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Zeeman Effect in the $^2P_{1/2}$ Level of Atomic Fluorine

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The position of the $(F, M_F) = (1, 0) \longleftrightarrow (1, -1)$ transition in the $^2P_{1/2}$ level of atomic fluorine has been accurately measured and a g factor calculated. The result is $g_J(F; {}^2P_{1/2}) = 0.665\,611\,7 \pm 0.000\,002\,1$. This result is in excellent agreement with the previously published value of $0.665\,61 \pm 0.000\,03$, but differs by 25 parts per million from a recent calculation carried out to order α^2 in relativistic contributions according to the theory of Kambe and Van Vleck. The result is discussed in terms of the theories of Abragam and Van Vleck, and Kambe and Van Vleck.

INTRODUCTION

Atomic g factors may be calculated to a precision of several hundred parts per million (ppm) by using the Landé formula as corrected for the anomalous spin factor of the electron.[1] Further corrections, attributable to departures from L-S coupling, motion of the nucleus,[2] and relativistic and diamagnetic effects, must be applied before a calculated g factor can be meaningfully compared with a precision measurement. The theory for the relativistic and diamagnetic corrections in many electron atoms has been developed by Abragam and Van Vleck,[3] who considered terms linear in magnetic field to order $\alpha^2\beta H$. They used a spherically averaged potential to simplify calculations, but the theory was later extended to include exchange terms by Kambe and Van Vleck.[4] The simpler theory of Abraham and Van Vleck, which we will refer to as the AVV theory, has been used extensively to calculate atomic g factors,[3, 5–8] although there is evidence that it consistently overestimates the relativistic and diamagnetic corrections by as much as 10%. On the other hand, the extended theory of Kambe and Van Vleck, which we will refer to as the KVV theory, has been tested for very few atoms. In the ground multiplet of oxygen,[4, 9] it appears to underestimate the relativistic and diamagnetic corrections by about 5%, although this error may be due largely to the approximate Hartree-Fock wave functions used. In the ground multiplet of fluorine,[10] perfect agreement has been obtained for the $J = \frac{3}{2}$ level using quite accurate Hartree-Fock functions. The only available g-factor measurement in the $J = \frac{1}{2}$ level[11] is not of sufficient accuracy to test the theory. In view of the current flood of quite accurate atomic wave functions, it is expected that the KVV theory will, in the future, be much more extensively applied.

This paper reports a new experimental determination of the g factor in the $J = \frac{1}{2}$ level of the ground multiplet of fluorine to a precision of 3 ppm. This g factor is a particularly favorable one for testing the AVV and KVV theories for a number of reasons. Most important, perhaps, is the fact that the contribution of the relativistic and diamagnetic corrections to the fluorine $J = \frac{1}{2}$

level g factor is larger (in ppm) than for any other conveniently measurable light atom. This is illustrated in Table I. Also, in oxygen, the KVV corrections to the g factors in the $J=2$ and $J=1$ levels of the ^3P ground multiplet contain a large number of identical terms. This does not occur in fluorine so that each g-factor measurement is individually more meaningful. Departures from L-S coupling are expected to be negligible[6,10] in fluorine and one uncertainty in the theory is therefore removed. Finally, in two independent calculations of the fluorine $J=\frac{3}{2}$ level g factor using the AVV theory,[6,7] remarkable agreement with experiment was obtained. It would be most interesting to see if this agreement extends to the $J=\frac{1}{2}$ level.

TABLE I. Magnitudes of the relativistic and diamagnetic corrections to g_J in a selection of atomic species. These are approximate values based on available data.

Element	Level	Relativistic and diamagnetic correction (ppm)
N	$^2D_{5/2}$	80
	$^2D_{3/2}$	100
O	$^3P_2$	160
	$^3P_1$	120
F	$^2P_{3/2}$	180
	$^2P_{1/2}$	410
Cl	$^2P_{3/2}$	130
	$^2P_{1/2}$	340
Ne	$^3P_2$	180
A	$^3P_2$	130

Our measurement of the fluorine $J=\frac{1}{2}$ level g factor differs from the AVV calculations by 35 ppm, and from the KVV calculations by 25 ppm. These discrepancies are somewhat larger in magnitude than those found for other light atoms, but in terms of the percentage error that they indicate for the small relativistic and diamagnetic corrections, are consistent with other measurements. These aspects, and some suggestions which have been made in connection with the AVV and KVV theories, are discussed in the final section.

