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Ab Initio Calculation of Screening Effects on $|\psi(0)|^2$ for Heavy Atoms*

M. Wilson†
Physics Department, The Johns Hopkins University, Baltimore, Maryland

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Hartree-Fock calculations are used to investigate screening effects on the values of $|\psi(0)|^2$ for heavy atoms. It is shown that such calculations represent reasonably well the actual screening behavior derived from observed isotope (and isomer) shifts. In addition to the already known importance of $5p$ and $5d$ electron screening effects, it is found, in the case of the actinides, that $5f$ screening effects are also important.

INTRODUCTION

The current theory of isotope shifts[1] in the spectra of the heavy elements attributes the observed shifts predominantly to the so called volume effect which for two isotopes of the same element is due to the difference in the values of $|\psi(0)|^2$, the total electron-charge density in the neighborhood of the nucleus.

Similarly the interpretation of recent studies of isomer shifts,[2] measured by means of the Mössbauer effect, in compounds of various isotopes requires an understanding of the effect on $|\psi(0)|^2$ caused by the different environments in which the nucleus is placed. Here, however, in addition to the various possible configurations of outer atomic electrons, ligand field effects and polarization caused by the environment may play an important role.

The evaluation of $|\psi(0)|^2$ is usually accomplished by using observed magnetic hyperfine splitting factors[3] or by use of the Fermi-Segrê formula.[4] The problem then becomes one of obtaining the appropriate experimental data, to which is added, in the case of the Fermi-Segrê formula, the more difficult task of choosing a suitable value to represent an effective nuclear charge.

An alternative and more enlightening procedure is to calculate the values of $|\psi(0)|^2$ directly from radial wave functions obtained by means of some suitable atomic model such as that of Hartree-Fock (HF).[5] The usefulness of this *ab initio* approach will be demonstrated below. It is known that in certain cases this simple procedure yields results that depart markedly from observed values.[6] Such deviations, when found, point the way for more detailed investigations.[7] However, it will be seen below that many useful results can be obtained by means of this simple model which often yields results in satisfactory accord with observation. In addition, some unexpected screening effects have been found.

Recent work on the assessment of relativistic effects[8] on the values of $|\psi(0)|^2$ indicate that the essential features of the behavior of $|\psi(0)|^2$ caused by electron rearrangement effects may be determined from the use of nonrelativistic radial wave functions.

More difficult to assess is the importance of various suggested improvements to the simple restricted HF model such as those of the spin-polarized HF,[9] the projected spin-polarized HF,[10] the use of strongly correlated wave functions,[11] and inclusion of explicit configuration mixing effects.[12] Since a widespread and detailed study of these suggested improvements is not presently available, it is of some interest to assess the usefulness of those values of $|\psi(0)|^2$ obtained by means of the unrestricted HF model.

We also select for consideration several questions that may be answered by means of a simple model study such as considered here. Firstly, do numerical inaccuracies in the radial wave functions mask the small differential effects being sought? Secondly, can the observed shielding effects on the total $|\psi(0)|^2$ caused by electron rearrangement (primarily amongst the valence shells) be reproduced by the model? Thirdly, can any systematics of electron shielding effects be deduced from the model behavior?

We present the results of some calculations and discuss the answers to these questions in the following sections.

RESULTS AND DISCUSSION

Atomic radial wave functions were obtained using a program developed by Froese[13] which solves the HF self-consistent-field equations with exchange with the restriction that orthogonality is maintained between functions of the same orbital angular momentum, but different principal quantum number. The details of the procedure for obtaining the HF solutions have been described elsewhere.[13]

As examples we consider a somewhat arbitrary selection of data, although the choice was influenced by a desire to consider those heavy atoms for which a greater wealth of experimental data were available. We consider below the results of calculations for several sets of atomic configurations involving in turn $5p$, $5d$, and $5f$ electrons.[14]

