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Spin-Optimized Self-Consistent Field Wave Functions*

Uzi Kaldor†
Department of Chemistry, Stanford University, Stanford, California 94305

and

Frank E. Harris
Department of Physics, University of Utah, Salt Lake City, Utah 84112

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A method is given for determining a spin-optimized self-consistent-field (SO-SCF) function based on optimized spatial orbitals and a spin function which is optimum in the S, M_S spin space. Results are presented for Li(^2S), Li(^2P), Be$^+$(^2S), B^{++}(^2S), and Be(^1S). SO-SCF wave functions and energies are very similar to those obtained with restriction to the normally paired spin function, but the use of the entire spin space greatly improves the description of spin-dependent properties. Whereas single-spin-function calculations of the spin density at the nucleus are for Li(^2S) and Li(^2P), respectively, 9% and 100% in error, the corresponding SO-SCF errors are only 2% and 7%.

I. INTRODUCTION

There has been much recent interest in developing practical independent-particle methods capable of yielding good descriptions of spin-dependent properties of open-shell atoms. The methods receiving serious attention are all of the self-consistent-field (SCF) type in which the spatial orbitals are optimized by applying an energy-minimization principle. The simplest and most widely used such procedure, the restricted Hartree-Fock (RHF) method,[1] fails because the orbitals are optimized without regard for spin-dependent perturbations upon the closed-shell electrons. Early attempts to remedy this situation involved the separate optimization of α-spin and β-spin orbitals in a determinantal wave function.[2] This, the unrestricted Hartree-Fock (UHF) method, in general leads to a wave function which is not an eigenfunction of $\mathcal{S}^2$. Improvements beyond the UHF method involve the removal of this defect.

The generation of many-electron spin eigenfunctions was very early discussed by Pauling,[3] who gave rules for the handling of the several spin functions spanning an n-spin space of given $\mathcal{S}^2$ and $\mathcal{S}_z$. Serber[4] and Yamanouchi[5] considered the matrix representations of the permutation group having spin eigenfunctions as bases, and a comprehensive compilation of the formulas needed to generate spin eigenfunctions from arbitrary orbital products was given wide circulation by Kotani *et al.*[6] The production of a spin eigenfunction from a spin-orbital product was pointed out by Löwdin[7] to be a projection, and Pauncz, de Heer, and Löwdin[8] gave rules by which such projections could be characterized. Harriman[9] gave explicit formulas for density matrices involving projectors, and several workers[10] have given explicit formulas and discussions of the properties of the "Sanibel" coefficients occurring in the projector algebra. Essentially equivalent is the "spin-free" approach to quantum chemistry described by Matsen.[11] More recently Goddard[12] has applied these group-theoretical concepts to derive one-electron SCF-like equations for functions having arbitrary but specified spin coupling.

The necessity to consider all spin functions spanning the spin space of an atom was pointed out some time ago by Pratt.[13] Actual use of more than one spin function in calculations also has an appreciable history; for example, Harris and Taylor[14] found it advisable to include both spin functions in studies of Li and LiH. These calculations were not of the full SCF generality, but they indicated that the optimum spin function did not exactly correspond to singlet coupling of the Li 1*s* electrons. A similar result was reported by Ritter, Pauncz, and Appel,[15] and recent Hylleraas-type calculations by Larsson[16] on Li (^2S) indicate that for a given spatial function, optimization of the spin function usually improves the value calculated for the Fermi contact interaction. Kutzelnigg and Smith[17] have pointed out the increased generality produced by the use of general spin functions in wave functions based on spin-orbital products, and Smith and Larsson[18] have reiterated the role of the full spin space.