THE FLUORINE SPECTRUM

The paramagnetic-resonance spectrum of the ground multiplet of fluorine has been discussed extensively elsewhere.[7,11,12] For completeness, however, we will describe briefly the important features of the $^2P_{1/2}$ level. The ground electronic configuration of fluorine is $(1s)^2\,(2s)^2\,(2p)^5$ and the single vacancy in the $2p$ shell gives rise to only one L-S term, an inverted ^2P. The metastable $^2P_{1/2}$ level lies 404. 0 cm^{-1} above the ground $^2P_{3/2}$ level and, therefore, has about 7% of the ground-level population at room temperature. It has an intermediate field character at normal laboratory fields. The nuclear spin is $\frac{1}{2}$, giving rise to four $\Delta M_F=\pm 1$ transitions of which only two, the $(F, M_F)=(1,0)\longrightarrow(1,-1)$ and $(1,-1)\longrightarrow(0,0)$ transitions, are observable at a microwave frequency of the order of 9000 MHz.

The energy-level scheme has been found[7] to be adequately described by the Clendenin[13] formula for an l doublet with nuclear spin $I=\frac{1}{2}$. The constants in this formula, with the exception of $g_J\,(J=\frac{1}{2})$, are known with sufficient precision to predict the transition frequencies to within approximately 1 ppm. Those applicable to the $J=\frac{1}{2}$ level are: $a'''=-446\pm 10$ MHz, from measurements on the ground level by Radford, Hughes, and Beltrán-López;[7] $a_{1/2}=10\,244.21\pm 0.03$ MHz, from measurements of the $(1,-1)\longrightarrow(0,0)$ excited-level transition by Harvey[11]; and $g_I/g_P=0.940\,814$ $\pm 0.000\,009$, from NMR measurements in aqueous HF by Kanda, *et al.*[14] Harvey's measurements also give $g_J\,(J=\frac{1}{2})=0.665\,61\pm 0.000\,03$, where the large error (45 ppm) reflects the small dependence of this transition frequency on the value of the magnetic field. The $(1,0)\longrightarrow(1,-1)$ excited-level transition has also been observed,[12] but has not been measured precisely. This transition occurs at a high magnetic field, and is the one most sensitive to the value of g_J; it is the one that we measure in order to obtain an accurate g factor for the $J=\frac{1}{2}$ level.

APPARATUS

The experiment was performed with a precision X-band paramagnetic-resonance spectrometer similar in design to that of Hirshon and Fraenkel.[15] This spectrometer can be used with superheterodyne detection and high- or low-frequency field modulation, or with direct detection and high-frequency field modulation, and was designed primarily for ENDOR experiments. Up to 50 mW of power is available at the microwave cavity from a Varian X-13B klystron which can be stabilized with reference to either the sample cavity or a variable standard frequency. Magnetic fields of up to 13 000 G in a two-inch gap are provided by a commercial 12-in. electromagnet. The power supply for this magnet is rated at a short-term current stability of two ppm. In the present work, direct detection with high-frequency (100 KHz) field modulation was used and the klystron was locked to the variable standard frequency.

The sample, gaseous CF_4 obtained from the Matheson Company, was pumped rapidly through a 0.9-cm-diam quartz tube located axially in a TE_{011} reflection cavity, and was dissociated in a radio-frequency discharge just upstream from the cavity.

Of major concern in this experiment was the achievement of and measurement of a highly homogeneous magnetic field over the volume of the sample at 13 000 G. The value chosen for the cavity frequency represents the best compromise between increasing sample volume and deteriorating field homogeneity, although at that value the field variation over the sample was still about 40 ppm. The variation was further reduced, to less than 10 ppm, by the use of current shims[16] fed from a highly stable low-voltage power supply.

Because the magnetic field produced by this method may not have a uniform distribution, a special proton-resonance probe was built for the precise measurement of the field. This probe was designed to fit accurately into the center of the cavity and to occupy essentially the same volume as the sample. In addition, the radio-frequency coil surrounding the proton sample was designed to give approximately the same axial distribution of rf magnetic field as occurred in the microwave cavity. The proton sample itself was the same as that used by Harvey in previous measurements on the $J=\frac{1}{2}$ level of fluorine, a 0.163-M solution of nickel sulfate. The value of g_p taken for this sample is $g_p = -0.003\,041\,991\,0$.[17] The proton-resonance–detector head was developed from one used by Beringer and Heald.[18] It consists of a transistorized voltage-tuned oscillator, loosely coupled to the sample coil, and a Nuvistor high-impedance detector. For precise measurements, the oscillator was phase locked to the first or second harmonic of a stable 0- to 30-MHz signal generator, and the output of the detector was displayed on the panel meter of a phase-sensitive detector by slowly turning the vernier frequency control of the signal generator. The proton-resonance frequency, and that of the klystron oscillator, were measured with a Hewlett-Packard model 5245L counter whose time base was referenced to the laboratory frequency standard.

