and two antisymmetric functions with respect to the figure axis of the molecule. Two pure p orbitals of the As would then be combined with the antisymmetric H functions to form two π molecular orbitals, whereas the third bonding orbital, a σ molecular orbital, would be formed by combination of the symmetric H orbital with a hybridized atomic orbital of the As. This description will be elaborated elsewhere.

The magnetic coupling constant of $As^{75}H_3$, 0.33 Mc/sec, is the same as that of $Sb^{121}H_3$ while the nuclear g factor of As^{75}, 0.96, is less than that of Sb^{121}, 1.34. This result shows that the molecular magnetic field of AsH_3 at the As nucleus is larger than that of the Sb nucleus in SbH_3 by a factor of 1.40. If the molecular field is generated purely by rotation of the molecule, one might expect this factor to be approximately equal to the ratio of the two B_0 values, or about 1.3. The magnetic coupling constants of deuterated arsine and stibine are too small to be measured with accuracy. They are several times lower than those of the normal species and appear to be reduced by approximately the square of the B_0 ratios from the hydride values.

We wish to thank C. A. Burrus for assistance with the millimeter wave components.

PHYSICAL REVIEW VOLUME 97, NUMBER 3 FEBRUARY 1, 1955

Polarization Energy for $3d$ and $4p$ Electrons

R. E. TREES
National Bureau of Standards, Washington, D. C.
(Received September 23, 1954)

Meshkov has demonstrated the presence of an appreciable polarization energy associated with the combination of a $3d$ and a $4p$ electron in the $3d^2\,4p$ configuration of Ti II. He has shown that the mean deviation between theory and experiment is reduced from ± 332 K to ± 249 K when this energy is considered. It is here noted that by use of a modified form of Meshkov's approximation a further reduction to ± 180 K is produced. This modification requires only three adjustable parameters, as compared with the five required in Meshkov's original method. It is suggested that the agreement could be made even better if a breakdown of LS-coupling due to the closeness of three terms in this spectrum were considered.

I. INTRODUCTION AND RESULTS

In a recent paper, Meshkov has demonstrated the existence of an appreciable polarization energy associated with the combination of a $3d$ and a $4p$ electron in the $3d^2\,4p$ configuration of Ti II.[1] His method evaluates the d-p and d-d polarization energy of Ti II by utilizing the experimental data for Ti III in Bacher and Goudsmit's first approximation formula.[2,3] The parameters of Slater's formulas (more accurately, the differences in value of these parameters in Ti II and Ti III) were evaluated by least squares to get best agreement with the experimental data. His results are reproduced in columns A of Table I; the final mean deviation, obtained with five arbitrarily adjustable parameters, is ± 249 K.

Racah also has calculated term values for this configuration, by using a method that accounts for the d-d polarization energy only.[4,5] He assumes that the total d^2 energy is proportional to the energy of the d^2 parent term in Ti III. The parameters of Slater's formulas that refer to dp energy, together with the proportionality factor for the d^2 energy, were evaluated by least squares. His results are reproduced in columns B of Table I; the final mean deviation, obtained with four adjustable parameters, is ± 332 K. Since this calculation omits d-p polarization energy entirely, the smaller mean deviation obtained in Meshkov's calculation would be due primarily to its inclusion, though his use of an additional adjustable parameter also would help a little.[6]

Meshkov's method accounts for polarization by utilizing experimental data with Bacher and Goudsmit's first approximation, but only a part of the Slater energy is accounted for at the same time. Its main advantage, compared to using Slater's formulas together with the $L(L+1)$ correction,[3,7] is that it requires fewer adjustable parameters, so that the chance of getting accidental