Actual applications by SCF-type methods have lagged somewhat behind the ideas indicated in the preceding paragraph. Löwdin[7] made the concrete proposal that the spatial orbitals be optimized after spin projection of a Slater determinant built from pure-spin orbitals. This method, sometimes denoted spin-extended Hartree-Fock (SEHF), corresponds to the use of an *a priori* determined spin eigenfunction, and has the practical virtue that the spatial orbitals can be required to satisfy certain orthogonality relations.[19] SEHF calculations of first-row atoms have been carried out by Goddard[20] (who refers to this method as "GF"), Kaldor,[21] Sando,[22] and Lunell.[23]

A potential defect of the SEHF method is that its spin function does not correspond to close coupling of α and β spins into pairs, and it may often be better to optimize spatial orbitals using the spin eigenfunction which maximally couples pairs. We call this procedure "maximally paired Hartree-Fock" (MPHF); it is called the "G1" method by Goddard. The limited-basis-set studies of Ritter, Pauncz, and Appel[15] on Li, larger-basis-set studies of Goddard[24] and Lunell,[23] and numerical studies by Hardcastle, Gammel and Keown,[25] all indicate that MPHF energies can be appreciably better than SEHF energies. However, the arbitrary choice of the maximally paired spin function interferes with good estimation of spin-dependent properties. For example, MPHF functions have zero spin density at the nuclei of atoms having no *s* open shells, such as Li (^2P), N (^4S), or Mn (^6S), in contradiction with experiment.

The obvious next step is to choose an optimum spin eigenfunction as well as to optimize the spatial orbitals. This method, which we call spin-optimized SCF (SO-SCF), will be seen to yield considerable qualitative improvement in the description of spin-dependent quantities. In this paper we report SO-SCF studies of several three- and four-electron systems.[23]

II. THE SO-SCF FUNCTION

One way to write a wave function based on an orbital product and a general spin eigenfunction is the form

$$\Psi = \mathcal{A}\,\Xi\,\Theta \,, \tag{1}$$

where $\mathcal{A}$ is the antisymmetrizer, Ξ is a product of spatial one-electron functions,

$$\Xi = \chi_1(1)\chi_2(2)\cdots\chi_n(n) \tag{2}$$

and Θ is a linear combination of all independent spin functions spanning the space of appropriate S and M_S:

$$\Theta = \textstyle\sum_k t_k \theta_k \;. \tag{3}$$

The best function Ψ is obtained by simultaneous optimization of the orbitals in Ξ *and* the coefficients t_k in Θ. This is the function we call the spin-optimized self-consistent field (SO-SCF) function.

The SO-SCF functions presented in this paper can alternatively be described as an antisymmetrized spin-projected Hartree product of spin orbitals

$$\Psi = \mathcal{A}\,\mathcal{O}\,\varphi_1(1)\varphi_2(2)\cdots\varphi_n(n) \,, \tag{4}$$

where $\mathcal{O}$ projects a spin state characterized by S and M_S, and the spin orbitals φ_i are of the mixed-spin form

$$\varphi_i = \chi_i(a_i\alpha + b_i\beta) \,. \tag{5}$$

Both the χ_i and the ratios a_i/b_i are to be determined variationally.

However, a given wave function often corresponds to an infinite number of different sets of a_i/b_i ratios, so that these ratios cannot be determined uniquely. For a two-electron singlet state, for instance, both ratios are completely immaterial and cancel out upon projection,[26] as there is only one spin function describing this state, viz. $\alpha\beta-\beta\alpha$. A three-electron doublet state has two independent spin functions, which may be chosen as

$$\begin{aligned}\theta_1&=2^{-1/2}(\alpha\beta\alpha-\beta\alpha\alpha)\\ \theta_2&=6^{-1/2}(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)\end{aligned}\qquad(6)$$

so that although there are three a_i/b_i ratios, there is only one actual spin parameter to be determined variationally, namely the ratio t_2/t_1 in Eq. (3) for Θ. These illustrations indicate why the SO-SCF function is represented more conveniently by Eqs. (1)–(3) than by Eqs. (4) and (5). It may also be noted that there exist SO-SCF functions (such as that for ^4S N) which cannot assume the form given in Eqs. (4) and (5).

III. METHOD OF CALCULATION

The SO-SCF wave function is determined by a procedure similar to that used by one of us[21] for the SEHF function. It can be shown that the operator H-EI has vanishing matrix elements between the SO-SCF function and all states singly excited therefrom (within the space spanned by the basis orbitals). This extension of Brillouin's theorem is the basis for the following operations.

