Hartree total energy is larger by as much as 38.53 Ry for plutonium.

Total energies calculated from the relativistic solutions are of about the same magnitude as those obtained from the nonrelativistic solutions at low values of atomic number, but are significantly larger at high atomic numbers. This difference increases uniformly with increasing atomic number from 1.06% for germanium to 9.02% for plutonium.

Magnetic Susceptibility of 2 ³S₁ State of Helium and Some Like Ions

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The magnetic susceptibility of the 2 ³S₁ state of helium and some like ions is computed using a thirty-five term wave function of the type originally proposed by Hylleraas and Undheim. It is found that it is possible to obtain highly accurate values for the magnetic susceptibility using this wave function if the parameters are accurately determined. Finally, an argument is given which suggests that the magnetic susceptibility obtained in the present work is accurate to at least five significant figures.

I. INTRODUCTION

IN atomic helium the only electronic states of practical importance are those for which at least one electron is in the ground state. Thus, as is well known,[1] the Pauli antisymmetry principle is satisfied for wave functions for which either the spatial function is symmetric and the spin function is antisymmetric or for wave functions having antisymmetric spatial functions and symmetric spin functions. These two possibilities lead to two term schemes, the former giving the singlet system whose lowest member is 1 ¹S₀ while the latter leads to the triplet system whose lowest member is 2 ³S₁.

Inasmuch as the 2 ³S₁ triplet state lies above the ground state by 19.8 eV and transitions to the ground state 1 ¹S₀ are rather rigorously forbidden, both by the orthogonality of the spin functions and by the symmetry differences of the spatial functions, this metastable state has of late been the subject of a number of investigations. Experimentally this state is an attractive metastable system to study as it is possible to obtain an appreciable concentration of these metastable atoms under experimental conditions. From the point of view of the theorist it is attractive as an approximate wave function and triplet state energy are obtained in which the energy is a rigorous upper bound to the true triplet energy simply by requiring that the spatial part of ones variational wavefunction be antisymmetric.

To mention just a few of the recent papers on 2 ³S₁ helium, Pekeris,[2] Hart and Herzberg,[3] Davis,[4,5] and Traub and Foley[6] have all made accurate variational calculations of the energy. Hughes[7–9] and his co-workers have made rather definitive experimental and theoretical studies of the magnetic moment in this state. Finally, Benton, Ferguson, Matsen, and Robertson[10] have recently made a number of measurements of the cross sections for de-excitation of the metastable atom by collisions with other atoms.

[1] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Academic Press Inc., New York, 1957), p. 124.

[2] C. L. Pekeris, Phys. Rev. 115, 1216 (1959).
[3] J. F. Hart and G. Herzberg, Phys. Rev. 171, 83 (1963).
[4] H. L. Davis, J. Chem. Phys. 37, 1508 (1962).
[5] H. L. Davis, J. Chem. Phys. 39, 1183 (1963).
[6] J. Traub and H. M. Foley, Phys. Rev. 111, 1098 (1958).
[7] V. Hughes, G. Tucker, E. Rhoderick, and G. Weinreich, Phys. Rev. 91, 828 (1953).
[8] V. Hughes, G. Tucker, E. Rhoderick, and G. Weinreich, Phys. Rev. 91, 842 (1953).
[9] V. Hughes, G. Tucker, E. Rhoderick, and G. Weinreich, Phys. Rev. 112, 627 (1958).
[10] E. E. Benton, E. E. Ferguson, F. A. Matsen, and W. W. Robertson, Phys. Rev. 128, 206 (1962).

The principal aim of this work is to obtain accurate values for the magnetic susceptibility of this metastable state. Calculations are presented for helium and for a number of ions in the isoelectronic series. To be successful in this task it is found that an accurate wave function must be used, and that the linear and nonlinear parameters be known to high accuracy. It is for this reason that a rapidly converging type of wave function is obtained and the calculations are performed using a large number of significant figures (12 places).