A. Configurations Involving 5*p* Electrons

Recent interest in the interpretation of studies of the Mössbauer effect in compounds of some of the short period elements[15] has prompted examination of screening effects on the s-electron density at the nucleus ($|\psi(0)|^2$) by p electrons. Let us take for our model study the case of iodine. Mössbauer-effect studies of isomer shifts of iodine isotopes has led to discussions concerning the effect on $|\psi(0)|^2$ caused by various possible configurations of outer atomic electrons.[16] Some of the simplifying assumptions used in these discussions would bear closer examination. It has been assumed, for example, that the $|\psi(0)|_{5s}{}^2$ is linearly dependent on the number of $5p$ holes. An empirical estimate of this $5p$-electron screening effect has recently been obtained by Perlow and Perlow[16] who concluded that for configurations close to $5s^25p^6$ that a $5s$-electron loss is about four times as effective in causing a shift as a $5p$-electron loss, and that it is of opposite sign. The variation in $|\psi(0)|^2$ due to relaxation of the core has usually been assumed negligible, and the occupation of a $5d$ orbital has been assumed to have little or no effect on $|\psi(0)|^2$ compared to those changes caused by rearrangement of electrons in the $5s$ and $5p$ shell.

We have evaluated HF values of $|\psi(0)|^2$ for all the s^np^m configurations belonging to the free ions of iodine (I^- to I^{7+}) and the results are given in Table I which contains values of $4\pi|\psi(0)|^2$ for the different ns orbitals. Also included in the Table are values of the total $4\pi|\psi(0)|^2$ due to all of the s electrons. This is obtained simply by summing the contributions from all of the s orbitals each being weighted by its occupation number.

Examination of the values in Table I shows that the effects of core relaxation contribute to an effective increase in $|\psi(0)|^2$ over that for a fixed core. For configurations containing a single $5s$ electron (i.e., $sp^0 - sp^6$) this increase, measured by the ratio

$$[\Delta|\psi(0)|_{\rm tot}{}^2 - \Delta|\psi(0)|_{5s}{}^2]/\Delta|\psi(0)|_{5s}{}^2,$$

is ~ 38% and for those containing two $5s$ electrons (i.e., $s^2p^0 - s^2p^6$) the corresponding increase is ~ 20%. A plot of the data of Table I in Fig. 1 shows that the effect on $|\psi(0)|^2$ of adding (or subtracting) $5p$ electrons is not linear in the number of $5p$ electrons. Indeed this is not surprising since linearity would imply that the mutual interaction between the $5p$ electrons be vanishingly small.

It can also be seen that care should be taken to specify which $5s$ electron is being lost when referring to the relative effectiveness of $5s$- and $5p$ electron loss in causing a shift. For example, for $5s^25p^m$ to $5s5p^m$ the $5s$-electron loss is from about 5 to 8 times more effective than a $5p$ electron loss, whereas for $5s5p^m$ to $5s^05p^m$ it is about 10 to 13 times more effective than a $5p$-electron loss. In both cases it is of opposite sign. Close to $5s^25p^6$ the calculated value is in reasonable accord with the empirical estimate of this effect.[16]

We include in Table II values of $4\pi|\psi(0)|^2$ for $5s5p^35d$ of I III compared with those for $5s5p^3$ of I IV. The $5s5p^35d$ values are seen to lie approximately midway between the corresponding points for $5s5p^3$ and $5s5p^4$ in Fig. 1. Thus the addition of a $5d$ electron has an effect on $|\psi(0)|^2$ in the case of

TABLE I. Values of $4\pi|\psi_s(0)|^2$ for iodine ions (in units of $a_0{}^{-3}$). Values in parentheses are: $4\pi|\psi(0)|_{\rm tot}{}^2 = 4\pi \sum\limits_{\text{all electrons}} (|\psi_{ns}(0)|^2 \times$ number of electrons in $n^{\rm th}$ shell.