[1] S. Meshkov, Phys. Rev. **91**, 871 (1953).
[2] R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).
[3] R. E. Trees, J. Research Nat. Bur. Standards **53**, 35 (1954), Research Paper 2515. Section 2.2 of this paper discusses the use of a linear approximation [such as Bacher and Goudsmit's first approximation, or the $L(L+1)$ correction] for the polarization energy, and lists other references on this subject. Referred to as A.
[4] G. Racah, Phys. Rev. **62**, 438 (1942).
[5] T. Yamanouchi [Proc. Phys.-Math. Soc. Japan **22**, 841 (1940)] has analyzed this configuration by using still another method which would account for the d-d polarization energy. He regards the energies of the parent term in d^2 as adjustable parameters, so that the number of parameters needed is six. His results are not given in numerical form.
[6] Racah's calculation A in Table I of reference 4 shows that the mean deviation is ± 430 K if neither d-d nor d-p polarization energy is included. Five parameters are used in this calculation.
[7] In a term $d^n(\beta SL)pS'L'$ the correction would be generalized to the form $(\alpha_d-\alpha_p)L(L+1)+\alpha_p L'(L'+1)$ to include both d-d and d-p polarization effects, so that two additional parameters would be needed. Rigorously, corrections proportional to $S(S+1)$ and $S'(S'+1)$ should be included also, but these seem to have a small effect. However, it should be noted that formula (2) does include these latter corrections.

agreement is decreased. Indirectly, the method checks the theory in the spectra in which the polarization is evaluated (i.e., in Ti III as well as Ti II) and the number of experimental values that determine the parameters is effectively increased. The disadvantages are that approximations are involved in the procedure and the errors are likely to be greater than those obtained by using Slater's formulas and the $L(L+1)$ correction; also the results are obtained in a form that is not as easy to interpret.

In this paper Meshkov's method is modified to a form which requires only three adjustable parameters instead of five. This modification evaluates both the polarization energy and the Slater energy with experimental data taken from Ti III and Sc II. The final mean deviation obtained with this method is ± 180 K as given in calculation C of Table I. Meshkov's calculation is based on the assumption that the d-p polarization energy in the d^2p configuration of Ti II is equal to that in the dp configuration of Ti III. The improved agreement obtained in the present paper may be attributed to the fact that this energy is more nearly equal to the larger effect present in the dp configuration of Sc II, which is approximately the assumption made.

II. EXPLANATION OF PROCEDURE

The energy of a term in the d^4p configuration of Ti I can be calculated from observed energies in Ti II and Ti III without introducing any arbitrary parameters by use of Bacher and Goudsmit's second approximation. For this approximation to lead to correct results, one requirement is that the parameters in any one spectrum (i.e., Ti I, Ti II, or Ti III) have the same ratios with respect to each other as the parameters in either of the other two spectra.[8] If this were the case, then it would be much easier to calculate the energies by using the simpler formulas for Bacher and Goudsmit's first approximation and introduce a single arbitrary parameter as a scale factor. In the notation of A this procedure is defined by the following formula:

$$W_{\text{Ti II}}(d^2p) = e[\overline{W}_{\text{Ti III}}(d^2p; d^2) + 2\overline{W}_{\text{Ti III}}(d^2p; dp)]. \quad (1)$$

In this formula, $\overline{W}_{\text{Ti III}}(d^2p; dp)$ is the average energy of the combination of a $3d$ and a $4p$ electron in some term (assumed specified) of the $3d^24p$ configuration approximated from experimental data in the $3d4p$ configuration of Ti III.[9] The factor 2 occurs because the p electron can be combined with either of the two d electrons. A similar interpretation holds for $\overline{W}_{\text{Ti III}}(d^2p; d^2)$.

[8] Section 7 of A. Racah has noted that even if this condition is satisfied the second approximation would fail to account fully for the first-order energy and he has modified the Bacher and Goudsmit theory to overcome this defect; these points are covered in Secs. 4 and 5 of A. This defect of the theory would not invalidate formula (1) of the present paper. Formula (2) was suggested in part by Racah's modification.

[9] The necessary formulas are given explicitly in Table IV of reference 1. A general procedure for setting up these formulas is given in reference 1, and a different procedure is given in Sec. 3 of A.