THEORY

The diamagnetic susceptibility of the $2\,{}^3S_1$ metastable state is computed in the usual way from[11]

$$\chi_D = \frac{Ne^2}{6mc^2} \int \psi_0{}^*(\sum_i r_i{}^2)\psi_0 d\tau = \frac{Ne^2}{6mc^2}\langle r_1{}^2 + r_2{}^2\rangle_{\text{av}} \quad (1)$$

and the paramagnetic susceptibility from

$$\chi_P = NJ(J+1)g^2\mu_0{}^2/3kT. \quad (2)$$

Since the electrostatic fields exerted by single nuclei are spherically symmetric, the Van Vleck paramagnetic terms are zero. Here ψ_0 is the solution of the field-free Schrödinger equation, and N, J, g, μ_0, k, and T all have their usual meanings.[12]

The particular choice of the wave function ψ_0 was decided by the requirement of rapid convergence to the experimental energy for the state as mentioned earlier. A comparison of the results in the papers referenced earlier[13] seemed to indicate that the type of wave function utilized by Hart and Herzberg, and Traub and Foley converged more quickly than either the configuration interaction approach, used by Davis, or the function developed by Pekeris. This latter, though yielding accurate results, required over 200 terms to give convergence of the energy calculations to seven significant figures. Thus, the wave function used here is of the form proposed by Hylleraas and Undheim,[14] and is given by

$$\psi = \sum_{i=1}^{N} c_i e^{-(kcs/2)} k^{(l_i+m_i+n_i)} s^{l_i} u^{m_i} t^{n_i} \frac{\sinh}{\cosh}(\tfrac{1}{2}kt), \quad (3)$$

where k is a scaling parameter, c is the other nonlinear parameter, c_i are linear variation coefficients, l_i, m_i, n_i are the integral powers whose values will be chosen later, N is the number of terms in the wave function, which is taken up to a maximum of 35, $s = r_1 + r_2$, $u = r_{12}$, and $t = r_1 - r_2$.

The hyperbolic functions $\sinh(\tfrac{1}{2}kt)$, and $\cosh(\tfrac{1}{2}kt)$ are

[11] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), pp. 206–226.
[12] See Ref. 11.
[13] See Refs. 2–6.
[14] E. A. Hylleraas and B. Undheim, Z. Physik **65**, 759 (1930).

chosen according to whether n_i is even or odd so as to maintain the odd symmetry of the wave function.

The major computing effort here lies in minimizing the energy of the wave function [Eq. (3)] with respect to both of the nonlinear parameters c and k. A significant reduction in the computing time required for this task is achieved by considering k to be a scaling factor. Thus, since the field free Hamiltonian H_0 contains only homogeneous operators T and V, one can minimize the energy on both c and k with recalculation of the energy integrals needed only for various values of c. This is because the dependence of these integrals on k is particularly simple.

Thus the wave function [Eq. (3)] is written as

$$\psi(s,u,t) = \phi(ks,ku,kt), \quad (4)$$

where $\phi(s,u,t)$ is given by

$$\phi(s,u,t) = \sum_{i=1}^{N} c_i e^{-(cs/2)} s^{l_i} u^{m_i} t^{n_i} \frac{\sinh}{\cosh}(\tfrac{1}{2}t). \quad (5)$$

Then, in atomic units, the kinetic energy operator T is $-\tfrac{1}{2}\nabla_1{}^2 - \tfrac{1}{2}\nabla_2{}^2$ and the potential energy operator is $V = -(Z/r_1) - (Z/r_2) + (1/r_{12})$ so that one obtains for the energy

$$E = \frac{\int \psi^*(s,u,t)(T+V)\psi(s,u,t)d\tau}{\int \psi^*(s,u,t)\psi(s,u,t)d\tau} = \frac{k^2M - kL}{N}, \quad (6)$$

where

$$M = \int \phi^*(s,u,t)T\phi(s,u,t)d\tau, \quad (7a)$$

$$L = \int \phi^*(s,u,t)V\phi(s,u,t)d\tau, \quad (7b)$$

and

$$N = \int \phi^*(s,u,t)\phi(s,u,t)d\tau. \quad (7c)$$

The L, M, N can be expanded as follows:

$$L = \sum_{i,j} c_i{}^* c_j M_{ij}, \quad (8a)$$

$$M = \sum_{i,j} c_i{}^* c_j L_{ij}, \quad (8b)$$

$$N = \sum_{i,j} c_i{}^* c_j N_{ij}, \quad (8c)$$

where

$$M_{ij} = \int \phi_i{}^*(s,u,t)T\phi_j(s,u,t)d\tau, \quad (9a)$$

$$L_{ij} = \int \phi_i{}^*(s,u,t)V\phi_j(s,u,t)d\tau, \quad (9b)$$

$$N_{ij} = \int \phi_i{}^*(s,u,t)\phi_j(s,u,t)d\tau, \quad (9c)$$

and when the coordinates s, u, t are used to describe the coordinate system, these functions become

$$L_{ij} = 2\pi^2 \int_0^\infty ds \int_0^s du$$

$$\times \int_0^u dt \{ 4Zsu\phi_i^*\phi_j - [s^2 - t^2]\phi_i^*\phi_j \}, \quad (10a)$$

$$N_{ij} = 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt \{ u(s^2 - t^2)\phi_i^*\phi_j \}, \quad (10b)$$

$$M_{ij} = 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt \bigg\{ u(s^2 - t^2)$$

$$\times \left[\frac{\partial\phi_i}{\partial s}\frac{\partial\phi_j}{\partial s} + \frac{\partial\phi_i}{\partial u}\frac{\partial\phi_j}{\partial u} + \frac{\partial\phi_i}{\partial t}\frac{\partial\phi_j}{\partial t} \right]$$

$$+ 2s(u^2 - t^2)\left[\frac{\partial\phi_i}{\partial s}\frac{\partial\phi_j}{\partial u} + \frac{\partial\phi_i}{\partial u}\frac{\partial\phi_j}{\partial s} \right]$$

$$+ 2t(s^2 - u^2)\left[\frac{\partial\phi_i}{\partial u}\frac{\partial\phi_j}{\partial t} + \frac{\partial\phi_i}{\partial t}\frac{\partial\phi_j}{\partial u} \right] \bigg\}. \quad (10c)$$

Inspection shows that each of the integrals in Eqs. (10) will reduce to a sum of integrals of the three types

$$FINT = 2\pi^2 \int_0^\infty ds \int_0^s du$$

$$\times \int_0^u dt [e^{-cs}s^l u^m t^n \sinh^2(\tfrac{1}{2}t)], \quad (11a)$$

$$FJNT = 2\pi^2 \int_0^\infty ds \int_0^s du$$

$$\times \int_0^u dt [e^{-cs}s^l u^m t^n \cosh^2(\tfrac{1}{2}t)], \quad (11b)$$

$$FKNT = 2\pi^2 \int_0^\infty ds \int_0^s du$$

$$\times \int_0^u dt [e^{-cs}s^l u^m t^n \sinh(\tfrac{1}{2}t) \cosh(\tfrac{1}{2}t)], \quad (11c)$$

when the wave function is as in Eq. (7). Then, since

$$\sinh^2(\tfrac{1}{2}t) = \tfrac{1}{2}(\cosh t - 1), \quad (12a)$$

$$\cosh^2(\tfrac{1}{2}t) = \tfrac{1}{2}(\cosh t + 1), \quad (12b)$$

$$\sinh(\tfrac{1}{2}t)\cosh(\tfrac{1}{2}t) = \tfrac{1}{2}\sinh t, \quad (12c)$$

we need only compute the integrals

$$A = \int_0^\infty ds \int_0^s du \int_0^u dt [e^{-cs}s^l u^m t^n \cosh t], \quad (13a)$$

$$B = \int_0^\infty ds \int_0^s du \int_0^u dt [e^{-cs}s^l u^m t^n \sinh t], \quad (13b)$$

$$D = \int_0^\infty ds \int_0^s du \int_0^u dt [e^{-cs}s^l u^m t^n]. \quad (13c)$$

Then

$$FINT = \pi^2(A - D), \quad (14a)$$

$$FJNT = \pi^2(A + D), \quad (14b)$$

$$FKNT = \pi^2 B. \quad (14c)$$

Detailed formulas relating the auxiliary functions [Eq. (14)] to the matrix elements M_{ij}, L_{ij}, and N_{ij} are given elsewhere.[15]

Solution of the secular equation

$$DET | k^2 M_{ij} - kL_{ij} - EN_{ij} | = 0 \quad (15)$$

leads to a value for the energy E and then the set of simultaneous equations resulting from Eq. (6) can be solved for the coefficients c_i.

