried out at the Institut für Instrumentelle Mathematik, Bonn, using the IBM 7090.

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PHYSICAL REVIEW VOLUME 152, NUMBER 1 2 DECEMBER 1966

Dipole Polarizabilities of the 2^3S_1 and 2^1S_0 States of He and Li^+†

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(Received 28 October 1965; revised manuscript received 15 July 1966)

Variational calculations of the dipole polarizabilities of the two lowest excited states $2\,{}^3S_1$ and $2\,{}^1S_0$ of He and Li^+ are made with 72-term variational wave functions. Because of the slow convergence for the He $2\,{}^1S_0$ state, the wave function for this system is extended to include 96 terms. The polarizabilities are determined from the interaction energy of the atomic system with a uniform external electric field. The most complete calculations gave 315.63 atomic units and 801.95 a.u. for He, and 46.88 a.u. and 98.19 a.u. for Li^+, for the $2\,{}^3S_1$ and $2\,{}^1S_0$ states, respectively. The only previous calculations are those for helium, in which Dalgarno and Kingston used theoretical oscillator strengths. They obtained 313 and 788 a.u. for the $2\,{}^3S_1$ and $2\,{}^1S_0$ states, respectively. The ground states are also calculated as a check on the method used. Excellent agreement with the previous calculations and with experiment is obtained for the ground states of H^-, He, and Li^+.

I. INTRODUCTION

In recent years, great effort has been expended in the study of two-electron systems. In addition to the intrinsic interest in these systems themselves, they are sufficiently simple that they are of special interest in the study of various approximation methods. Thus, even under the usual assumptions of a nonrelativistic, infinite-nuclear-mass Hamiltonian, they cannot be solved exactly. However, variational calculations, with the help of high speed computers, have approximated the energy of the unperturbed Hamiltonian to as high an accuracy as obtained in experiment.[1-3] For this reason most of the interest now centers on properties other than the energy, such as the polarizabilities. The electric polarizabilities of the ${}^1S_0$ ground state of He and two-electron ions have been obtained theoretically and are in good agreement with experiment. However, for higher energy states, the theoretical and experimental data are more limited.

In the presence of a uniform external electric field the total energy of the atomic system will be decreased. To fourth order in the electric field, the interaction

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† Work supported by U. S. Air Force Office of Scientific Research, Grant Number AF-AFOSR-191-63.

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energy ΔE in atomic units[4] is given by

$$-\Delta E=\frac{1}{2!}\alpha F^2+\frac{1}{4!}\beta F^4+\cdots. \tag{1}$$

Here α and β are the dipole polarizability and dipole-hyperpolarizability, respectively. Then,

$$\alpha=\lim_{F\to 0}-2\Delta E/F^2. \tag{2}$$

An alternative point of view is to consider the effect of the external field on the wave function. Thus, when the uniform field is introduced the wave function of the atomic system is distorted and a dipole moment μ is then induced according to

$$\mu=\alpha F+\tfrac{1}{6}\beta F^3+\cdots. \tag{3}$$

This implies

$$\alpha=\lim_{F\to 0}\mu/F. \tag{4}$$

The polarizability of the $1\,{}^1S_0$ ground state of helium and two electron ions have been computed by Winker and Das[5] using a variation-perturbation approach. Sternheimer[6] solved directly the first-order equation both analytically and numerically. More recent work has been carried out by McNamee and Dalgarno[7] Yoshimine and Hurst[8] and Langhoff and Hurst[9] using uncoupled Hartree-Fock approximations. McNamee and Dalgarno[7] and Cohen[10] have used coupled Hartree-Fock approximations. Geltman[11] used an absorption coefficient integral over the wavelength in calculating the polarizability of H$^-$ and obtained a result in close agreement with Schwartz,[12] who used an 18-term Hylleraas-type zero-order wave function with a more general form of first-order perturbed wave function. Schwartz's calculation probably gave the most accurate results that have thus far been obtained for the ground state of H$^-$.

As to the excited states, the only ones which are bound are those with one electron in the ground state.[13] The primary aim of the present work is to obtain the polarizabilities of the metastable states $2\,{}^3S_1$ and $2\,{}^1S_0$. These states are of special importance because they are metastable. Dipole transitions to the ground state from the state $2\,{}^3S_1$ are forbidden by both spin and spatial symmetries whereas the $2\,{}^1S_0$ transition to the ground state is forbidden by the spatial symmetry alone. Thus, while both of these excited states are metastable, the $2\,{}^3S_1$ transition to the ground state can be obtained only from consideration of higher order effects than for the $2\,{}^1S_0$ state.