TABLE I. Calculated and observed term values in $3d^2\,4p$ of Ti II.[a]

	Term	Obs	A Calc	A Diff	B Calc	B Diff	C Calc	C Diff.
z	$(^3F)^4G$	29 936	30 001	65	29 823	−113	30 113	177
z	$(^3F)^4F$	31 108	31 123	15	31 125	17	31 061	−47
z	$(^3F)^2F$	31 369	31 387	18	31 471	102	31 394	25
z	$(^3F)^2D$	31 918	32 003	85	32 251	333	31 794	−124
z	$(^3F)^4D$	32 690	32 711	21	32 890	+200	32 452	−238
z	$(^3F)^2G$	34 657	34 175	−482	34 109	−548	34 673	16
z	$(^3P)^2S$	37 431	37 413	−18	37 628	197	37 516	85
y	$(^1D)^2D$	39 380	39 928	548	40 000	620	39 848	468
z	$(^1D)^2P$	39 627	39 321	−306	39 496	−131	39 300	−327
y	$(^1D)^2F$	40 011	39 662	−349	39 507	−504	39 936	−75
z	$(^3P)^4S$	40 027	40 260	233	40 237	210	40 239	212
y	$(^3P)^4D$	40 612	40 506	−106	40 441	−171	40 615	3
z	$(^3P)^4P$	42 127	42 018	−109	42 100	−27	41 965	−162
y	$(^1G)^2G$	43 763	43 721	−42	43 675	−88	43 760	−3
x	$(^3P)^2D$	44 907	44 897	−10	44 737	−170	45 083	176
y	$(^3P)^2P$	45 524	45 814	+290	45 673	149	45 587	63
z	$(^1G)^2H$	45 802	45 459	−343	45 184	−618	45 676	−126
x	$(^1G)^2F$	47 535	47 801	266	48 078	543	47 411	−124
	$(^1S)^2P$		(66 060)		(64 465)		(64 053)	
		Mean deviation		±249		±332		±180

[a] The symbols A, B, and C refer to the following calculations: A: S. Meshkov, Phys. Rev. **91**, 871 (1953), Table VI. B: G. Racah, Phys. Rev. **62**, 438 (1942), Table I, Calculation B. C: Formula 2, this paper.

The adjustable parameter "e" is introduced as a scaling factor.

The approximation (1) gives poor results because the parameter ratios do not behave as required. This can be seen from inspection of the parameters for Ti II, Ti III and Sc II which are listed in Table II. The parameters B and C defined by the two $3d$-electrons do have approximately the same ratio in all three spectra ($B/C = 0.29 \pm 0.03$). However, the parameters defined by a $3d$ and a $4p$ electron (i.e., F_2, G_1, and G_3) have mutual ratios, and ratios with respect to B and C, that differ in all three spectra. In particular, the ratio G_1/F_2 has the values 1.4, 1.2, and 1.0 in Sc II, Ti II and Ti III, respectively. Roughly speaking, the d^2 parameters in Ti II are nearly equal to the ones in Ti III, but the dp parameters are more nearly equal to those in Sc II. This is understandable from shielding considerations.

The preceding discussion shows that there will be a point intermediate between Sc II and Ti III where B and C will have the same values as in Ti II; this point is defined by "e_1," which is our first adjustable parameter. There will be also a point where the ratio G_1/F_2 will be equal to the value of this ratio in Ti II. The ratio

TABLE II. Radial parameters in spectra with $3d$ and $4p$ electrons.[a]

Parameter	Sc II (1)	Sc II (2)	Ti III (1)	Ti III (2)	Ti II (3)	Ti II (4)	Ti II (5)	Ti II (6)
B	481	502	695	718	669	681	682	684
C	1789	1535	2911	2629	2563	2493	2481	2459
F_2	242	259	444	450	290	288	291	281
G_1	380	360	435	441	332	337	357	346
G_3	8	7	46	46	18	20	22	16
α_d		31		35		33	35	34
α_p		100		35			35	75
Deviation					±430	±332	±249	±180

[a] The column numbers refer to the following calculations: (1) W. M. Cady, Phys. Rev. **43**, 322 (1933). (2) R. E. Trees (unpublished). (3) G. Racah, Phys. Rev. **62**, 438 (1942), Calculation A of Table I. (4) G. Racah, Phys. Rev. **62**, 438 (1942), Calculation B of Table I combined with calculation (2) for Ti III given above. (5) S. Meshkov, Phys. Rev. **91**, 871 (1953). Calculation of Table V combined with calculation (2) for Ti III given above. (6) Results of this paper.