The integrals involved in Eq. (13) were solved by expanding $\cosh(t)$ and $\sinh(t)$ in infinite series in (t) and summing the resulting series

$$A = \int_0^\infty ds \int_0^s du \int_0^u dt [e^{-cs}s^l u^m t^n \cosh t]$$

$$= \sum_{i=0}^\infty \frac{(2i+m+n+l+2)!}{(2i+n+1)(2i+m+n+2)(2i)! c^{(2i+l+m+n+3)}}, \quad (16a)$$

$$B = \int_0^\infty ds \int_0^s du \int_0^u dt [e^{-cs}s^l u^m t^n \sinh t]$$

$$= \sum_{i=0}^\infty \frac{(2i+l+m+n+3)!}{(2i+n+2)(2i+m+n+3)(2i+1)! c^{(2i+l+m+n+4)}}, \quad (16b)$$

$$C = \int_0^\infty ds \int_0^s du \int_0^u dt [e^{-cs}s^l u^m t^n]$$

$$= \frac{(l+m+n+2)!}{(m+n+2)(n+1)c^{l+m+n+3}}, \quad (16c)$$

to the computational limits of convergence of the computer.

The method employed for optimizing the nonlinear parameters c and k, so as to minimize the energy, con-

[15] J. T. McMullan, MA thesis, The State University of New York at Buffalo, Buffalo, New York, February 1964 (unpublished).

TABLE I. Six-term energy results.

Ion	He I	Li II	Be III	B IV	C V
No. of terms	6	6	6	6	6
Energy in a.u.	-2.1752033	-5.1106952	-9.2971275	-14.733853	-21.420708
Power of					
S　U　T			Eigenvector in units of $a_0/4$		
0　0　0	5.9307974×10^{-1}	1.7194193	2.9002536	3.9856805	4.9465544
1　0　0	-3.1679337×10^{-1}	-8.9293931×10^{-1}	-1.4988541	-2.0542439	-2.5435356
0　0　1	-3.0595637×10^{-1}	-8.6475907×10^{-1}	-1.4525374	-1.9936387	-2.4730489
0　1　0	-8.9885579×10^{-2}	-1.7585617×10^{-1}	-2.2837918×10^{-1}	-2.5729235×10^{-1}	-2.7100190×10^{-2}
0　1　1	2.3859716×10^{-2}	5.4722199×10^{-2}	7.5427172×10^{-2}	8.7553838×10^{-2}	9.4073133×10^{-2}
1　1　0	-1.4028536×10^{-2}	-3.0478014×10^{-2}	-4.0786586×10^{-2}	-4.6222169×10^{-2}	-4.8840536×10^{-1}

sists in calculating the energy for three values of one of the parameters holding the other one fixed. These three energy values are then fitted to a parabola.[16] Then the value of the parameter being varied which minimizes the parabola is taken as the new value of this parameter. Then the other parameter is varied in the same manner while the improved one is held fixed.

Thus, if γ is c or k the curve of E versus γ is represented by

$$E(\gamma)=E(\gamma_0)+\frac{E(\gamma_1)-E(\gamma_0)}{\Delta}(\gamma-\gamma_0)$$
$$+\frac{E(\gamma_2)-2E(\gamma_1)+E(\gamma_0)}{2\Delta^2}(\gamma-\gamma_0)(\gamma-\gamma_1),\quad(17)$$

where

$$\Delta=\gamma_n-\gamma_{n-1}.\quad(18)$$

On requiring $\partial E/\partial\gamma=0$ we obtain

$$\gamma^*=\frac{\gamma_0+\gamma_1}{2}-\frac{\Delta[E(\gamma_1)-E(\gamma_0)]}{E(\gamma_0)-2E(\gamma_1)+E(\gamma_2)}.\quad(19)$$

The new parameter γ^* is generally better than any of the other three.