In 1958, Dalgarno and Kingston[14] used the theoretically calculated values of dipole transition oscillator strengths in obtaining the polarizabilities of helium $2\,{}^3S_1$ and $2\,{}^1S_0$ states. In the present work, variation functions are used to obtain the perturbation energy due to the uniform external electric field. The resulting values of polarizabilities are in good agreement with Dalgarno and Kingston's calculations.

As a check on the method, the same computer programs are used for the ${}^1S_0$ ground states. The results for the ground states are in excellent agreement with previous accurate calculations and with experiment.

In Sec. II the choice of the wave function and its symmetry are discussed and the problem is formulated. Section III gives results of computations, including α of the ground state of H$^-$. In addition are presented results for the $1\,{}^1S_0$, $2\,{}^3S_1$, and $2\,{}^1S_0$ states of He and Li$^+$ in the presence of an external field. Finally, Sec. IV is a summary and discussion of results.

II. THEORY

In the absence of an electric field the zero-order wave functions for the $2\,{}^3S_1$ and $2\,{}^1S_0$ states have spherical symmetry so that the permanent electric moment is zero. Thus, from Eq. (4) in the presence of a uniform electric field in the Z direction the polarizability α is given from the induced moment μ according to

$$\alpha=\lim_{F\to 0}\mu/F=\lim_{F\to 0}\frac{\langle\bar{\Psi}|z_1+z_2|\bar{\Psi}\rangle}{F\langle\bar{\Psi}|\bar{\Psi}\rangle}. \tag{5}$$

Alternatively α can be computed from the interaction energy ΔE according to

$$\alpha=\lim_{F\to 0}-2\Delta E/F^2. \tag{6}$$

The basic problem then reduces to obtaining a variational wave function, which has the proper distortion in the external field and in using this wave function to obtain α according to Eq. (5) and Eq. (6).

Perhaps the simplest function one could conceive of which would have distortion in the presence of the external field and none when the field is zero, is given by

$$\begin{aligned}\bar{\Psi}&=\psi^0+(z_1+z_2)\psi_1+(z_1-z_2)\psi_1'+\cdots\\&\approx\psi^0+\psi^{\mathrm{I}}+\psi^{\mathrm{II}}.\end{aligned} \tag{7}$$

On substituting Eq. (7) into the usual energy integral one obtains,

$$E=\frac{\langle\bar{\Psi}|H|\bar{\Psi}\rangle}{\langle\bar{\Psi}|\bar{\Psi}\rangle}\approx\frac{\langle\psi^0+\psi^{\mathrm{I}}+\psi^{\mathrm{II}}|H_0+H^1|\psi^0+\psi^{\mathrm{I}}+\psi^{\mathrm{II}}\rangle}{\langle\psi^0+\psi^{\mathrm{I}}+\psi^{\mathrm{II}}|\psi^0+\psi^{\mathrm{I}}+\psi^{\mathrm{II}}\rangle}, \tag{8a}$$

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[4] 1 a.u. of electric field strength $=e^2/a_0{}^2=5.142\times10^9$ V/cm.

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where

$$H_0=-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2-q/r_1-q/r_2+1/r_{12} \qquad (8b)$$

and

$$H^1=F(z_1+z_2). \qquad (8c)$$

The wave function Ψ is that function which minimizes the total energy of Eqs. (8) in the field.

The explicit form of the trial functions ψ^0, ψ^{I}, and ψ^{II} must represent reasonable compromises in speed of convergence and difficulty of evaluating the integrals. Chosen from these points of view the zero order wave function used here are of the form first proposed by Hylleraas and Undheim.[15] Specifically,

$$\psi^0(ks,ku,kt)=\sum_{i=1}^{N} c_i e^{-kcs/2}k^{l_i+m_i+n_i}s^{l_i}u^{m_i}t^{n_i}\begin{Bmatrix}\sinh(\tfrac{1}{2}kt)\\ \cosh(\tfrac{1}{2}kt\ )\end{Bmatrix}$$

