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Hyperpolarizabilities of H^-, He, and Li^+*

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The Ritz variational approximation is used to calculate the energy of the ground state of He, Li^+, and H^- in the presence of a uniform external electric field. The interaction energies are expressed as power series in the electric-field intensity. From the coefficients of these expansions, the polarizabilities α and the hyperpolarizabilities γ are obtained. In this study the hyperpolarizabilities are computed with Hylleraas-type wave functions consisting of 78, 96, 102, and 150 terms. The convergence of α and γ are satisfactory for He and Li^+, but not for H^-. For H^- it is suggested that in order to obtain proper convergence one would need to include more terms in the wave function than would be tractable for our computer. Thus, a different type of function should be used for this ion. The 150-term wave functions gave 169, 1.383, and 0.1925 atomic units (a.u.) for the polarizabilities of H^-, He, and Li^+, respectively. This 150-term function also gave 1.74×10^7, 42.8, and 0.244 a.u. for the hyperpolarizabilities of these same atoms. It is suggested from a study of the convergence of α and γ as more terms are included in the wave function, of the accuracy of the computed α's, and of the free atom energies that the computed γ results are correct to within a few percent or better for He and Li^+, but that the γ computed for H^- is unreliable. The only available measurement of γ, for these ions, gave 51.6 ± 7.9 a.u. for the helium atom.

I. INTRODUCTION

WHEN an S-state atom, such as helium, is placed in a static external electric field $\mathbf{F}$, its electronic charge distribution is distorted. Assuming the applied field to be uniform, this distortion is described by the induced moment $\boldsymbol{\mu}$ which, to a first approximation, is proportional to the first power of the field, i.e.,

$$\boldsymbol{\mu}=\boldsymbol{\alpha}\cdot\mathbf{F}. \tag{1.1}$$

Here $\boldsymbol{\mu}$ and $\mathbf{F}$ are vectors and $\boldsymbol{\alpha}$ is a second-rank tensor, generally called the polarizability. The polarizability has been the subject of many early and recent investigations.[1-4]

If, however, the field strength is increased, the charge distribution undergoes further distortion and this linear relation is no longer adequate as higher-order terms contribute significantly to $\boldsymbol{\mu}$. Thus, Eq. (1.1) must be modified to give

$$\boldsymbol{\mu}=\boldsymbol{\alpha}\cdot\mathbf{F}+\tfrac{1}{2}\boldsymbol{\beta}:\mathbf{F}^2+\tfrac{1}{6}\boldsymbol{\gamma}\vdots\mathbf{F}^3+\cdots. \tag{1.2}$$

Here the third- and fourth-order tensors $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ have been called by Buckingham and Orr[5] the first, and second hyperpolarizabilities, respectively. On very general geometrical arguments one can show for S-state atoms that the $\boldsymbol{\beta}$ term is zero so that $\boldsymbol{\gamma}$, the second hyperpolarizability, gives the lowest-order nonlinear contributions to $\boldsymbol{\mu}$. Equation (1.2) can, of course, be extended to include even higher-order terms; however, with presently available experimental methods these higher-order terms would be exceedingly difficult to detect. Thus, since $\boldsymbol{\gamma}$ is the only hyperpolarizability we shall consider here, for simplicity, we shall refer to $\boldsymbol{\gamma}$ as the hyperpolarizability throughout this paper.

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

[1] A. Dalgarno, Advan. Phys. **11**, 281 (1962).

[2] K. S. Pitzer, in *Advances in Chemical Physics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1959), Vol. 2, p. 59.

[3] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1951); **102**, 731 (1956); **107**, 1565 (1957); **115**, 1198 (1959); **127**, 1220 (1962); **130**, 1423 (1963); **132**, 1637 (1963).

[4] P. W. Langhoff and R. P. Hurst, Phys. Rev. **139**, A1415 (1965).

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

Alternatively, the energy of interaction ΔE associated with the induction of the moment can be expressed as

$$\Delta E = -\tfrac{1}{2}\boldsymbol{\alpha}:\mathbf{F}^2 - \tfrac{1}{6}\boldsymbol{\beta}\vdots\mathbf{F}^3 - (1/24)\boldsymbol{\gamma}\,\vdots\!\vdots\,\mathbf{F}^4\cdots, \quad (1.3)$$

so that the polarizability term is second order and the γ term is fourth order in the energy with respect to the field.