The method then is to choose a value γ_1, for the nonlinear parameter and a value for the optimization increment Δ. Then γ_0 and γ_2 are calculated from Eq. (18) and γ^* is obtained from Eq. (19). The whole process is repeated as many times as necessary with gradual reduction of the optimization increment until the required accuracy is obtained.

Having obtained the wave function in this way, the diamagnetic susceptibility is computed from Eq. (1) by using the relation

$$r_1^2+r_2^2=\tfrac{1}{2}(s^2+t^2).\quad(20)$$

Hence

$$\langle r_1^2+r_2^2\rangle_{av}=2\pi^2k^{-2}\Big\{\sum_{i=1}^N\sum_{j=1}^N c_i^*c_j\int ds\int du$$

$$\times\int dt[\phi_i^*u(s^4-t^4)\phi_j]\Big\}.\quad(21)$$

[16] R. P. Hurst, J. D. Gray, G. H. Brigman, and F. A. Matsen, Mol. Phys. 1, 2, 189 (1958).

Finally, using this result the susceptibilities are obtained from Eqs. (1) and (2).

RESULTS AND DISCUSSION

The computed values for the energy of the $2\,^3S_1$ state of He I, Li II, Be III, B IV, and C V using the six-term wave function are as shown in Table I and those for He I, and Li II using the thirty-five term wave function are given in Table II. In both cases the coefficient as-

TABLE II. Thirty-five term energy results.

Ion	He I	Li II
No. of terms	35	35
Energy in a.u.	-2.1752288	-5.1107268
Experimental	-2.17522937	-5.1107
Power of		
S　U　T	Eigenvector in Hylleraas units of $a_0/4$	
0　0　0	4.7515763×10^{-1}	1.3278706
1　0　0	-2.1297433×10^{-1}	-6.4743414×10^{-1}
0　0　1	-2.3595717×10^{-1}	-6.6060270×10^{-1}
0　1　0	-5.4054036×10^{-2}	-1.2200908×10^{-1}
0　1　1	2.2244468×10^{-2}	4.5255803×10^{-2}
1　1　0	-3.1617821×10^{-2}	-4.9843953×10^{-2}
0　0　2	7.4304450×10^{-3}	6.1758189×10^{-3}
0　0　3	-1.1314525×10^{-4}	4.8014926×10^{-4}
0　1　2	-1.4770588×10^{-3}	-2.0103314×10^{-3}
0　2　0	6.2799498×10^{-3}	6.4228812×10^{-3}
0　2　1	-6.9498491×10^{-4}	-3.6682981×10^{-3}
0　3　0	-1.5902550×10^{-3}	-8.6006201×10^{-3}
1　0　1	-9.7955047×10^{-3}	-3.5915761×10^{-2}
1　0　2	1.5904228×10^{-3}	3.8458913×10^{-3}
1　1　1	2.8108215×10^{-3}	8.5321579×10^{-3}
1　2　0	3.9112128×10^{-3}	2.4434584×10^{-2}
2　0　0	-4.6895605×10^{-3}	-2.3866696×10^{-2}
2　0　1	-1.0306888×10^{-3}	-2.5018333×10^{-3}
2　1　0	-2.9498338×10^{-3}	-2.1956618×10^{-2}
3　0　0	-2.0583545×10^{-4}	4.4842797×10^{-3}
0　0　4	-1.3331422×10^{-5}	-4.9063179×10^{-5}
0　1　3	8.5168555×10^{-5}	2.1854306×10^{-4}
0　2　2	-4.4517142×10^{-5}	-1.9473620×10^{-4}
0　3　1	1.3483542×10^{-4}	1.9130504×10^{-4}
0　4　0	4.7905459×10^{-5}	-1.0589895×10^{-4}
1　0　3	-2.3735311×10^{-5}	-1.0808635×10^{-4}
1　1　2	-7.1967346×10^{-5}	-8.3084609×10^{-5}
1　2　1	-3.4457473×10^{-4}	-2.2965488×10^{-4}
1　3　0	-7.1356653×10^{-5}	1.2571919×10^{-3}
2　0　2	-3.0739998×10^{-5}	-2.1771461×10^{-6}
2　1　1	3.8242851×10^{-4}	1.7749086×10^{-4}
2　2　0	1.5833393×10^{-5}	-2.8356107×10^{-3}
3　0　1	-1.0637398×10^{-5}	6.3008506×10^{-5}
3　1　0	-3.6033713×10^{-5}	2.2570131×10^{-3}
4　0　0	-3.7331584×10^{-5}	-6.7572069×10^{-4}