First, an arbitrary guess is made for Ψ, choosing Ξ and Θ in the forms given by Eqs. (2) and (3). Then all possible linearly independent singly excited states

$$\Psi_i^{\,a}=\mathcal{A}\,\Xi_i^{\,a}\,\Theta\qquad(7)$$

are form, where Ξ_i^a indicates the replacement of χ_i in Ξ by χ_a, with χ_a orthogonal to χ_i. The same Θ is used for Ψ and all Ψ_i^a. A configuration-interaction (CI) calculation is made to find the optimum wave function of the form $\Psi+\sum_{i,a}\times C_{ia}\Psi_i^{\,a}$, following which the effects of configuration mixing are incorporated (to first order) in Ψ by modifying the orbitals:

$$\chi_i'=\chi_i+\textstyle\sum_a C_{ia}\chi_a\ .\qquad(8)$$

This process is repeated until convergence is achieved.

The spin function Θ is then optimized by per-

TABLE I. SO-SCF wave functions for ^2S states of three-electron systems.

Basis orbital[a]	χ_{1s}	$\chi_{1s'}$	χ_{2s}
Li (^2S): $\Theta=0.999\,9928\,\theta_1-0.003\,7864\,\theta_2$[b]			
$1s(3.0000)$	1.143 59	0.609 95	0.028 04
$3s(5.4000)$	−0.077 79	0.078 39	0.000 60
$3s(2.9972)$	0.007 11	0.271 38	0.020 58
$3s(1.3465)$	0.011 55	−0.002 30	0.284 75
$3s(0.8451)$	−0.007 64	0.002 43	0.649 13
$4s(5.3300)$	−0.104 62	0.128 27	−0.002 30
$4s(0.7257)$	0.003 22	−0.001 22	0.114 76
$\chi(0)$[c]	3.352 56	1.788 13	0.082 21
Be$^+$ (^2S): $\Theta=0.999\,985\,1\theta_1-0.005\,458\,1\theta_2$			
$1s(4.000)$	1.143 92	0.670 73	0.040 74
$4s(6.870)$	−0.076 21	0.101 20	−0.002 30
$3s(6.870)$	−0.107 80	0.111 23	0.000 49
$3s(4.040)$	0.012 09	0.190 32	0.025 25
$3s(2.002)$	0.003 82	−0.000 89	0.387 74
$4s(1.327)$	0.000 32	−0.000 58	0.625 80
$\chi(0)$	5.163 09	3.027 34	0.183 88
B^{++}(^2S): $\Theta=0.999\,9823\,\theta_1-0.005\,9523\,\theta_2$			
$1s(5.000)$	1.141 19	0.710 21	0.047 70
$4s(7.860)$	−0.022 54	0.059 39	−0.001 29
$3s(7.860)$	−0.161 03	0.176 96	0.000 99
$3s(4.840)$	0.021 15	0.117 14	0.026 54
$3s(2.702)$	−0.002 32	−0.001 88	0.390 35
$3s(1.875)$	0.003 12	−0.001 13	0.609 52
$\chi(0)$	7.198 42	4.479 89	0.300 87

[a] Orbital exponents are given in parentheses.

[b] $\theta_1=(\alpha\beta\alpha-\beta\alpha\alpha)/\sqrt{2}$; $\theta_2=(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)/\sqrt{6}$.

[c] Wave function at nucleus.

forming a CI calculation including the functions Ψ_k,

$$\Psi_k = \mathcal{A}\Xi\,\theta_k\,, \tag{9}$$

where Ξ is the spatial function calculated in the previous step and θ_k are the spin functions spanning the space of appropriate S and M_S. The resulting CI coefficients are used to construct a new approximation to Θ according to Eq. (3). The spatial orbital variation and the spin function optimization are repeated until the changes fall below a prescribed limit. In practice we do not wait for orbital convergence to carry out the spin function optimization; the fastest way is to determine Θ after each Ξ iteration. It should be noted that whereas the Ξ optimization is an iterative procedure, the best Θ for a particular Ξ is found in one step, which is in general faster than a step in the orbital variation. It therefore does not take significantly longer to optimize both Ξ and Θ than to optimize Ξ for a predetermined Θ. However, unlike the SEHF case, any transformation among the occupied orbitals will in general alter the wave function (this is generally true for any form of Θ but the SEHF function[27]). No orthogonalization is therefore possible, and the improvement in the wave function is paid for by having to calculate more complicated matrix elements.