These relations can be placed in clear perspective if we regard Eq. (1.3) to be simply a power series of the total energy in the field. Then, including all terms up to fourth order in the field, we have, adopting Cartesian tensor notations,[6,7]

$$E = E^0 - p_iF_i - \tfrac{1}{2}\alpha_{ij}F_iF_j - (1/3!)\beta_{ijk}F_iF_jF_k - (1/4!)\gamma_{ijkl}F_iF_jF_kF_l. \quad (1.4)$$

Here the usual convention of repeated indices implies summation, E^0 is the field-free energy, p_i is the permanent dipole moment, α_{ij} is the second-rank polarizability tensor, β_{ijk} is the third-rank first hyperpolarizability tensor, and γ_{ijkl} is the fourth-rank second hyperpolarizability tensor. For spherically symmetric systems, all of these tensors must be isotropic.[7] Then, since there is no isotropic tensor of first order other than zero and since a scalar multiple of the Levi-Civita density[8] is the only nonzero tensor of third order, these odd power terms vanish. Further, since the only isotropic tensor of second order is a scalar multiple of δ_{ij}, the substitution tensor, we have

$$\alpha_{ij} = \alpha\delta_{ij}. \quad (1.5)$$

Finally, one can show that any component of the isotropic tensor γ_{ijkl} is zero unless i, j, k, and l occur in pairs, and that the most general isotropic tensor of fourth order can be written

$$\gamma_{ijkl} = \lambda\delta_{ij}\delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \nu(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}), \quad (1.6\text{a})$$

where

$$\gamma_{1111} = \gamma_{2112} + \gamma_{1212} + \gamma_{1122} = \lambda + 2\mu. \quad (1.6\text{b})$$

Thus, using these results, Eq. (1.4) reduces to

$$\Delta E = E - E_0 = -\tfrac{1}{2}\alpha F^2 - (1/24)\gamma F^4 - \cdots, \quad (1.7\text{a})$$

where

$$F^2 = F_iF_i, \quad (1.7\text{b})$$

$$F^4 = (F_iF_i)(F_jF_j), \quad (1.7\text{c})$$

and

$$\gamma = \gamma_{1111} = \gamma_{2222} = \gamma_{3333}. \quad (1.7\text{d})$$

Then, we see there is only one independent component in α_{ij} and one in γ_{ijkl}. These conclusions are, as we have shown, results from arguments which are entirely geometrical in nature.

Recently, calculations of γ for helium have been made from an uncoupled Hartree-Fock approximation[9]; however, it has been suggested by Drake and Cohen[10] that the uncoupled Hartree-Fock approximation cannot yield reliable hyperpolarizabilities. The only other theoretical result for helium is that of Boyle, Buckingham, Disch, and Dunmar[11] (BBDD) who also give an experimental value. The BBDD experimental value, which was obtained from the birefringence induced in helium gas by an electric field, is larger than their calculated value by a factor of 1.5, although their experimental result seems to agree with the uncoupled Hartree-Fock number.[9] Thus, it seems quite clear that additional effort will be required to obtain a reliable γ for He.

The purpose of this paper is to present accurate variational calculations of the hyperpolarizability of H$^-$, He, and Li$^+$. These calculations are made with Hylleraas-type variational wave functions and include up to 150 terms. In Sec. II we present the theory of the method, Sec. III gives the formulation of the problem, and in Sec. IV the results are presented. Finally, Sec. V is a summary and discussion of results.

II. THEORY OF METHOD

In previous calculations of hyperpolarizabilities from Hartree-Fock perturbation theory,[9] it is shown that if the Fock orbitals are known to nth order the energy can be determined to the $2n+1$ order. This result is entirely analogous to the $2n+1$ theorem of many-electron theory in that if the many-electron perturbation wave functions are known to nth order the many-electron energy can be obtained to the $2n+1$ order.[12] In the present work, however, these calculations are made from the variational technique without direct recourse to perturbation theory. Thus, the purpose of this section is to present an alternative variational form of the $2n+1$ theorem of perturbation theory in that we show that if the variational wave function is accurate to the nth order in some expansion parameter λ then the energy is determined to order $2n+1$.

First we assume the Hamiltonian has the usual form for perturbation problems, namely,

$$H = H^0 + \lambda H^1, \quad (2.1)$$

and that the usual expansions of E and ψ in powers of

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[6] A. D. Buckingham and M. J. Stephen, Trans. Faraday Soc. **53**, 884 (1957).