It was not found possible to obtain a field outside the cavity that was sufficiently homogeneous for precise monitoring of the magnetic field. Since a slow drift of the field consistently occurred, and since some time necessarily elapsed between the observation of the line and the insertion of the probe in place of the quartz tube, it was necessary to adopt the regression line procedure outlined in the next section in order to obtain the actual field value at which the fluorine resonance occurred.

EXPERIMENTAL PROCEDURE AND RESULTS

At the start of each day's run, the magnet pole caps were adjusted until the position of the field maximum was within 0.5 mm of the central axis of the cavity and current shim assembly; this tolerance ensuring that the shims would accurately compensate for the radial fall off of magnetic field. No more than two measurements were completed without repeating this procedure, and it was carried out after every measurement for which there was evidence of deterioration in the field homogeneity. The current through the shims was adjusted initially to give a good proton-resonance line shape with the probe located in the cavity, and finally, for each measurement, to give the best fluorine-resonance line shape. With this technique, and with a gas pressure of 50 μ upstream from the discharge, the $J=\frac{1}{2}$ level $(1,0)\longrightarrow(1,-1)$ fluorine transition was observed consistently with a signal to noise ratio of about 30/1, and a peak to peak line width of 0.25 G (20 ppm). The proton-resonance line width in the same field was about 0.10 G (8 ppm), thus indicating that the fluorine transition was appreciably pressure broadened. Further reduction of pressure actually reduced sensitivity, however, owing to the creation of greater ion densities in the cavity.

Because of the poor field homogeneity outside the cavity, the following procedure for measuring the line position was adopted. After accurately setting the field on the center of the transition and recording the klystron frequency, the quartz tube was removed from the cavity and the proton-resonance probe inserted in its place. Readings of the proton-resonance frequency were then recorded over a period of about one half hour and a least-squares regression line was calculated to give the value at the time of the original setting. A typical set of data is shown in Fig. 1. It is possible, of course, for undetected short-term field variations to occur upon cessation of the discharge, but to the limiting sensitivity of a Hall-effect incremental gaussmeter (better than 0.1 G), we were unable to observe any such effects.

The results of twelve measurements on the excited level transition are shown in Table II. In this table we also include the results of six measurements on the ground level $(2,-1)\longrightarrow(2,-2)$ transition which were performed in order to check the validity of our field measuring procedure. Of the three highest transitions in the ground level, this one has the simplest dependence on g_J. In one of the latter measurements, an abnormal field instability was noted and the result lies well outside the standard deviation of the remaining five. This value was rejected. Such instabilities, occurring in the magnet current regulator, should have little effect on the excited level measurements due to saturation of the magnet core at a field of 13 000 G. The g factors are those which exactly fit the observed line positions and were computed on an IBM 7094 computer using the

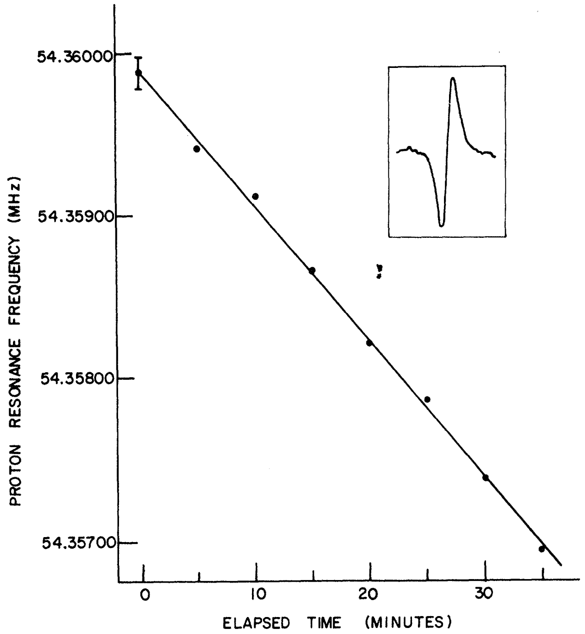

FIG. 1. A typical plot of magnetic field variation (in terms of proton-resonance frequency) versus elapsed time after setting on the $(1,0) \longleftrightarrow (1,-1)$ transition. The calculated regression line is shown with an error bar at zero time representing a tolerance of ± 2 ppm in the calculated frequency. The insert shows a chart record of the transition made with a time constant of 1 sec.