IV. RESULTS AND DISCUSSION

SO-SCF calculations were carried out for the ^2S ground state of Li, Be$^+$, and B^{++}. The basis sets were those used by Goddard[24] in his MPHF calculations. No exponent reoptimization was necessary, as the SO-SCF orbitals differ only slightly from the MPHF orbitals. Our SO-SCF wave functions are given in Table I. In addition, we determined the SEHF, MPHF, and SO-SCF wave functions for the lowest ^2P excited state of Li (Table II). The nine-orbital basis set of Weiss[28] was used. The basis orbital exponents were optimized for the SO-SCF function by the method of steepest descent with parabolic interpolation,[21] and these exponents were also used for the MPHF function. Weiss's original exponents were found to be optimal for the SEHF function, Finally, we determined MPHF and SO-SCF functions for the ^1S ground state of Be, using a five-orbital set with exponents optimized for the SO-SCF function. These wave functions are shown in Table III.

The energy, spin density at the nucleus, and orbital overlaps given by the SO-SCF functions for the three-electron systems are collected in

TABLE II. Wave functions for Li (^2P).

Basis orbital[a]	χ_{1s}	$\chi_{1s'}$	Basis orbital	χ_{2p}
SEHF function: $\Theta = (2\alpha\beta\alpha - \alpha\alpha\beta - \beta\alpha\alpha)/\sqrt{6}$				
$1s(3.00)$	0.889 13	0.893 41	$2p(1.500)$	0.132 91
$3s(9.60)$	−0.000 82	−0.000 98	$4p(2.120)$	0.044 36
$3s(3.38)$	0.104 54	0.110 34	$4p(1.275)$	0.324 86
$3s(2.52)$	0.058 21	0.044 14	$4p(0.785)$	0.506 49
			$4p(0.566)$	0.160 75
$\chi(0)$[b]	2.606 60	2.619 14		0.0
MPHF function: $\Theta = (\alpha\beta\alpha - \beta\alpha\alpha)/\sqrt{2}$				
$1s(2.9440)$	1.170 57	0.627 94	$2p(1.5053)$	0.130 56
$3s(9.5460)$	−0.001 01	−0.009 05	$4p(2.1161)$	0.055 27
$3s(4.3055)$	−0.237 53	0.239 17	$4p(1.2041)$	0.388 40
$3s(2.9228)$	0.041 48	0.216 48	$4p(0.7316)$	0.510 10
			$4p(0.5316)$	0.085 56
$\chi(0)$	3.336 04	1.789 58		0.0
SO-SCF function: $\Theta = 0.999\,994\,0\theta_1 + 0.003\,445\,04\theta_2$[c]				
$1s(2.9440)$	1.170 54	0.627 97	$2p(1.5053)$	0.130 63
$3s(9.5460)$	−0.001 01	−0.009 04	$4p(2.1161)$	0.055 29
$3s(4.3055)$	−0.237 38	0.239 02	$4p(1.2041)$	0.388 43
$3s(2.9228)$	0.041 35	0.216 62	$4p(0.7316)$	0.510 07
			$4p(0.5316)$	0.085 50
$\chi(0)$	3.335 93	1.789 67		0.0

[a] Orbital exponents are given in parentheses.

[b] Wave function at nucleus.

[c] $\theta_1 = (\alpha\beta\alpha - \beta\alpha\alpha)/\sqrt{2}$; $\theta_2 = (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)/\sqrt{6}$.

TABLE III. Wave functions for Be (^1S).