[7] H. Jeffreys, *Cartesian Tensors* (Cambridge University Press, London, 1952), p. 66.

[8] H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1950), p. 129.

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

[10] C. W. F. Drake and M. Cohen, Bull. Am. Phys. Soc. **12**, 701 (1967).

[11] L. L. Boyle, A. D. Buckingham, R. L. Disch, and D. A. Dunmar, J. Chem. Phys. **45**, 1318 (1966).

[12] A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **A238**, 269 (1956).

λ can be made ,i.e.,

$$E=\sum_{i=0}^{\infty}\lambda^i E^i, \tag{2.2a}$$

$$\psi=\sum_{i=0}^{\infty}\lambda^i\psi^i. \tag{2.2b}$$

Further, to simplify the notation, we shall let

$$\psi(m)=\psi^0+\lambda\psi^1+\lambda^2\psi^2+\cdots+\lambda^m\psi^m \tag{2.3a}$$

and

$$E(m)=\epsilon^0+\lambda\epsilon^1+\lambda^2\epsilon^2+\cdots+\lambda^m\epsilon^m. \tag{2.3b}$$

Here ϵ^i and ψ^i are the ith-order energies and wave functions, respectively.

On constructing the Schrödinger equation from Eqs. (2.1) and (2.2), we have

$$H\psi=E\psi \tag{2.4a}$$

or

$$[H^0+\lambda H^1-E(2n+1)]\psi(2n)=(-H^0\psi^{2n+1}+\epsilon^0\psi^{2n+1})\lambda^{2n+1}+O(\lambda^{2n+2}). \tag{2.4b}$$

Then, if we multiply (2.4b) by ψ^{0*} and integrate over all space, we have

$$\langle\psi^0|H^0+\lambda H^1-E(2n+1)|\psi(2n)\rangle=O(\lambda^{2n+2}). \tag{2.5}$$

Also, from Eq. (2.4b), we obtain

$$\langle\lambda\psi^1+\lambda^2\psi^2+\lambda^3\psi^3+\cdots+\lambda^n\psi^n|H^0+\lambda H^1-E(2n+1)\times|\psi(2n)\rangle=O(\lambda^{2n+2}), \tag{2.6}$$

so that on adding Eqs. (2.5) and (2.6) we obtain

$$\langle\psi(n)|H^0+\lambda H^1-E(2n+1)|\psi(2n)\rangle=O(\lambda^{2n+2}). \tag{2.7}$$

Equation (2.7) can be written

$$\langle\psi(n)|H^0+\lambda H^1-E(2n+1)|\psi(n)\rangle+\langle\psi(n)|H^0+\lambda H^1-E(2n+1)|\lambda^{n+1}\psi^{n+1}+\lambda^{n+2}\psi^{n+2}+\cdots+\lambda^{2n}\psi^{2n}\rangle=O(\lambda^{2n+2}). \tag{2.8}$$

In the same manner as (2.4) is obtained, one can show

$$[H^0+\lambda H^1-E(2n+1)]\psi(n)=O(\lambda^{n+1}), \tag{2.9}$$

so that Eq. (2.8) can be written

$$\langle\psi(n)|H^0+\lambda H^1-E(2n+1)|\psi(n)\rangle=O(\lambda^{2n+2}). \tag{2.10}$$

Finally, we have the desired result

$$E(2n+1)=\frac{\langle\psi(n)|H^0+\lambda H^1|\psi(n)\rangle}{\langle\psi(n)|\psi(n)\rangle}+O(\lambda^{2n+2}). \tag{2.11}$$

From the variational theorem we have

$$E(2n+1)\geq W_0, \tag{2.12}$$

where W_0 is the true lowest eigenvalue. In applying the result given as Eq. (2.11), one constructs a wave function $\psi(n)$ as a linear combination of trial functions. Each trial function contains a number of adjustable parameters and has the proper symmetry so as to represent ψ^i. Thus, if we require the variation

$$\delta E(2n+1)=0, \tag{2.13}$$

we obtain approximations to the perturbation energies ϵ^i up to and including order $2n+1$ and approximations to ψ to order n.