$$=\sum_{i=1}^{N} c_i\phi_i{}^0(ks,ku,kt). \qquad (9a)$$

By analogy to Eq. (9a) the first-order functions are chosen to be of the form

$$\psi^1(ks,ku,kt,kz_1,kz_2)=$$

$$(z_1+z_2)\sum_{i=1}^{N} d_i e^{-kcs/2}k^{l_i+m_i+n_i+1}s^{l_i}u^{m_i}t^{n_i}\begin{Bmatrix}\sinh(\tfrac{1}{2}kt)\\ \cosh(\tfrac{1}{2}kt)\end{Bmatrix}$$

$$=\sum_{i=1}^{N} d_i\phi_i{}^1(ks,ku,kt,kz_1,kz_2), \qquad (9b)$$

$$\psi^{\text{II}}(ks,ku,kt,kz_1,kz_2)=$$

$$(z_1-z_2)\sum_{i=1}^{N} e_l e^{-kcs}k^{l_i+m_i+n_i+-}s^{l_i}u^{m_i}t^{n_i}\begin{Bmatrix}\sinh(\tfrac{1}{2}kt)\\ \cosh(\tfrac{1}{2}kt)\end{Bmatrix}$$

$$=\sum_{i=1}^{N} e_i\phi_i{}^{\text{II}}(ks,ku,kt,kz_1,kz_2) \qquad (9c)$$

Here k is a scaling parameter, c is a nonlinear parameter, c_i, d_i, and e_i are linear variation coefficients and l_i, m_i, n_i are integral powers. Further s, t, and u are defined according to

$$s=r_1+r_2,\quad t=r_1-r_2,\quad u=r_{12}. \qquad (10)$$

The hyperbolic functions $\sinh(\tfrac{1}{2}kt)$ and $\cosh(\tfrac{1}{2}kt)$ are chosen accordingly so as to maintain the proper symmetry. Thus, for the case of the zero-order functions, for the singlet states the spatial part of the function must be symmetric so that if n_i is even the $\cosh(\tfrac{1}{2}kt)$ function is taken and if n_i is odd the $\sinh(\tfrac{1}{2}kt)$ is used. Similarly, for the triplet states the spatial part of the function must be antisymmetric so that when n_i is even the $\sinh(\tfrac{1}{2}kt)$ function is taken and when n_i is odd $\cosh(\tfrac{1}{2}kt)$ is used.

Substituting Eq. (7) and Eq. (9) into Eq. (8), one can, then, minimize this energy integral with respect to the linear parameters c_i, d_i, e_i and nonlinear parameters c and k.

Preceeding in the usual way,[13,15] one obtains the secular equation:

$$\begin{vmatrix} (k^2M-kL-EN)_{ij}{}^{(0,0)} & P_{ij}{}^{(0,\text{I})}/k & P_{ij}{}^{(0,\text{II})}/k \\ P_{ij}{}^{(0,\text{I})}/k & (k^2M-kL-EN)_{ij}{}^{(\text{I},\text{I})} & (k^2M-kL-EN)_{ij}{}^{(\text{I},\text{II})} \\ P_{ij}{}^{(0,\text{II})}/k & (k^2M-kL-EN)_{ij}{}^{(\text{I},\text{II})} & (k^2M-kL-EN)_{ij}{}^{(\text{II},\text{II})} \end{vmatrix}=0 \qquad (11)$$

in which, the superscripts correspond to the wave functions $\phi_i{}^0$, $\phi_i{}^{\text{I}}$, $\phi_i{}^{\text{II}}$, respectively. The integrals M, L, P, N correspond to the kinetic energy, Coulomb potential, perturbation potential and normalization integrals, respectively. Specifically these integrals represent

$$M_{ij}{}^{(0,0)}=\int \phi_i{}^0(s,u,t,)(-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2)\phi_j{}^0(s,u,t)d\tau, \qquad (12a)$$

$$L_{ij}{}^{(0,0)}=\int \phi_i{}^0(s,u,t)\left(\frac{q}{r_1}+\frac{q}{r_1}-\frac{1}{r_{12}}\right)\phi_j{}^0(s,u,t)d\tau, \qquad (12b)$$

$$N_{ij}{}^{(0,0)}=\int \phi_i{}^0(s,u,t)\phi_j{}^0(s,u,t)d\tau, \qquad (12c)$$

$$P_{ij}{}^{(0,\text{I})}=\int \phi_i{}^0(s,u,t)F(z_1+z_2)\phi_j{}^{\text{I}}(s,u,t,z_1,z_2)d\tau, \qquad (12d)$$