	I^-	I	I^+	I^{2+}	I^{3+}	I^{4+}	I^{5+}	I^{6+}	I^{7+}
	$5s^25p^6$	$5s^25p^5$	$5s^25p^4$	$5s^25p^3$	$5s^25p^2$	$5s^25p$	$5s^2$		
1s	583 569.374	583 570.760	583 570.865	583 571.652	583 572.300	583 574.179	583 575.661		
2s	61 537.974	61 538.515	61 538.992	61 539.838	61 540.978	61 542.135	61 543.884		
3s	12 211.202	12 211.521	12 212.010	12 212.728	12 213.649	12 214.910	12 216.445		
4s	2 482.586	2 483.041	2 483.954	2 485.290	2 487.107	2 489.496	2 492.521		
5s	271.447	287.262	307.003	329.314	353.502	379.153	405.995		
Total	(1320 145.166)	(1320 182.198)	(1320 225.648)	(1320 277.644)	(1320 335.072)	(1320 399.746)	(1320 469.012)		
		$5s5p^6$	$5s5p^5$	$5s5p^4$	$5s5p^3$	$5s5p^2$	$5s5p$	$5s$	
1s		583 569.227	583 570.677	583 570.750	583 571.307	583 573.083	583 574.952	583 577.088	
2s		61 536.198	61 536.653	61 537.200	61 537.974	61 539.177	61 540.674	61 542.315	
3s		12 208.698	12 209.020	12 209.613	12 210.119	12 211.112	12 212.349	12 213.764	
4s		2 476.887	2 447.284	2 478.067	2 479.244	2 481.023	2 483.384	2 486.427	
5s		297.706	316.877	338.821	362.838	388.438	415.335	443.325	
Total		(1319 879.726)	(1319 904.145)	(1319 930.081)	(1319 960.126)	(1319 997.228)	(1320 038.053)	(1320 082.513)	
			$5p^6$	$5p^5$	$5p^4$	$5p^3$	$5p^2$	$5p$	$4d^{10}$
1s			583 569.073	583 570.083	583 570.338	583 571.556	583 573.287	583 575.274	583 577.884
2s			61 534.190	61 534.688	61 535.351	61 536.210	61 537.345	61 538.843	61 540.676
3s			12 206.121	12 206.468	12 206.891	12 207.618	12 208.542	12 209.729	12 211.290
4s			2 473.717	2 474.325	2 475.380	2 476.976	2 479.168	2 482.040	2 485.617
Total			(1319 566.202)	(1319 571.128)	(1319 575.920)	(1319 584.720)	(1319 596.684)	(1319 611.772)	(1319 630.934)

TABLE II. The effect of a $5d$ electron on the values of $4\pi\ |\psi(0)|^2$ (in units of a_0^{-3}). Values in parentheses as in Table I.

	$I^{2+}5s5p^35d$	$I^{3+}5s5p^3$
$1s$	583 572.440	583 571.307
$2s$	61 537.883	61 537.974
$3s$	12 209.445	12 210.119
$4s$	2478.025	2479.244
$5s$	351.857	362.838
Total	(1319 947.445)	(1319 960.126)

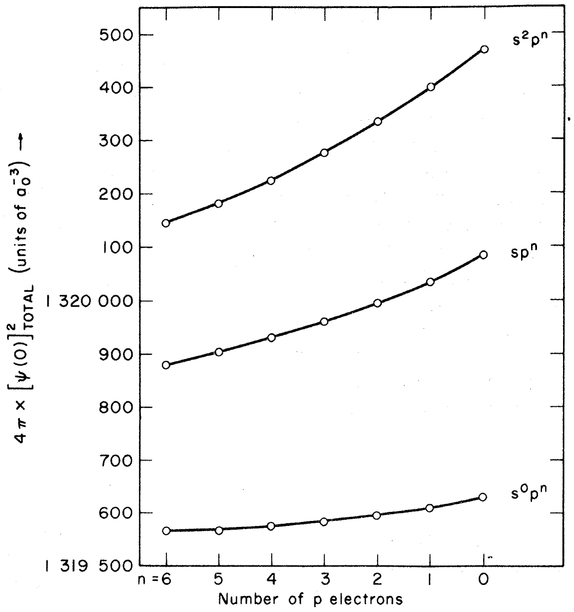

FIG. 1. Variation of $|\psi(0)|_{\text{tot}}^2$ versus (number of p-electrons) for I^- to I^{7+}

a singly occupied $5s$ orbital of about half that of the addition of a $5p$ electron.