One can show that the present technique is equivalent, in principle, to the variation-perturbation method.[13] The present method, however, has the advantage that one needs only to solve a single secular equation for the lowest eigenvalue. On the other hand, to use the variation-perturbation method, one must first obtain ϵ^0 and ψ^0; then solve each of the increasingly complex perturbation equations to obtain ψ^1, ψ^2, $\cdots\psi^n$. Finally, additional expressions must be evaluated to obtain the energies ϵ^{n+1}, ϵ^{n+2}, $\cdots$, ϵ^{2n+1}. Of the two methods, it seems the present method is much more straightforward and its use results in a substantial saving in computer time. By either method *the same integrals must be evaluated.*

The primary disadvantage of the present method, for the application considered here, as compared with the variation-perturbation approach, lies in the fact that for the present method one must make the calculations carrying a large number of significant figures. This is because one must solve rather large secular equations and because the size of the fourth-order energy term is usually fairly small when compared with ϵ^0. On the other hand, if it is already necessary to employ double precision arithmetic (16 significant figures for the IBM 7044) to obtain reliable results from the variation-perturbation technique, as is the case here, this disadvantage is not particularly significant. It is of interest to note that the present method has given highly accurate results for the dipole polarizability of the ground state and several excited states of two electron ions.[14]

III. FORMULATION

The variational wave function chosen for this problem is based on the functional form first proposed by Hylleraas.[15] The Hylleraas function, originally intended to describe the free-atom ground state of helium, has the form

$$\psi(s,t,u)=\phi^0(Ks,Kt,Ku), \tag{3.1a}$$

where

$$\phi^0(s,t,u)=e^{-(1/2)s}\sum_{i=1}^{N}a_i s^{l_i}u^{m_i}t^{2n_i}, \tag{3.1b}$$

$$s=r_1+r_2, \tag{3.1c}$$

$$u=r_{12}, \tag{3.1d}$$

$$t=r_1-r_2. \tag{3.1e}$$

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[13] J. O. Hirschfelder, W. B. Brown, and S. T. Epstein, in *Advances in Quantum Chemistry*, edited by Per-Olov Löwdin (Academic Press Inc., New York, 1964), Vol. 1, p. 256.

[14] Kwong T. Chung and R. P. Hurst, Phys. Rev. **152**, 35 (1966).

[15] E. A. Hylleraas, Z. Physik, **54**, 347 (1930).

TABLE I. Powers of l_i, m_i, and n_i for the 78-term wave function [see Eq. (3.4b)].

l_i	0	0	0	0	0	0	1	1	1	1	2	2	3
m_i	0	0	1	1	2	3	0	0	1	2	0	1	0
n_i	0	1	0	1	0	0	0	1	0	0	0	0	0

K is a scaling factor and the a_i are the linear variation coefficients.

Earlier studies[14] have shown that a form for the wave function accurate to the first power in the field is

$$\phi=\phi^0+(z_1+z_2)\phi_1{}^{(1)}+(z_1-z_2)\phi_2{}^{(1)}. \qquad (3.2)$$

Here ϕ^0, $\phi_1{}^{(1)}$, and $\phi_2{}^{(1)}$ have the same form as Eqs. (3.1b) except $\phi_2{}^{(1)}$ includes odd powers of t to maintain the proper spatial symmetry. Then a reasonable means of extending Eq. (3.2) to the second power in the field is to include a general quadratic function in z_1 and z_2. Thus the final form chosen is

$$\phi=\phi^{(0)}+(z_1+z_2)\phi_1{}^{(1)}+(z_1-z_2)\phi_2{}^{(1)}+(z_1+z_2)^2\phi_1{}^{(2)} +(z_1-z_2)^2\phi_2{}^{(2)}+(z_1{}^2-z_2{}^2)\phi_3{}^{(2)}. \qquad (3.3)$$

Explicitly, then, the wave function chosen has the form

$$\psi=\phi(Ks,Kt,Ku,Kz_1,Kz_2)\,, \qquad (3.4a)$$

where

$$\phi(s,t,u,z_1,z_2)=\sum_{i=1}^{N} e^{-s/2}s^{l_i}u^{m_i}t^{2n_i} \times[a_i+b_i(z_1+z_2)+c_i(z_1-z_2)t+d_i(z_1+z_2)^2 +e_i(z_1-z_2)^2+f_i(z_1{}^2-z_2{}^2)t] \qquad (3.4b)$$