$$P_{ij}{}^{(0,\text{II})}=\int \phi_i{}^0(s,u,t)F(z_1+z_2)\phi_j{}^{\text{II}}(s,u,t,z_1,z_2)d\tau, \qquad (12e)$$

$$M_{ij}{}^{(\text{I},\text{I})}=\int \phi_i{}^1(s,u,t,z_1,z_2)$$
$$\times(-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2)\phi_j{}^1(s,u,t,z_1,z_2)d\tau, \qquad (12f)$$

$$L_{ij}{}^{(\text{I},\text{I})}=\int \phi_i{}^{\text{I}}(s,u,t,z_1,z_2)$$
$$\times\left(\frac{q}{r_1}+\frac{q}{r_2}-\frac{1}{r_{12}}\right)\phi_j{}^1(s,u,t,z_1,z_2)d\tau, \qquad (12g)$$

$$N_{ij}{}^{(\text{I},\text{I})}=\int \phi_i{}^{\text{I}}(s,u,t,z_1,z_2)\phi_j{}^{\text{I}}(s,u,t,z_1,z_2)d\tau, \qquad (12h)$$

$$M_{ij}{}^{(\text{I},\text{II})}=\int \phi_i{}^{\text{I}}(s,u,t,z_1,z_2)$$
$$\times(-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2)\phi_j{}^{\text{II}}(s,u,t,z_1,z_2)d\tau, \qquad (12i)$$

$$L_{ij}{}^{(\text{I},\text{II})}=\int \phi_i{}^{\text{I}}(s,u,t,z_1,z_2)$$
$$\times\left(\frac{q}{r_1}+\frac{q}{r_2}-\frac{1}{r_{12}}\right)\phi_j{}^{\text{II}}(s,u,t,z_1,z_2)d\tau, \qquad (12j)$$

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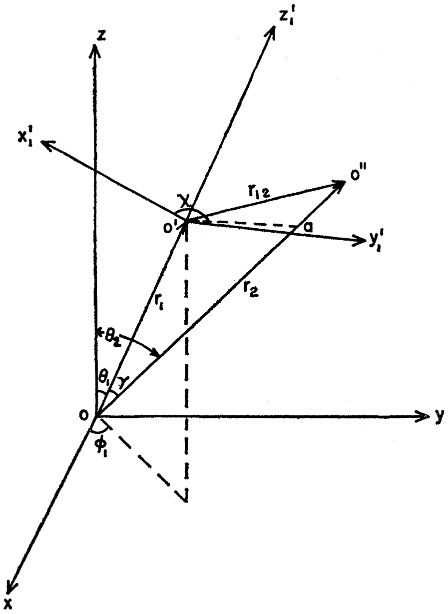

FIG. 1. Coordinate system in integration. [In this figure the direction of X_1' is so chosen that the X_1' axis intersects with the z axis. $0'A$ is the intersection of $(\mathbf{r}_1,\mathbf{r}_2)$ and $X'Y'$ plane.]

$$N_{ij}^{(\mathrm{I,II})}=\int \phi_j^{\mathrm{I}}(s,u,t,z_1,z_2)\phi_j^{\mathrm{II}}(s,u,t,z_1,z_2)d\tau\,, \tag{12k}$$

$$M_{ij}^{(\mathrm{II,II})}=\int \phi_i^{\mathrm{II}}(s,u,t,z_1,z_2) \times(-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}{}_2{}^2)\phi_j^{\mathrm{II}}(s,u,t,z_1,z_2)d\tau\,, \tag{12l}$$

$$L_{ij}^{(\mathrm{II,I}c)}=\int \phi_i^{\mathrm{II}}(s,u,t,z_1,z_2) \times\left(\frac{q}{r_1}+\frac{q}{r_2}-\frac{1}{r_{12}}\right)\phi_j^{\mathrm{II}}(s,u,t,z_1,z_2)d\tau\,, \tag{12m}$$

$$N_{ij}^{(\mathrm{II,II})}=\int \phi_i^{\mathrm{II}}(s,u,t,z_1,z_2)\phi_j^{\mathrm{II}}(s,u,t,z_1,z_2)d\tau. \tag{12n}$$

The differential volume element of integration in this coordinate system is[16]:

$$d\tau=\tfrac{1}{4}u(s^2-t^2)dsdudt\,\sin\theta_1 d\theta_1 d\phi_1 d\chi\,. \tag{13}$$