B. Configurations Involving 5*d* Electrons

Next let us consider the question of how well the calculated values of $|\psi(0)|^2$ reproduce the behavior of the observed isotope shifts. We select isotope rather than isomer shifts for our comparison since the interpretation of the former, in the sense of assigning specific causes to the observed shifts, is much more secure than that of the latter. It will be assumed that the observed isotope shifts are due entirely to the different values of $|\psi(0)|^2$ in the different configurations of valence electrons.

We present in Table III the calculated values of $4\pi|\psi(0)|^2$ for the configurations

$5d^{10}6s^2$, $5d^{10}6s6p$, $5d^96s^26p$ of Hg I

and $5d^{10}6s$, $5d^96s^2$, $5d^96s6p$ of Hg II.

In Fig. 2 are plotted the observed isotope shifts for these configurations versus the corresponding values of $4\pi|\psi(0)|_{\text{tot}}^2$. Similar plots for Tl III and Pt I are given in Figs. 3 and 4.

Error brackets are often difficult to assess for several reasons. The first is that the observed values are usually the result of careful appraisal of many data, which, if relating shifts in different stages of ionization, must be referred to some convenient datum in order to obtain isotope-shift values on some continuous scale. A theoretically convenient datum is usually provided by a suitable series limit, which of necessity forms an estimate based on extrapolation of measurements with the possibility of attendant (and sometimes unsuspected) errors. Therefore, although the accuracy or relative shifts within a single ionization stage may be high, the shifts relating different ionization stages may be somewhat less accurate.

Another source of difficulty in assessing errors is that the observed isotope shifts of levels of a complex configuration are usually scattered over some range of values. This scatter is not necessarily entirely due to experimental uncertainties, since configuration-mixing effects between levels

TABLE III. Values of $4\pi\ |\psi_s(0)|^2$ for Hg I and II (in units of a_0^{-3}). Values in parentheses as in Table I.

Hg I	$5d^{10}6s^2$	$5d^{10}6s6p$	$5d^96s^26p$
$1s$	2 019 611.	2 019 613.	2 019 611.
$2s$	224 202.3	224 202.4	224 204.2
$3s$	50 526.52	50 525.97	50 529.30
$4s$	12 550.63	12 549.39	12 552.62
$5s$	2 298.50	2 293.61	2 325.80
$6s$	150.11	166.83	194.51
Total	(4 618 678.9)	(4 618 536.0)	(4 618 835.5)
Hg II	$5d^{10}6s$	$5d^96s^2$	$5d^96s6p$
$1s$	2 019 615.	2 019 614.	2 019 612.
$2s$	224 202.8	224 204.2	224 203.2
$3s$	50 526.30	50 529.39	50 528.17
$4s$	12 549.42	12 553.09	12 551.16
$5s$	2 293.20	2 326.30	2 319.97
$6s$	192.40	221.10	232.68
Total	(4 618 565.9)	(4 618 896.4)	(4 618 661.9)

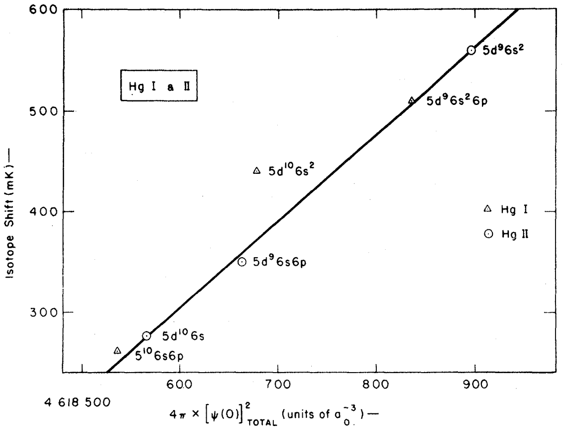

FIG. 2. Isotope shifts versus $|\psi(0)|_{tot}^2$ for Hg I and II. Experimental data from Kopfermann (Ref. 18).

of configurations with different isotope shifts result in mixing of isotope shift values. However, some single value representing the isotope shift of a complex configuration can usually be judiciously chosen. Such representative values have been used in constructing Figs. 2, 3 and 4.