TABLE II. Powers of l_i, m_i, and n_i for the 96-term wave function [see Eq. (3.4b)].

l_i	0	0	0	0	0	0	1	1	1	1	1	2	2	2	3	3
m_i	0	0	1	1	2	2	0	0	1	1	2	0	0	1	0	1
n_i	0	1	0	1	0	1	0	1	0	1	0	0	1	0	0	0

or

$$\phi(s,t,u,z_1,z_2)=\sum_{i=1}^{N}(a_i\chi_i{}^0+b_i\chi_i{}^1+c_i\chi_i{}^2 +d_i\chi_i{}^3+e_i\chi_i{}^4+f_i\chi_i{}^5)\,, \qquad (3.4c)$$

where a_i, b_i, c_i, d_i, e_i, and f_i are linear variation coefficients, s, u, and t are defined in Eq. (3.1), and K is a scaling parameter.

As seen from Eq. (3.4b), the total number of terms in ψ is $6N$. In Tables I–IV are listed the values of l_i, m_i, and n_i for the 78-, 96-, 102-, and 150-term functions.

Proceeding in the usual way[16] one obtains the following $6N$ by $6N$ secular determinant:

$$|K^2M_{ij}{}^{mn}-KL_{ij}{}^{mn}+P_{ij/k}{}^{mn}-EN_{ij}{}^{mn}|=0\,, \qquad (3.5)$$

where

$$M_{ij}{}^{mn}=\int\chi_i{}^m(-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2)\chi_j{}^n d\tau\,, \qquad (3.6a)$$

$$L_{ij}{}^{mn}=\int\chi_i{}^m(q/r_1+q/r_2-1/r_{12})\chi_j{}^n d\tau\,, \qquad (3.6b)$$

$$P_{ij}{}^{mn}=\int\chi_i{}^m(z_1+z_2)\chi_j{}^n d\tau\,, \qquad (3.6c)$$

$$M_{ij}{}^{mn}=\int\chi_i{}^m\chi_j{}^n d\tau\,. \qquad (3.6d)$$

Here, $\chi_i{}^m$ are defined according to Eqs. (3.4b) and (3.4c) and q is the nuclear charge. Details of how these integrals are evaluated are given elsewhere.[17]

TABLE III. Powers of l_i, m_i, and n_i for the 102-term wave function [see Eq. (3.4b)].

l_i	0	0	0	0	0	0	1	1	1	1	1	2	2	2	2	3	3
m_i	0	0	1	1	2	2	0	0	1	1	2	0	0	1	2	0	1
n_i	0	1	0	1	0	1	0	1	0	1	0	0	1	0	0	0	0

Finally, the secular equation [i.e., Eq. (3.5)] is solved for the lowest eigenvalue for zero electric field and various finite fields. Then, α and γ are obtained from the interaction energy according to Eq. (1.3). Further details of this process are given in Sec. IV.

IV. RESULTS

Inasmuch as α and γ are defined for zero field, the scaling factor K is determined in each case such that K is chosen to give the minimum energy for $F=0$. These results for the optimum values of K are presented in Table V.

Since the contribution of the field-dependent terms of the energy expansion, Eq. (1.7a), is ordinarily very small, it is found necessary to make the calculations using large external fields, i.e., 10^{-1}–10^{-3} a.u. With fields of this size, on careful study of the interaction energies, it is found that the sixth-order term of Eq. (1.7a) partially contributes. Consequently, α, γ, and ζ are determined from the interaction energies, $E-E_0$, for three finite values of the field. In particular, α, γ, and ζ are evaluated from the simultaneous solution of the

TABLE IV. Powers of l_i, m_i, and n_i for the 150-term wave function [see Eq. (3.4b)].

l_i	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	2	2	2	2	2	2	3	3	3	3
m_i	0	0	1	1	2	2	3	3	0	0	1	1	2	2	3	0	0	1	1	2	3	0	0	1	2
n_i	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	0	1	0	1	0	0	0	1	0	0

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[16] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 149.

[17] M. N. Grasso, M.A. thesis, State University of New York at Buffalo, 1968 (unpublished).

TABLE V. Optimized scaling factors for 1^1S state of two-electron systems [see Eq. (3.1a)].