Since the wave function contains $\cos\theta_2$, in order to express it in terms of the integration variable, the axis of coordinate system is so directed that the x' axis passes through the z axis (see Fig. 1). Hence, from geometry, one can prove that[16]

$$\cos\theta_2=\cos\theta_1\cos\gamma+\sin\theta_1\sin\gamma\cos\chi\,, \tag{14}$$

where

$$\cos\gamma=\frac{r_1{}^2+r_2{}^2-r_{12}{}^2}{2r_1r_2}=\frac{s^2+t^2-2u^2}{s^2-t^2}. \tag{15}$$

Finally in the (s,u,t) coordinate system, the matrix element of the Laplacian operator can be written as[13,15]:

$$\int \bar{\Psi}(-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2)\bar{\Psi}dt=\int\left[\left(\frac{\partial\bar{\Psi}}{\partial s}\right)^2+\left(\frac{\partial\bar{\Psi}}{\partial u}\right)^2+\left(\frac{\partial\bar{\Psi}}{\partial t}\right)^2 +\frac{2s(u^2-t^2)}{u(s^2-t^2)}\left(\frac{\partial\bar{\Psi}}{\partial s}\right)\left(\frac{\partial\bar{\Psi}}{\partial u}\right) +\frac{2t(s^2-u^2)}{u(s^2-t^2)}\left(\frac{\partial\bar{\Psi}}{\partial u}\right)\left(\frac{\partial\bar{\Psi}}{\partial t}\right)\right]d\tau\,. \tag{16}$$

Using Eqs. (13)–(16), explicit expressions are obtained for the integrals listed as Eqs. (12). Further details on evaluation of these integrals are given elsewhere.[16]

Once the integrals are evaluated the secular equations are constructed for both the singlet and triplet systems. For the 2 $^3S_1$ state the appropriate secular equation is solved for the lowest root. Since the second root of the secular equation, corresponding to the singlet states, is an upper bound to the energy of the 2 $^1S_0$ state,[17] the energies of the 1 $^1S_0$ and 2 $^1S_0$ states are taken as the first and second roots of this equation, respectively.

For all states considered here the parameters c and k, are taken as the corresponding optimized parameters for zero field. This approximation is at least partially justified because the polarizability is determined from the limiting value of the interaction energy as the field approaches zero. In any event, both c and k are exceedingly insensitive to the field for fields of the size considered in this work.

III. RESULTS

In all calculations presented here, the nonlinear parameters c and k are optimized for the 14-term field-free wave functions. Preliminary study has indicated that extending the wave function to more terms or including the field-dependent terms results in only small changes in the optimized c and k. The computational effort, saved by making this approximation, of course, is very large. In Table I is given a list of these nonlinear parameters corresponding to the appropriate 14-term field-free wave functions for each of these states.

The energy corresponding to the 14 term zero order functions, with and without the applied field are given

TABLE I. The values of nonlinear parameters of two-electron systems optimized for 14-term wave function (dimensionless).

Ion	H^-	He			Li^+		
	1 $^1S_0$	1 $^1S_0$	2 $^3S_1$	2 $^1S_0$	1 $^1S_0$	2 $^3S_1$	2 $^1S_0$
c/a_0[a]	3.046	6.047	1.889	1.890	8.506	2.420	2.422
k	0.505	0.6270	1.412	1.4395	0.7002	1.7321	1.751

[a] $a_0=0.52917$ Å.

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TABLE II. The polarizability calculations for the 42-term wave functions (in a.u.).

Ion	State	F (10^{-5} a.u.)	E_0[a]	E	$-2\Delta E/F^2$
H$^-$	$1\,^1S_0$	2	−0.52769913689586	−0.52769917635228	197.282
		4		−0.52769929947229	197.284
		6		−0.52769949201295	197.287
He	$1\,^1S_0$	20	−2.90362994382937	−2.90362997149437	1.38325
		40		−2.90363005448435	1.38325
		60		−2.90363019281777	1.38325
He	$2\,^1S_1$	2	−2.175225639039099	−2.17522570214046	315.506
		4		−2.17522589144309	315.505
		6		−2.17522620964469	315.503
He	$2\,^1S_0$	1	−2.14563164291700	−2.14563168329705	807.601
		2		−2.14563180443620	807.596
		3		−2.14563200633189	807.589
Li$^+$	$1\,^1S_0$	100	−7.27979268148201	−7.27979277772253	0.192480
		200		−7.27979306644393	0.192480
		300		−7.27979354764769	0.192480
Li$^+$	$2\,^3S_1$	5	−5.11072218577530	−5.11072224435210	46.8612
		10		−5.11072242008217	46.8613
		15		−5.11072271296409	46.8614
Li$^+$	$2\,^1S_0$	10	−5.040408359149628	−5.04040885092036	98.3561
		20		−5.04041036217434	98.3512
		30		−5.04041278473672	98.3463