Clendenin formula. They are quoted without rounding.

Our measurements of the ground-level g factor yield

$$g_J(F;{}^2P_{3/2}) = 1.333\,861\,0 \pm 0.000\,001\,1,$$

where the error is the standard deviation for five measurements. This value is in very good agreement with the known value[19] and provides further evidence that no significant errors in field measurement occur.

The distribution curve for the $J=\frac{1}{2}$ excited level measurements is highly skewed and suggests a possible bias in the method of field alignment. However, we find the following explanation more plausible. In Fig. 2, the deviations of the twelve measured g factors from their mean are plotted against cavity frequency. A trend is discernible which is too large to be attributed to small discrepancies in the theory, and probably is due to an apparatus effect. Variations in the position of the axial quartz tube change the cavity frequency by most ±0.25 MHz, but a temperature rise of 25°C, which could be caused by poor adjustment of the radio-frequency discharge operating conditions, lowers the frequency by 1 MHz. We have qualitatively established that short-term temperature changes of this magnitude have an observable effect on the flux distribution over the sample, probably due to local heating of the magnet

TABLE II. Experimentally determined g factors for the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ levels of atomic fluorine.

Level	Run	Proton resonance frequency (MHz)	Transition frequency (MHz)	g factor
${}^2P_{1/2}$	1	54.357 912	8667.273	0.665 610 06
	2	54.362 049	8668.102	0.665 612 18
	3	54.358 475	8667.399	0.665 611 19
	4	54.358 113	8667.353	0.665 612 70
	5	54.359 890	8667.677	0.665 611 55
	6	54.361 228	8667.953	0.665 612 75
	7	54.361 376	8667.974	0.665 612 28
	8	54.361 377	8667.980	0.665 612 65
	9	54.361 011	8667.869	0.665 610 07
	10	54.359 018	8667.470	0.665 609 06
	11	54.362 219	8668.136	0.665 612 27
	12	54.364 511	8668.568	0.665 611 70
	unweighted mean and standard deviation = 0.665 611 5 ± 0.000 001 2			
${}^2P_{3/2}$	1	21.473 563	8668.642	1.333 860 99
	2	21.472 908	8668.370	1.333 862 19
	3	21.474 716	8669.037	1.333 846 49[a]
	4	21.471 863	8667.918	1.333 861 66
	5	21.473 649	8668.666	1.333 859 04
	6	21.473 879	8668.778	1.333 860 99
	unweighted mean and standard deviation = 1.333 861 0 ± 0.000 001 1			

[a] Run rejected; see text for details.

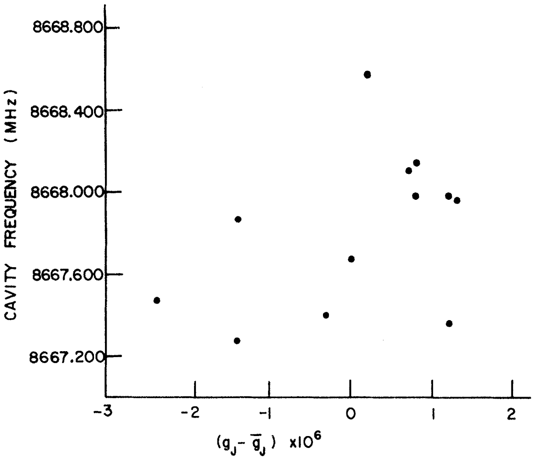

FIG. 2. Deviations of the twelve measurements of the $J=\frac{1}{2}$ level g factor from their unweighted mean, plotted against cavity frequency.

pole caps, and conclude that the lowest frequency measurements are also the least reliable. This judgment would appear to be confirmed by Fig. 2. The ground-level measurements were made with slightly lower discharge power and this effect is not discernible.

Giving the four lowest frequency measurements a rather arbitrary weighting factor of 0.5, we obtain from the twelve measurements of the excited-level transition the following value for the g factor:

$$g_J(F;{}^2P_{1/2}) = 0.665\,611\,7 \pm 0.000\,002\,1,$$

where the quoted error is twice the standard deviation and includes all measurements but one to which we have given half weight.