sociated with each term in the expansion is listed. The numbers on the left of both Tables I and II are the powers of s, u, and t used in the wave function. These powers were chosen in a systematic manner in that the sum of l, m, and n is a constant I, i.e., $l+m+n=I$. On including all terms for which $I=0$, 1, 2, 3 and 4 the thirty-five term wave function is obtained.

In Table III are listed the results for the magnetic

TABLE III. Magnetic susceptibility results (at 300°K).
(In each case $\chi_P=3343.72\times10^{-6}$ cm³/mole.)

Ion	Number of terms in wave function	$\langle r_1^2+r_2^2\rangle_{av}$ in (au)²	$-\chi_D\times10^6$ in cm³/mole	$\chi=\chi_P+\chi_D$ in cm³/mole
He	6	22.8235650761	18.0838433	33.25636 $\times10^{-4}$
	35	22.9291760176	18.1675222	33.25552 $\times10^{-4}$
Li⁺	6	7.54233220883	5.97603191	33.37744 $\times10^{-4}$
	35	6.91934660531	5.48242042	33.382380 $\times10^{-4}$
Be⁺⁺	6	3.76318283315	2.98169053	33.4073800 $\times10^{-4}$
B⁺⁺⁺	6	2.25588738761	1.78741200	33.419320 $\times10^{-4}$
C⁺⁺⁺⁺	6	1.50314828011	1.1909926	33.425900 $\times10^{-4}$

susceptibilities. The value of g used is that obtained by Hughes et al.[17]

It is interesting to compare the energy value obtained for helium with that obtained by other authors. These are shown in Table IV. A rough interpolation between Pekeris'[18] energy results, as additional terms are added,

TABLE IV. Energy comparison.

Author	No. of terms	Energy in a.u.
Pekeris	125	-2.17522097961
	252	-2.17522925888
	400	-2.17522937680
	715	-2.17522937822
Davis	80	-2.1752246
	80	-2.1752259
Traub & Foley	12	-2.1752176
Hart & Herzberg	20	-2.1752192
Present work	6	-2.17520330532
	35	-2.17522877618

[17] See Refs. 7, 8, and 9.
[18] See Ref. 2.

seems to indicate that the present 35-term function is equivalent in accuracy to about 220 terms in the Pekeris wave function.

TABLE V. $\langle r_1^2+r_2^2\rangle_{av}$ in a.u.

Author	No. of terms	$\langle r_1^2+r_2^2\rangle$
Pekeris	125	22.8746354
	252	22.9270248
	444	22.9286082
	715	22.9286426
Present work	3	24.38180716
	6	22.8235650761
	35	22.9291760176

Pekeris has also reported a number of values for the expectation value corresponding to each of his various wave functions and these are shown in Table V together with the helium values in the present work using 3, 6, and 35 term functions. We can immediately notice that the value obtained from our 35-term function differs from the Pekeris 715-term value by 0.0005334 au whereas the Pekeris 252-term value differs from the 715-term value by -0.0016178 au. Thus it seems possible that, even though the Hylleraas wave function with 35 terms is less accurate than the 252-term Pekeris function for the short-range Hamiltonian operator, it may be more accurate for the long-range operators such as r^2. In any event it is gratifying to note that the two wave functions which differ so much in the manner in which they are constructed and in the number of terms they contain give agreement in the computed r_1^2 values to five places. It is, therefore, highly likely that the susceptibility is now known to five places.

Finally, it is of interest to note that when the computation of the energy was performed using the 35-term function and 8-place arithmetic the computed result was below the experimental value, showing that the round-off error inherent in these long computations had become a limiting factor. Thus any extension of this type of work must be performed on a machine with a long word-length.