of the other two adjustable parameters "e_3" and "e_2" defined this point. The scaling factor needed to make the values of F_2 and G_1 themselves the same as in Ti II is the second parameter "e_2." The complete formula is expressed as follows:

$$W_{\mathrm{Ti\ II}}(d^2p) = \bar{W}_{\mathrm{Sc\ II}}(d^2p; d^2) + e_1[\bar{W}_{\mathrm{Ti\ III}}(d^2p; d^2) - \bar{W}_{\mathrm{Sc\ II}}(d^2p; d^2)] + 2e_2\bar{W}_{\mathrm{Sc\ II}}(d^2p; dp) + 2e_3[\bar{W}_{\mathrm{Ti\ III}}(d^2p; dp) - \bar{W}_{\mathrm{Sc\ II}}(d^2p; dp)]. \quad (2)$$

The average energies evaluated from experimental data in Sc II and Ti III are listed in Table III. The parameters were adjusted by least squares to give the best fit with the experimental data in Ti II, and were found to have the following values:

$$(A = 26423.8),\ e_1 = 0.84492,\ e_2 = 0.90551,\ e_3 = 0.24163.$$

The calculated values are given in column C of Table I; the mean deviation between theory and experiment is ± 180 K.

The values of e_1, e_2, and e_3 obtained above were used to interpolate between the values of the parameters in Sc II and Ti III (given in columns (2) of Table II) to obtain the parameters of the linear theory which would give the same results as formula (2); the results are given in column (6) of Table II. This correspondence is not exact, since the parameters used for Sc II and Ti III do not fit the experimental data in these spectra exactly. A check in the rational roots indicates that these parameters would lead to values that differ from those of calculation C by about 100 K, which is within the over-all accuracy of the original calculation. It will be noted that the parameter for the dp-polarization energy (i.e., α_p) is greater than the one for the d^2 energy (i.e., α_d), and that the value of this parameter depends strongly on the degree of ionization.

Two parameter formulas were considered also. A formula the same as (2) except that $e_2 = 1$, lead to a mean deviation of ± 293 K with the parameter values $e_1 = 0.8418$ and $e_3 = 0.2942$. This mean deviation could probably be reduced to about ± 280 K by fuller use of least squares in evaluating e_1 and e_3. A simpler two-parameter relation of the form

$$W_{\mathrm{Ti\ II}}(d^2p) = e_1 W_{\mathrm{Ti\ III}}(d^2p; d^2) + 2e_2 W_{\mathrm{Ti\ III}}(d^2p; dp) \quad (3)$$

was not tried, as it was clear from the start that this was not as good an approximation as the one used by Meshkov.

TABLE III. Average energies.

SL	$S'L'$	Sc II $\bar{W}(d^2(SL)pS'L'; d^2)$	Ti III $\bar{W}(d^2(SL)pS'L'; d^2)$
^3P		12 128	10 661
^3F		4909	242
^1G		14 261	14 398
^1S[a]		26 324	34 020
^1D		10 944	8473
		$2\bar{W}(d^2(SL)pS'L'; dp)$	
		−53 000	−151 000
^3P	^2S	154	422
^3P	^4S	3132	3506
^3P	^4P	4308	7419
^3F	^4F	3581	5355
^3F	^4G	2467	4494
^1G	^2H	4676	7328
^3P	^4D	2995	4842
^3F	^4D	5028	7734
$^3P, ^3F$	^4D	944	1854
^3F	^2G	7824	10 569
^1G	^2G	2562	3286
$^3F, ^1G$	^2G	−2153	−2365
^1S	^2P	4313	6721
^3P	^2P	8033	12 749
^1D	^2P	4041	6266
$^1S, ^3P$	^2P	−1912	−1697
$^1S, ^1D$	^2P	1757	3474
$^3P, ^1D$	^2P	17	553
^3P	^2D	6025	8570
^1D	^2D	4886	7882
^3F	^2D	4982	9177
$^3P, ^1D$	^2D	−2270	−2255
$^3P, ^3F$	^2D	3165	5137
$^1D, ^3F$	^2D	425	1063
^1D	^2F	4020	6086
^3F	^2F	4508	7028
^1G	^2F	5994	10 184
$^1D, ^3F$	^2F	−2422	−2559
$^1D, ^1G$	^2F	986	1950
$^3F, ^1G$	^2F	647	1240

[a] Calculated values.