DISCUSSION

The value of the fluorine $J=\frac{1}{2}$ level g factor measured in this experiment is in excellent agreement with the previously published value[11] of $0.665\,61 \pm 0.000\,03$. In contrast with the ground-level g factor, however, it is not in agreement with theory.

Radford, Hughes, and Beltrán-López have calculated the relativistic and diamagnetic corrections for the ground level of fluorine using the AVV theory. They used Brown's[20] self-consistent-field wave functions for the dominant kinetic-energy correction and Slater's[21] approximate screened hydrogenic functions for the spherically averaged radial integrals, and obtained a g factor in agreement with experiment to within 2 ppm. Harvey, Kamper, and Lea,[6] in a similar calculation using Brown's wave functions throughout, also obtained agreement to within 2 ppm. This quite remarkable agreement does not, however, extend to the excited level where the two calculations yield g factors differing by 50 ppm. In an independent calculation, we have confirmed the values obtained with Brown's wave functions and obtain for the $J=\frac{1}{2}$ level, $g_J(J=\frac{1}{2}) = 0.665\,589$. This value differs from the experimental one by 35 ppm.

Beltrán-López, Ley Koo, Segovia, and Blaisten[10] have calculated the g factors for both levels in the ground multiplet of fluorine using the KVV theory and quite accurate Hartree-Fock self-consistent-field wave functions. They obtain essentially perfect agreement in the ground level and give for the excited level, $g_J(J=\frac{1}{2}) = \frac{2}{3} - (1072 \pm 2) \times 10^{-6}$. This value differs from our experimental result by 25 ppm. In this calculation, in contrast to the previous ones, the motion of the nucleus was found to make a significant contribution.

To facilitate a discussion of these differences, we have listed in Table III a number of theoretical values for $g_J(J=\frac{1}{2})$. These have been calculated using a spin factor anomaly correction of -733×10^{-6}, obtained by inserting $g_S = 2 \times (1.001\,159\,622)$ in the Landé formula,[10] and several significant combinations of available motion of the nucleus corrections and relativistic and diamagnetic corrections. For each value, we also list the percentage error in the relativistic and diamagnetic corrections; that is, the change required in these corrections to bring the theoretical value into agreement with experiment. Since departures from L-S coupling are very small in fluorine, these should reflect the actual errors in the relativistic and diamagnetic terms to within the uncertainty in the motion of the nucleus correction. In the following discussion, we take the best available atomic parameters to be those of Beltrán-López *et al.*

Table III shows that the use of an improved value for the kinetic energy, and for the motion of the nucleus correction, both cause a greater disagreement between the AVV theory and experiment. Together, they bring the discrepancy up to about 80 ppm. The good agreement obtained for the ground-level g factor cannot, therefore, be indicative of the accuracy to be expected in applying this theory to many electron atoms. Incorporating the best values for the kinetic energy and the motion of the nucleus correction, the relativistic and diamagnetic corrections computed with the AVV theory appear to be in error by 17%. It has been stated[8] that, with reasonably accurate wave functions, these corrections should be accurate to within 10%. Although fluorine may be an anomalous case, it would be desirable to check their accuracy for more substances.

The KVV theory gives better agreement with experiment. Surprisingly, the agreement is almost perfect when the corrections are calculated with Brown's wave functions, although a 13-ppm error then occurs in the ground-level g factor,

TABLE III. Theoretical g factors for the $J=\frac{1}{2}$ level of fluorine. The motion of the nucleus (MN) corrections and the relativistic and diamagnetic (RD) corrections are explained in the notes. The final column shows the apparent percentage error in the RD corrections.

Notes	MN corrections	RD corrections	g_J(theory)	RD error
(a)	0	-305×10^{-6}	0.665 589	8%
(b)	0	-326×10^{-6}	0.665 568	13%
(c)	-10×10^{-6}	-326×10^{-6}	0.665 558	17%
(d)	-15×10^{-6}	-268×10^{-6}	0.665 611	0%
(e)	-10×10^{-6}	-289×10^{-6}	0.665 595	6%

[a] Motion of nucleus assumed negligible and AVV corrections calculated with Brown's wave functions as in Ref. 6.

[b] As in footnote a except that the best available value for the kinetic energy is used. This change and those following make use of Ref. 10.

[c] As in footnote b except that the best available motion of the nucleus correction is used.