The proportionality between observed isotope shifts and calculated values of $|\psi(0)|^2$ in Figs. 2, 3, and 4 is seen to be quite good thus demonstrating the usefulness of such calculations.

It is perhaps worth noting that the isotope shift of the 6s $^2S_{1/2}$ level of Tl III has not yet been observed directly. Crawford and Schawlow[17] estimated its value to be about 0.38 cm^{-1}, basing their estimate on observed shifts of levels of the configurations $5d^96s^2$ and $5d^96s6p$. This estimate therefore ignored the possibility of non-negligible screening effects on the value of $|\psi(0)|_{6s}^2$ due to the different number of 5d electrons.[18] The HF value of $4\pi|\psi(0)|_{tot}^2$ for the configuration $5d^{10}6s$ is 4796 253 a_0^{-3}. Thus, if we take the line of Fig. 3 as a calibration, we obtain a value of about 0.285 cm^{-1} for the isotope shift of the $6s^2S_{1/2}$ level of Tl III.

Figure 2 suggests the possibility that once a set of calculated values of $|\psi(0)|^2$ has been calibrated for a particular ionization stage (in principle two points should suffice), values of isotope shifts could be estimated for configurations belonging to other ionization stages.

C. Configurations Involving 5*f* Electrons

Crawford and Schawlow,[17] in their discussion of screening effect estimates, stressed the need for accurate radial wave functions in order that numerical inaccuracies in the wave functions of the inner electrons not obscure the changes (being sought) caused by the different configurations of outer electrons. A severe test on numerical accuracy is afforded by HF solutions obtained for the actinides. These contain 17 to 19 orbitals according to the type of valence configuration studied.

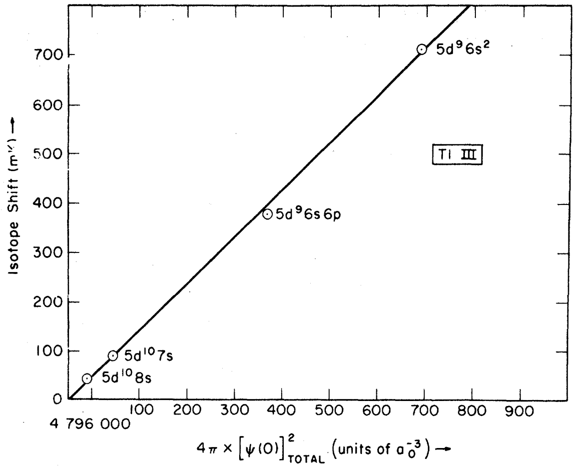

FIG. 3. Isotope shifts versus $|\psi(0)|_{tot}^2$ for Tl III. Experimental data from Kopfermann (Ref. 18) and Crawford *et al.* (Ref. 17).

Table IV contains the HF values of $4\pi|\psi(0)|^2$ for a variety of configurations in Pu I and II. Comparison of these values for the innermost 1s and 2s electrons shows that the variation amounts to only a few percent of the corresponding values obtained for the outermost 7s electron. Thus, these solutions are sufficiently accurate to yield direct estimates of screening and isotope (and isomer) shift behaviors.

Several simplifying assumptions are also usually made in the interpretation of measured isotope shifts. One is often to assume (as in the case of some isomer shift interpretations) that the valence shells alone contribute to the greater part of the cause of the resulting shifts. However, examination of the values given in Table IV reveals the existence of a hitherto unsuspected screening effect on the values of $|\psi(0)|^2$ for the 5s and 6s orbitals according to the different number of electrons in the 5f shell. Thus, although the 5s and 6s orbitals are not considered as being part of the valence shells, inasmuch as their occupation numbers remain unchanged, they do nevertheless contribute significantly to the resulting differences in the values of $|\psi(0)|_{tot}^2$ between the different configurations.