N[a]	H^-	He	Li^+
13	1.3583	3.8107	6.1784
16	1.5820	4.1122	6.5139
17	1.5584	4.1022	6.5842
25	1.5996	4.1639	6.5360

[a] N is the number of terms in the zero-order wave function.

resulting linear equations of the following form:

$$E-E^0-(\alpha/2!)F^2-(\gamma/4!)F^4-(\zeta/6!)F^6. \qquad (4.1)$$

It is well to note that the coefficient ζ is not determined accurately as the wave function does not contain all the proper symmetries required to supply this sixth-order term. In Tables VI–VIII are summarized the free-atom energies E_0, the interaction energies ΔE for various fields F, and α, and γ for the He, Li^+, and H^- systems.

One reasonable suggestion as to the probable accuracy of α and γ is obtainable from a comparison of the computed isolated atom energies E_0. Such a comparison is made in Table IX. One will note that in place of the customary experimental results for E_0 we have included the very accurate calculations of Pekeris. For these ions, the Pekeris results are the most accurate calculations that have yet appeared and are widely believed to be more accurate than the available experimental values. No attempt is made to review all of the many calculations made for E_0 for these systems, as this is done elsewhere.[18] However, the calculations of E_0 of Chung and Hurst[14] are included as these authors used a similar approach to obtain α. (See Table X.)

TABLE VI. The energies, polarizabilities, and hyperpolarizabilities for the 1^1S state of helium.

N	F (a.u.)	E_0 (a.u.)	ΔE (10^{-4} a.u.)	α (a.u.)	γ (a.u.)
13	0.00	−2.903671775196			
	0.01		0.69129011	1.3822	41.86
	0.02		2.76726217		
	0.03		6.23427496		
16	0.00	−2.903704339255			
	0.01		0.69163581	1.3829	42.48
	0.02		2.76867680		
	0.03		6.23758015		
17	0.00	−2.903712596223			
	0.01		0.69163931	1.3829	42.52
	0.02		2.76869296		
	0.03		6.23762548		
25	0.00	−2.903721055126			
	0.01		0.69169314	1.3830	42.81
	0.02		2.76982321		
	0.03		6.23820267		

An additional indication as to the probable accuracy of the computed hyperpolarizabilities is obtainable from a study of the accuracy of the polarizabilities. For this reason, in Table X are summarized the present as well as recent calculations and experimental values of the dipole polarizabilities α for the H^-, He, and Li^+ ions.

Finally, in Table XI are summarized previous experimental and theoretical hyperpolarizabilities, γ, as well as the most reliable values of γ obtained in the present study.

TABLE VII. The energies, polarizabilities, and hyperpolarizabilities for the 1^1S state for Li^+.

N	F (a.u.)	E_0 (a.u.)	ΔE (10^{-3} a.u.)	α (a.u.)	γ (a.u.)
13	0.00	−7.27986248926			
	0.05		0.24058060	0.19241	0.2400
	0.10		0.96307567		
	0.15		2.16976369		
16	0.00	−7.27988553213			
	0.05		0.24062507	0.19245	0.2419
	0.10		0.96325971		
	0.15		2.17020242		
17	0.00	−7.27989659621			
	0.05		0.24062310	0.19245	0.2419
	0.10		0.96325169		
	0.15		2.17018389		
25	0.00	−7.27990905860			
	0.05		0.24063008	0.19245	0.2327
	0.10		0.96328215		
	0.15		2.17026290		

V. SUMMARY AND CONCLUSIONS

No definitive conclusions can be made as to the accuracy of the hyperpolarizabilities computed in the present work. Nevertheless, the convergence studies given in Tables VI–VIII, the accuracy study of the zero-order energies given in Table IX, and the study of the com-

TABLE VIII. The energies, polarizabilities, and hyperpolarizabilities for the 1^1S state for H^-.

N	F (a.u).	E_0 (a.u.)	ΔE (10^{-4} a.u).	α (a.u.)	γ (10^{-8} a.u.)
13	0.000	−0.5273117425868			
	0.001		0.842622772	167.19	0.1581
	0.002		3.456213882		
	0.003		8.137925928		
16	0.000	−0.5273845254993			
	0.001		0.846590953	167.97	0.1596
	0.002		3.473041036		
	0.003		8.180665141		
17	0.000	−0.5273907661071			
	0.001		0.848741110	168.37	0.1629
	0.002		3.483798789		
	0.003		8.215866995		
25	0.000	−0.5273957740522			
	0.001		0.853580571	169.24	0.1736
	0.002		3.510963959		
	0.003		8.321144603		

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[18] E. A. Hylleraas, in *Advances in Quantum Chemistry*, edited by Per-Olov Löwdin (Academic Press Inc., New York, 1964), Vol. 1, p. 1.