[d] KVV theory computed with Brown's wave functions.

[e] KVV theory computed with quite accurate self-consistent-field wave functions.

but an apparent error of 6% remains in the relativistic and diamagnetic corrections when more accurate self-consistent-field functions are used. This error is very similar to that found in the $J=2$ and $J=1$ levels of oxygen.

Radford and Hughes,[22] in discussing the discrepancy found for oxygen, point out that a 5% change in the kinetic energy would bring both theoretical g factors into perfect agreement with experiment, and that this is well within the accuracy with which other atomic parameters are predicted by one-electron Hartree-Fock wave functions. They conclude that the lack of agreement in oxygen is readily attributable to deficiencies in the wave functions used. The comparison between our result and the g factors calculated for fluorine with the KVV theory forces us to a similar conclusion, but with one significant difference. Because of the way in which the kinetic-energy operator enters into the KVV corrections for fluorine, a change in the value of the kinetic energy which removes the 25 ppm discrepancy in the excited level produces an equal discrepancy in the ground level, and thus brings about no improvement. In fluorine, therefore, suspicion falls primarily on the calculated two-electron integrals which make up the major part of the remaining terms.

In order to obtain agreement with experiment, an accuracy of about 1% is required in the calculated relativistic and diamagnetic corrections. It does not seem reasonable to assume that this can be achieved with single-electron Hartree-Fock-type wave functions, no matter how precisely they are computed, as the important polarization and correlation effects are not adequately treated within the Hartree-Fock formalism. Probably the best hope for an ultimate test of the KVV theory of atomic moments lies in the use of more accurate configuration interaction type wave functions.

It would be most useful to have more comparisons between the KVV theory and experiment. A promising candidate for this is chlorine, for which the ground-level g factor has been accurately measured,[6] and the excited-level transitions observed.[12] We hope to be able to undertake the measurement of the excited-level g factor in the near future.

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[19] Radford, Hughes, and Beltrán-López (Ref. 7) quote the ratio $g_J(F; {}^2P_{3/2})/g_p = -438.4839 \pm 0.0003$, where g_p refers to protons in a cylindrical sample of mineral oil of length-to-diameter ratio 5/1. To obtain a value for g_J, we have multiplied this ratio by the value of g_p used in Radford and Hughes's (Ref. 22) interpretation of the ^{16}O spectrum. This refers to a mineral-oil sample of the same geometry. We find $g_J(F; {}^2P_{3/2}) = 1.333\,860\,6$.

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Many-Electron Pseudopotential Formalism for Atomic and Molecular Excited-State Calculations*

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The pseudopotential approach of Phillips and Kleinman is extended beyond the one-electron approximation for the purpose of obtaining correlated low-energy continuum and excited bound states of atomic and molecular systems with a minimum of computational effort. Pseudopotential equations are derived by a variational method. These and other nonvariational pseudopotential methods are shown to be quite useful in conjunction with either adiabatic or close-coupling methods. Calculations are performed on the following two-electron systems: e-H ^1S-wave elastic scattering, e-He$^+$ ^1S and ^3S elastic scattering, and ^1S and ^3S Rydberg states of He. In general, good results are obtained. The calculated Rydberg-state quantum defects usually agree with the experimental values to three decimal places, and the calculated e-H ^1S zero-energy scattering length of 5.90 ± 0.08, which is a strict upper bound to the true value, compares favorably with the value 5.965 ± 0.003 obtained by Schwartz in a very much more involved calculation. The possible extension of these methods to larger atomic systems and to molecules is discussed. A differential equation method for obtaining bound-state wave functions and energies based on asymptotic properties of Coulomb functions is outlined in the Appendix.

I. INTRODUCTION

Calculations of Rydberg and electronic continuum wave functions can be useful in describing many dynamic atomic and molecular processes such as photo-ionization, autoionization, photodetachment, elastic and inelastic electron scattering, etc. However, wave functions calculated by the Hartree-Fock method are frequently not good enough for this purpose. Accurate correlated wave functions are often needed.

The object of this paper is to develop *a priori* methods, based on the pseudopotential approach, by which one can calculate accurate correlated (bound or continuum) excited-state wave functions, but which involve only a small increase in computational effort over the Hartree-Fock method.

The "pseudopotential" approach developed by Phillips and Kleinman[1] for application to solid-state problems has recently been applied by several workers to the calculation of atomic and molecular wave functions.[2-11] The pseudopoten-