Calculations for rare-earth configurations involving 4f electrons[19] reveal a similar effect on the 4s-

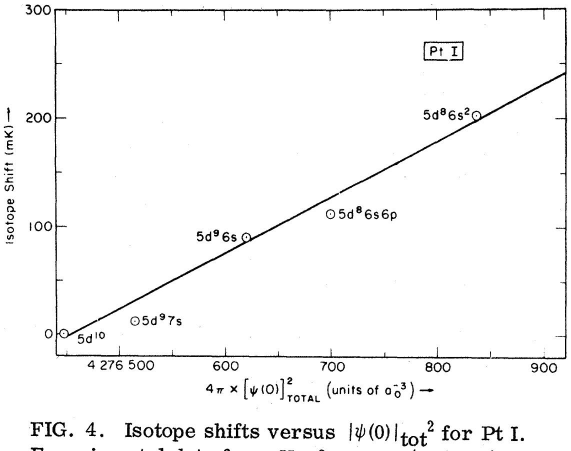

FIG. 4. Isotope shifts versus $|\psi(0)|_{tot}^2$ for Pt I. Experimental data from Kopfermann (Ref. 18).

TABLE IV. Values of $4\pi|\psi_s(0)|^2$ for Pu I and II (in units of a_0^{-3}). Values in parentheses as in Table I.

Pu I	$5f^6 7s^2$	$5f^6 7s7p$	$5f^6 7s6d$	$5f^5 7s^2 7p$	$5f^5 7s^2 6d$	$5f^5 7s7p6d$	$5f^5 7s6d^2$
1s	3 282 529.	3 282 532.	3 282 531.	3 282 527.	3 282 526.	3 282 526.	3 282 526.
2s	370 049.5	370 049.7	370 049.6	370 043.6	370 044.0	370 043.2	370 042.6
3s	86 261.63	86 261.69	86 261.19	86 262.87	86 261.97	86 261.88	86 260.77
4s	23 409.11	23 408.86	23 408.42	23 413.45	23 412.71	23 412.19	23 411.73
5s	5 772.67	5 771.94	5 771.86	5 796.21	5 795.20	5 794.50	5 794.01
6s	973.12	970.59	958.39	1 039.74	1 021.42	1 018.32	1 004.91
7s	65.69	73.25	51.58	98.09	76.25	84.18	60.58
Total	(7 538 121.6)	(7 538 063.8)	(7 538 012.2)	(7 538 362.7)	(7 538 274.2)	(7 538 196.6)	(7 538 141.5)
Pu II	$5f^6 7s$	$5f^6 7p$	$5f^6 6d$	$5f^5 7s7p$	$5f^5 7s6d$	$5f^5 7p6d$	$5f^5 6d^2$
1s	3 282 532.	3 282 527.	3 282 531.	3 282 528.	3 282 529.	3 282 527.	3 282 529.
2s	370 049.3	370 049.0	370 048.7	370 044.2	370 042.6	370 043.5	370 043.1
3s	86 261.13	86 260.93	86 260.39	86 262.56	86 261.43	86 261.28	86 260.50
4s	23 408.57	23 408.14	23 407.78	23 413.12	23 412.51	23 411.79	23 411.44
5s	5 772.04	5 771.04	5 771.21	5 795.46	5 794.61	5 793.49	5 793.18
6s	971.44	969.29	955.63	1 037.19	1 018.70	1 016.18	1 001.50
7s	90.29	• • •	• • •	122.47	102.06	• • •	• • •
Total	(7 538 079.0)	(7 537 971.2)	(7 537 949.2)	(7 538 283.9)	(7 538 220.3)	(7 538 106.5)	(7 538 078.5)

and 5s-electron wave functions. This effect can readily be understood in terms of screening effects in which the addition of a 5f electron causes an increase in the shielding of the 5s, 5p, 5d, 6s, and 6p closed-shell orbitals. This increased shielding produces an expansion of these orbitals with a corresponding decrease in the values of $|\psi(0)|^2$ for the 5s and 6s orbitals.

The fractional changes in magnitude of $|\psi(0)|^2$ for these closed-shell orbitals is not large, although because of their large absolute values of $|\psi(0)|^2$ they still make a significant contribution to the differences in $|\psi(0)|_{\text{tot}}{}^2$ from one configuration to another over and above that due to the differences in the values of $|\psi(0)|_{7s}{}^2$. This effect on closed shells below 5s is seen to be almost negligible.