[a] E_0 is the field free energy and E is the field-dependent energy. The wave function contains 14 terms in each of ψ^0, ψ^{I}, and ψ^{II}. [See Eqs. (9) of text.]

in Table II. The field-dependent wave function has 42 terms. In addition, the polarizabilities computed from the interaction energies, i.e., $-2\Delta E/F$, are also given in this table.

TABLE III. The polarizability calculations for the 72-term wave function (in a.u.).

Ion	State	E_0 (Pekeris)[a]	E_0 (present work)	F (10^{-5} a.u.)	$-2\Delta E/F$
H$^-$	$1\,^1S_0$	−0.52775100	−0.52773389606	2	202.117
				4	202.120
				6	202.125
He	$1\,^1S_0$	−2.90372437	−2.90370799598	20	1.38405
				40	1.38405
				60	1.38405
He	$2\,^3S_1$	−2.175229378	−2.17522826506	2	315.628[b]
				4	315.627
				6	315.626
He	$2\,^1S_0$	−2.14597404	−2.14590723586	1	798.988
				2	798.988
Li$^+$	$1\,^1S_0$	−7.27991324	−7.27988396961	100	0.192515
				200	0.192515
				300	0.192515
Li$^+$	$2\,^3S_1$	−5.11072737	−5.11072612263	3	46.8795
				6	46.8795
				9	46.8795
Li$^+$	$2\,^1S_0$	−5.04087673	−5.04076794916	2	98.1899
				4	98.1899
				6	98.1899

[a] E_0 is the field free energy and F is the field intensity. The wave function contains 24 terms in each of ψ^0, ψ^{I}, and ψ^{II}. [See Eqs. (9) of text.] C. L. Pekeris, Phys. Rev. **136**, 143 (1962); **136**, 1470 (1962).

[b] The 96-term results agree for this state, with these values to 5 places.

In Table III is given the polarizabilities for the 72 term wave function calculation. Also the energy values given by Pekeris[1] are listed so as to show the energy convergence in the present wave functions.

In order to obtain high accuracy for the polarizability calculations with reasonably small fields, it is found necessary to make all computations carrying a large number of significant figures. Thus, the numerical calculations are made first on the University of Texas CDC 1604 computer and later on an IBM 7044 computer using double precision arithmetic. In the first case the CDC gave 12 place accuracy and the IBM 7044 gave 16 with double-precision arithmetic. Some preliminary work shows that, with this accuracy the polarizability calculated from the energy of interaction ΔE and the induced moment μ agree to at least six places for every state. For this reason only the results as computed from the interaction energy are included.

TABLE IV. The 96-term polarizability calculations for He 2^1S_0 and H$^-$ $1\,^1S_0$ (in a.u.).

		E_0[a]	F (10^{-5}a.u.)	$-2\Delta E/F^2$
H$^-$	$1\,^1S_0$	−0.527745632599	2	205.878
			4	205.882
He	$2\,^1S_0$	−2.1459277430165	1	801.952
			2	801.943

[a] E_0 is the field free energy and F is the field intensity. The wave function contains 32 terms in each of ψ^0, ψ^{I}, and ψ^{II}. [See Eqs. (9) of text.]

TABLE V. Comparison of calculated and experimental polarizabilities of two-electron systems (in a.u.).