Basis orbital[a]	χ_{1s}	$\chi_{1s'}$	χ_{2s}	$\chi_{2s'}$
	MPHF function: $\Theta=\theta_1=(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha-\alpha\beta\beta\alpha-\beta\alpha\alpha\beta)/2$			
$1s(5.6858)$	−0.049 04	0.469 05	0.008 44	0.041 60
$1s(2.9479)$	1.088 03	0.651 36	0.004 95	−0.023 68
$3s(3.6747)$	−0.045 66	−0.160 56	0.018 59	−0.117 70
$2s(1.3767)$	−0.047 40	0.048 89	−0.256 46	0.927 41
$2s(0.8441)$	0.042 30	−0.011 85	1.205 11	0.175 91
$\chi(0)$[b]	2.731 9	5.447 9	0.078 7	0.419 9
	SO-SCF function: $\Theta=0.999\,86615\theta_1-0.016\,63999\theta_2$[c]			
$1s(5.6858)$	−0.050 33	0.468 60	0.010 52	0.036 83
$1s(2.9479)$	1.095 46	0.649 41	0.019 72	−0.055 45
$3s(3.6747)$	−0.044 10	−0.161 37	0.017 11	−0.115 73
$2s(1.3767)$	−0.058 96	0.055 32	−0.256 63	0.937 94
$2s(0.8441)$	0.029 99	−0.006 00	1.202 86	0.176 36
$\chi(0)$	2.743 2	5.438 9	0.136 8	0.419 9

[a] Orbital exponents are given in parentheses.

[b] $\theta_2=(2\alpha\alpha\beta\beta+2\beta\beta\alpha\alpha-\alpha\beta\alpha\beta-\beta\alpha\beta\alpha-\alpha\beta\beta\alpha-\beta\alpha\alpha\beta)/\sqrt{12}$.

[c] Wave function at nucleus.

TABLE IV. SO-SCF results for three-electron systems.

	Energy (hartree)	Spin density at nucleus	Orbital overlaps $\langle\chi_{1s}\vert\chi_{1s'}\rangle$	$\langle\chi_{1s}\vert\chi_{2s}\rangle$	$\langle\chi_{1s'}\vert\chi_{2s}\rangle$
Li(^2S)	−7.447 565	0.2265	0.928 32	0.136 15	0.227 60
Li(^2P)	−7.380 087	−0.0169	0.927 66	• • •	• • •
Be$^+$(^2S)	−14.291 620	0.9937	0.949 15	0.200 42	0.299 92
B^{++}(^2S)	−23.389 919	2.5166	0.960 65	0.237 14	0.333 65

TABLE V. Comparison of calculated and experimental results for Li.

	Energy (hartree)	Spin density at nucleus[a]	Orbital overlaps $\langle\chi_{1s}\vert\chi_{1s'}\rangle$	$\langle\chi_{1s}\vert\chi_{2s}\rangle$	$\langle\chi_{1s'}\vert\chi_{2s}\rangle$
			Li(^2S)		
RHF[b]	−7.432 726	0.1666 (28%)	1.000 00	0.0	0.0
SEHF[21]	−7.432 813	0.2412 (4%)	0.999 90	0.0	0.0
MPHF[24]	−7.447 560	0.2100 (9%)	0.928 22	0.140 05	0.233 09
SO-SCF[c]	−7.447 565	0.2265 (2%)	0.928 32	0.136 15	0.227 60
Expt.	−7.478 0[d]	0.2313[e]	• • •	• • •	• • •
			Li(^2P)		
RHF[28]	−7.365 068	0.0 (100%)	1.000 00	• • •	• • •
SEHF[c]	−7.365 091	−0.0218 (20%)	0.999 96	• • •	• • •
MPHF[c]	−7.380 082	0.0 (100%)	0.927 66	• • •	• • •
SO-SCF[c]	−7.380 087	−0.0169 (7%)	0.927 65	• • •	• • •
Expt.	−7.410 16[28]	−0.0181[f]	• • •	• • •	• • •

[a] Error in percent of experimental value is given in parentheses.

[b] E. Clementi, IBM J. Res. Develop. Suppl. 9, 2 (1965).

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TABLE VI. Comparison of calculated and experimental results for Be(^1S).