Several other features may be noted from the values given in Table IV. The difference in $4\pi|\psi(0)|_{7s}{}^2$ upon changing a 7p to a 6d (so as to change $5f^6 7s7p$ to $5f^6 7s6d$ and $5f^5 7s^2 7p$ to $5f^5 7s^2 6d$ in Pu I, and $5f^5 7s7p$ to $5f^5 7s6d$ in Pu II) have a constant value ($-22a_0^{-3}$). To a lesser extent the $4\pi|\psi(0)|_{6s}{}^2$ changes reflect a similar behavior. In addition, the difference in $4\pi|\psi(0)|_{7s}{}^2$ upon changing 7s to 7p (so as to change $5f^6 7s^2$ to $5f^6 7s7p$ and $5f^5 7s^2 6d$ to $5f^5 7s7p6d$ in Pu I) is also a constant value ($+8a_0^{-3}$). Again, the $4\pi|\psi(0)|_{6s}{}^2$ values show a corresponding behavior, but in this case are of opposite sign.

Comparison of these HF values of $|\psi(0)|^2$ with preliminary values of observed isotope shifts[20] for configurations in Pu I show a fairly good proportionality, thus lending further support to the usefulness of such sets of model calculations.

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[†] Present address: J. J. Thomson Physical Laboratory, University of Reading, Reading, Berks, England.

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Calculation of the ^1S State of the Beryllium Atom in Hylleraas Coordinates*

R. F. Gentner
Department of Physics, Adelphi University,† Garden City, New York, and Department of Chemistry, St. John's University, Jamaica, New York

and

E. A. Burke
Department of Physics, Adelphi University,† Garden City, New York, and Department of Physics, Brookhaven National Laboratory,‡ Upton, New York

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The ^1S state of the Be atom is calculated in Hylleraas coordinates using a 25-term single-determinant wave function having the proper spin-angular-momentum symmetry. A ground-state energy of −29.3158 Ry is obtained, as compared with the experimentally observed value of −29.337 Ry and the best Hartree-Fock value of −29.145 96 Ry, indicating that the application of the procedure to larger systems should be fruitful. Suggestions are given to improve the accuracy of the present method and to extend it to atoms of higher atomic number. Solutions of the integrals and procedures for manipulating them in storage are presented.

INTRODUCTION

It is well known that the main defect in using the Hartree-Fock formalism for an approximate solution of the many-electron Schrödinger equation is its failure to represent adequately the correlations between the motions of the individual electrons. Several methods have been employed in order to circumvent this failure. The simplest one, computationally, is the method of configuration interaction in which the wave function is approximated by a linear combination of hydrogen-like orbitals, the coefficients being chosen to minimize the energy. Although this method is readily applied to a great many multielectron problems (both atomic and molecular), difficulties with convergence have lead some investigators[1,2] to suggest as an alternative, a trial wave function which explicitly contains the interparticle coordinates r_{ij}. Recently generalized methods for including interparticle coordinates in the wave functions for atoms and molecules have been developed by Sinanoğlu[3] and Szasz.[4]

Hylleraas[5] applied this method to the helium atom. Using a six-term wave function depending on the variables $S = r_1 + r_2$, $t = r_2 - r_1$, and $u = r_{12}$ he calculated an energy within 0.02% of the experimental value. By carrying many more terms, more recent workers[6,7] have constructed wave functions that give energies within the current limits of experiment. However, when the method is extended to larger systems, extreme computational difficulties are encountered. James and Coolidge[8] calculated the ground-state energy of lithium using a wave function consisting of Slater-type orbitals multiplied by $r_{ij}^{\,n}$ (where $n = 0, 1, 2$) with the limitation that at most only one interelectronic separation coordinate is present in a given term. They did not, however, achieve the accuracy Hylleraas obtained for helium. As was later pointed out by James and Coolidge,[9] their wave function was not of pure doublet symmetry. Burke[10] has given an estimate of the error involved in this lack of proper symmetry. His calculation for lithium as well as the work of Berggren and Wood[11] and Smith and Larsson[12] have improved on the original results of James and Coolidge. All these workers used the correlated