TABLE IX. Comparison of the field-free energies for the 1^1S states for He, Li^+, and H^-.

Ion	E_0 (a.u.) (Pekeris[a])	E_0 (a.u.) (Chung and Hurst[b])	E_0 (a.u.) (Present work[c])
H^-	−0.527751006	−0.52773389	−0.52739577
He	−2.90372435	−2.90370799	−2.90372106
Li^+	−7.27991339	−7.27988397	−7.27990586

[a] E_0 is the field-free energy. These results correspond to 444 terms in ψ^0 for H^- and Li^+ and 1078 terms in ψ^0 for He. C. L. Pekeris, Phys. Rev. **115**, 1216 (1959); **126**, 143 (1962); **126**, 1470 (1962).

[b] The zero-order wave function contains 23 terms. K. T. Chung and R. P. Hurst, Phys. Rev. **152**, 35 (1966).

[c] The zero-order wave function contains 25 terms.

puted dipole polarizabilities as given in Table X clearly suggest certain trends. These trends are now discussed.

First of all, the convergence tests as more terms are included in ψ make it very probable that if the γ results are in error, they err by being too small. This is suggested by the fact that in every case inclusion of substantially more terms in ψ has increased α and γ. (In some cases α and γ are increased an insignificant amount.) For the case of H^-, all indications suggest that the computed γ is unreliable and may be much too small. This is suggested by the observations that for H^- the convergence of α and γ listed in Table VIII is unsatisfactory, the zero-order energy is quite poor, and the dipole polarizability α is shown in Table X to be about 20% too small.

TABLE X. Comparison of the calculated and experimental polarizabilities of He, Li^+, and H^- (in atomic units).

	H^-	He	Li^+
Uncoupled Hartree-Fock calculation[a]	112	1.486	0.205
Coupled Hartree-Fock calculation[b]	93	1.322	0.189
Variational method[c]	205.9	1.384	0.1925
Experimental or best	212[d]		
previous calculation	202[e]	1.384[f]	0.1907[g]
Present results	169.2	1.383	0.1925

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

[b] H. D. Cohen, J. Chem. Phys. **43**, 3558 (1965).

[c] K. T. Chung and R. P. Hurst, Phys. Rev. **152**, 35 (1966) (accurate calculation).

[d] C. Schwartz, Phys. Rev. **123**, 1700 (1961) (accurate calculation).

[e] S. Geltman, Astrophys. J. **136**, 935 (1962) (accurate calculation).

[f] A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) **73**, 455 (1960) (extrapolated from refractive index).

[g] K. Bockasten, Arkiv Fysik **10**, 567 (1956) (spectroscopic determination).

TABLE XI. Comparison of the calculated and experimental hyperpolarizabilities of He, Li^+, and H^- (in atomic units).

	H^-	He	Li^+
Uncoupled Hartree-Fock calculation[a]	0.8157×10^7	51.55	0.2852
Perturbation theory[b]	···	34.1	···
Experimental result[b]	···	51.6±7.9	···
Present results	0.17359×10^8	42.81	0.2427

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

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

In this connection, a calculation of α for H^- by Schwartz[19] indicates that the convergence is sufficiently slow that the present type of function is inadequate to obtain a reliable γ for this ion. In particular, if one included enough terms in ψ to insure convergence of α and γ, one would exceed the core memory of our computer. Finally, though γ for H^- is quite certain to be unreliable, it is still much larger than any previous calculation, so it is probably still the best result available.

The picture for He and Li^+ ions appears to be rather more encouraging. The convergence of α and γ of Table VI for He appears to be adequate: For Li^+, the convergence is even more satisfactory. Similarly, the free-atom energies are accurate to several units in the seventh place and the α's for the ions listed in Table X are in excellent agreement with the most accurate previous calculations and with experimental results. Thus, for these two ions one can reasonably expect the error in the computed γ's to be at most a few percent. It is of interest to note that the γ obtained here for helium lies just slightly below the rather large confidence limits of the only available experimental result.[11]

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[19] C. Schwartz (private communication).