	H^-		He			Li^+	
Energy state	$1\ {}^1S_0$	$1\ {}^1S_0$	$2\ {}^3S_1$	$2\ {}^1S_0$	$1\ {}^1S_0$	$2\ {}^3S_1$	$2\ {}^1S_0$
Uncoupled Hartree[a]-Fock calculation	112	1.486	···	···	0.205	···	···
Coupled Hartree[b]-Fock calculation	93	1.322	···	···	0.189	···	···
Present result	205.9	1.384	315.6	802.0	0.1925	46.88	98.19
Experimental or best previous calculation	212[c] 202[d]	1.384[e]	313[f]	788[f]	0.1907[g]	···	···

[a] M. Yoshimine and R. P. Hurst, Phys. Rev. **135**, A612 (1964).
[b] H. D. Cohen, J. Chem. Phys. **43**, 3558 (1965).
[c] C. Schwartz, Phys. Rev. **123**, 1700 (1961). (Accurate calculation.)
[d] S. Geltman, Astrophys. J. **136**, 935 (1962). (Accurate calculation.)
[e] A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) **73**, 455 (1960). (Extrapolated from refractive index.)
[f] A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London), **72**, 1053 (1958). (Calculated from theoretical oscillator strengths.)
[g] K. Bockasten, Arkiv. Fysik **10**, 567 (1956). (Spectroscopic determination.)

Because of the comparatively poor convergence of the polarizability of He $2\ {}^1S_0$ and $H^-\ 1\ {}^1S_0$, the wave functions for these states are extended to 96 terms. The results of these calculations are listed in Table IV. Because of limitations in the IBM 7044 computer memory on using double-precision arithmetic, further extension of the size of the wave function is hardly possible.

In Table V are summarized the polarizability results and a comparison is made with previous experimental and theoretical values. Table VI gives a comparison of the present field free energy results of He $2\ {}^3S_1$ with previous calculation of these energies. Finally, in Tables VII and VIII are given comparisons of computed $\langle r^2\rangle$ results with the highly accurate calculations of Pekeris.

IV. SUMMARY AND DISCUSSION

Inasmuch as the accuracy obtained for the computed polarizabilities and for $\langle r^2\rangle$ depends mostly on the accuracy of the outermost reaches of the wave function the comparisons of $\langle r^2\rangle$ values listed in Tables VII and VIII are of special interest. Inspection of these tables shows that the 26-term wave function of the present work gives values for $\langle r^2\rangle$ which agree with the highly accurate Pekeris results to five or six places except for the ground state of H^- and the $2\ {}^1S_0$ states of He and Li^+. A similar trend is found, as one should expect, in the study of the convergence of the polarizabilities as more terms are included in the wave function (see Tables II–IV). Specifically, on comparing the results of Tables II and III, it is seen that the polarizabilities have converged to at least three and usually four places in going from 42 to 72 terms except for the ground state of H^- and the $1\ {}^1S_0$ state of helium (see also Table III footnote b). In an attempt to achieve greater convergence the wave function for these two cases was extended to 96 terms. Nevertheless, it appears that the uncertainties in the polarizabilities, for these two states, are of the order of several atomic units or around 1%. Using an IBM 7044 computer it is not considered feasible to extend the wave function to include more terms.

It is gratifying to note from Tables II–IV that the contribution of the nonlinear terms to the dipole moment [see Eq. (3)] does not significantly effect the induced moments for fields of the size considered here. More specifically, in every case the error introduced in the polarizabilities resulting from the use of finite fields,

TABLE VI. Energy convergence of He $2\ {}^3S_1$ (no external field).

Author	No. of terms	Energy (a.u.)
Pekeris[a]	125	−2.17522097961
	252	−2.17522925888
	400	−2.17522937680
	715	−2.17522937822
Davis[b]	80	−2.1752246
	80	−2.1752259
Traub and Foley[c]	12	−2.1752176
Hart and Herzberg[d]	20	−2.1752192
Present work	14	−2.175225662
	26	−2.175228491
	38	−2.175229004
	78	−2.175229346

[a] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).
[b] H. L. Davis, J. Chem. Phys. **39**, 1183 (1963).
[c] J. Traub and H. M. Foley, Phys. Rev. **111**, 1098 (1958).
[d] J. F. Hart and G. Herzberg, Z. Physik **171**, 83 (1962).

TABLE VII. Expectation value of $\frac{1}{2}\langle(r_1^2+r_2^2)\rangle$ of He $2\ {}^3S_1$ (no external field).

Author	No. of terms	$\frac{1}{2}\langle(r_1^2+r_2^2)\rangle$ (in a.u.)
Pekeris[a]	125	11.437314
	252	11.463512
	444	11.464304
	715	11.464321
Present work	14	11.46176
	26	11.46477

[a] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

TABLE VIII. Comparison of expectation value $\frac{1}{2}\langle(r_1^2+r_2^2)\rangle$ with Pekeris value (a.u.).