	Energy (hartree)	Orbital overlaps					
		$\langle\chi_{1s}\vert\chi_{1s'}\rangle$	$\langle\chi_{2s}\vert\chi_{2s'}\rangle$	$\langle\chi_{1s}\vert\chi_{2s}\rangle$	$\langle\chi_{1s}\vert\chi_{2s'}\rangle$	$\langle\chi_{1s'}\vert\chi_{2s}\rangle$	$\langle\chi_{1s'}\vert\chi_{2s'}\rangle$
RHF[a]	−14.573 02	1.000 00	1.000 00	0.0	0.0	0.0	0.0
SEHF[20]	−14.587 21	0.953 13	0.995 47	0.0	−0.011 55	0.036 85	0.0
MPHF[b]	−14.589 485	0.951 06	0.873 92	0.180 70	0.362 93	0.115 34	0.246 37
SO-SCF[b]	−14.589 498	0.953 54	0.879 65	0.175 94	0.313 82	0.140 49	0.226 30
Expt.[c]	−14.667 4	⋯	⋯	⋯	⋯	⋯	⋯

[a] E. Clementi, IBM J. Res. Develop. Suppl. 9, 2 (1965).
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Table IV, and the Li calculations are compared in Table V with the RHF, SEHF, and MPHF results and with experimental data. It is obvious that the SO-SCF functions are almost identical with the corresponding MPHF functions, and that the contribution of the "open-shell" spin function is very small. These observations confirm those of earlier studies.[15,16] The energy improvement of the SO-SCF function over the MPHF function is insignificant, but the spin density at the nucleus is greatly improved. Whereas the MPHF spin density for Li (^2S) is 9% in error, the inclusion of both possible spin functions reduces the error to 2%. The effect is even more dramatic in the case of Li (^2P). The MPHF function yields an identically zero spin density at the nucleus for this state, as there are no unpaired *s* electrons. The very small contribution of the second spin function to the SO-SCF function brings the spin density to within 7% of the experimental value. These facts suggest that both spin functions are needed to obtain a good general description of the spin properties of lithium.

The results for Be (^1S) are qualitatively consistent with the observations already made for lithium. As shown in Table VI, the SO-SCF and MPHF energies are very nearly equal, and the second spin function appears with a very small coefficient in the SO-SCF function. In Be, as in Li, the increased flexibility provided by the second spin function results in a small, but significant decrease in the splitting of the spatial orbitals within each shell. We anticipate that these observations will probably apply also to heavier atoms, where UHF[29] and SEHF[21] calculations do not in general give good agreement with experiment.

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[†] Present address: Department of Chemistry, Tel Aviv University, Tel Aviv, Israel.

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Annihilation of Positrons in Argon I. Experimental

P. H. R. Orth* and G. Jones

Department of Physics, University of British Columbia, Vancouver 8, British Columbia, Canada

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The annihilation of positrons in argon has been investigated as a function both of argon density and applied electric field. The direct annihilation rate decreases with increasing field as observed in earlier work. These electric field results are compared with simple theoretical models of the positron-argon atom interaction in the following paper. A small nonlinear dependence on density of the direct annihilation rate became apparent at densities larger than about 10 amagats. The linear portion of the direct rate was characterized by $Z_{\text{eff}} = 27.3 \pm 1.3$. From the density dependence of the orthopositronium lifetime, the free orthopositronium annihilation rate (λ_1) and linear quenching rate in argon (λ_q) were found to be

$$\lambda_1 = (7.53 \pm 0.18) \times 10^6 \text{ sec}^{-1},$$

$$\lambda_q = (0.24 \pm 0.02) \times 10^6 \text{ sec}^{-1} \text{ amagat}^{-1}.$$

The role that impurities play in these measurements is also discussed.

I. INTRODUCTION

Recent investigations of the lifetime of positrons in argon have shown that the free positron annihilation rate cannot be described by a single exponential.[1-4] Time spectra of the annihilation γ rays show clear evidence of a shoulder followed by an exponential decay presumed to characterize annihilation of positrons at thermal velocities. It has been shown that the shoulder is removed, and the lifetime of the exponential increased, when a moderate static electric field is applied.[5] Typically, a field of about 80 V cm^{-1}amagat^{-1} is sufficient to increase the direct lifetime by a factor of 2. These results provide the only available experimental test of the validity of models that describe the positron-argon interaction at low relative velocities. A further series of these measurements has been made with improved instrumentation offering greater experimental precision; the measurements were performed to a greater degree of statistical accuracy. The results of these measurements are used to test the validity of several empirical potentials describing the effective positron-argon interaction in paper II which follows.

While engaged in this program, several other features of the decay of positrons in argon were measured in order to facilitate comparison with the results of other workers. These measure-