	H$^-$		He			Li$^+$	
Energy state	$1\,^1S_0$	$1\,^1S_0$	$2\,^1S_1$	$2\,^1S_0$	$1\,^1S_0$	$2\,^1S_1$	2^3S_0
Pekeris	11.91369[a]	1.1934830[b]	11.464321[c]	16.08913[d]	0.446279[e]	3.773589[f]	4.695098[g]
Present work[h]	11.85265	1.193475	11.46477	16.13428	0.446278	3.77369	4.70034

[a] C. L. Pekeris, Phys. Rev. **126**, 1470 (1962), for 444 terms.
[b] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959), for 715 terms.
[c] Reference b, for 715 terms.
[d] Reference a, for 615 terms.
[e] C. L. Pekeris, Phys. Rev. **126**, 143 (1962), for 308 terms.
[f] Reference e, for 308 terms.
[g] Reference e, for 444 terms.
[h] Present work, 26 terms.

is several orders of magnitude smaller than the error introduced because of incomplete convergence of the wave function.

The most comprehensive check on the reliability of the present method is, of course, the comparison of the computed dipole polarizabilities with the experimental values for the ground state of He and Li$^+$ (see Table V). In the case of helium the most recent experimental measurements of α from the dielectric constant give values somewhat larger than our calculated value. Thus, Essen[18] in 1953 obtained 1.40 ± 0.01 a.u. which agrees with the Johnson, Oudemans, and Cole[19] value of 1960 which is 1.396 ± 0.001. On the other hand, Dalgarno and Kingston,[20] from a careful extrapolation of refractive index data, obtained 1.384 a.u. which is in exact agreement with the present work. Inasmuch as refractive index data are usually more accurate than dielectric constant measurements it seems reasonable to give the Dalgarno and Kingston result preference as is indicated in Table V. In this connection, it is interesting to note that Schwartz[12] has computed α using an 18-parameter function for ψ_0 and a very flexible function for ψ_1. He obtains 1.383 a.u. for helium atom.

In the case of the Li$^+$ ion the most reliable experimental measurement of the ground state polarizability is the spectroscopic determination of Bockasten.[21] His value of 0.19073 a.u. was obtained by assuming that the difference between the observed term values and the hydrogen-like term values for the ^2D, ^2F, and ^2G terms are due to dipole and quadrupole polarization of the Li$^+$ ion. This is to be compared with 0.1925 a.u. obtained here. In Bockasten's work the accuracy of the experimental term values he used and the internal numerical consistency in the polarization formula support the assumption that his result is valid to all places quoted.[21] Nevertheless, the possibility remains that other effects not considered in this type of interpretation of the spectral data may have changed his experimental polarizability enough to account for the discrepancy between the present calculated value and his experimental result. In the present work this polarizability has converged to at least four places and experience with this and other $1\,^1S_0$ states strongly suggests (see Tables II–IV) including more terms in the wave function would most probably make α larger still thus very slightly increasing this discrepancy. In this connection it is interesting to note that Baber and Hasse[22] have computed a value of 0.1927 a.u. using a 6-parameter representation of ψ_0 and a 3-parameter function for ψ_1.

Finally, the only other previous determinations of the dipole polarizabilities of the $2\,^3S_1$ and $2\,^1S_0$ states of helium are the calculated values of Dalgarno and Kingston.[14]. Using theoretical oscillator strengths they obtained 313 and 788 a.u. to be compared with the present results of 315.6 and 802 a.u. for the $2\,^3S_1$ and $2\,^1S_0$ states respectively. In view of the problem of contributions from transitions to the continuum the agreement between the present results and those of Dalgarno and Kingston must be regarded as quite good.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor F. A. Matsen and and E. Rodriguez for the gracious hospitality extended to one of us (K. T. C.) at the University of Texas, while much of the results presented here were obtained on the Texas CDC 1604 computer. We are also grateful to Dr. K. Bockasten for his helpful comments concerning the accuracy of the Li$^+$ experimental results.

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[18] L. Essen, Proc. Phys. Soc. (London) **B66**, 189 (1953).

[19] D. R. Johnson, G. J. Oudemans, and R. H. Cole, J. Chem. Phys. **33**, 1310 (1960).

[20] A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. (London) **A259**, 424 (1960).

[21] K. Bockasten (private communication).

[22] T. D. Baber and H. T. Hassé, Proc. Cambridge Phil. Soc. **33**, 253 (1957).