III. ERRORS OF THE PROCEDURE

Because so few adjustable parameters were used in calculation C of Table I the inclusion or exclusion of any particular term has little effect on the resultant errors of other terms. The error in $y\,^2D$ is anomalously large since it exceeds twice the mean deviation. The mean deviation of the terms in calculation C, excluding the $y\,^2D$ in ± 146 K. If this term is omitted from the least squares calculation, the mean deviation of the other terms is reduced to ± 136 K,[10] which is only slightly less, so that including or excluding $y\,^2D$ does not make much difference in the over-all agreement. Comparison of the individual errors in calculation C with those of the least squares calculation with $y\,^2D$ omitted shows very little change; in particular, the $z\,^2P$ error is still the largest remaining error, though reduced slightly to -310 K in the latter calculation. When many adjustable parameters are used, there is more chance that terms with large errors will cause other terms in the calculation to have large errors and it is not easy to pick out the terms that are responsible for disagreements between theory and experiment.[11]

Unfortunately there are many sources of error in this

[10] We are indebted to Dr. P. Rabinowitz of the Computation Laboratory at NBS for making this calculation on SEAC. The parameter values of this least squares calculation were ($A = 26430.6$), $e_1 = 0.84547$, $e_2 = 0.87946$, $e_3 = 0.29553$. The SEAC code is a multiple purpose code based on the Gram-Schmidt orthogonalization process, and is described in National Bureau of Standards Report No. 3169.

[11] A case in point is the $a\,^1F$ of Ti I which is discussed in reference 25 of A.

theory that must be considered. One major source is configuration interaction, and the effects of this (as well as other less important effects) would have to be estimated in Sc II and Ti III before the errors in Ti II could be regarded as fully significant. The variation of the interaction parameter H_2 between the $3d^2$ and the $3d4s$ configuration is fairly well established,[12] and it can be shown that this configuration effect cannot explain the large errors in $y\,^2D$ and $z\,^2P$. However, the interaction parameters R_d and R_e between $3d4p$ and $4s4p$ cannot be estimated on the basis of previous work,[13] and it is not easy to evaluate the perturbation that would result from interaction between these two configurations. For this reason, the $3d4p$ parameters in calculation (2) of Table II might not indicate true behavior. The good agreement obtained would tend to indicate this is not the case and that configuration interaction can be neglected. If this latter assumption were not true, then the Ti II data would be even more perturbed and a linear theory (which includes this method) would be inapplicable.

With regard to the source of the large errors of $y\,^2D$ and $z\,^2P$ in calculation C it should be noted that $y\,^2D$, $z\,^2P$ and $y\,^2F$ have two pairs of interacting levels separated by 450 K in one pair ($J=2\frac{1}{2}$) and by 370 K in the other ($J=1\frac{1}{2}$), so that breakdown of LS-coupling could be appreciable. If the $J=2\frac{1}{2}$ and $J=1\frac{1}{2}$ term assignments were interchanged in these pairs, then the errors of $y\,^2D$, $z\,^2P$, and $y\,^2F$ would be changed from $+468$, -327, and -75 K, respectively, to $+51$, -80, and $+118$ K so that this procedure would remove all significant discrepancies between theory and experiment; the mean deviation of the revised errors would be ± 123 (a new least squares calculation would reduce this still more).

This interchange is probably not warranted, but an appreciable improvement should result if the actual correction were accurately evaluated and applied. It is likely that the classification of the levels given in Volume I of *Atomic Energy Levels* does specify the dominant component. However, the g-values, which would be the most decisive factor in deciding this, are uncertain. A strong interaction between $y\,^2D_{1\frac{1}{2}}$ and $z\,^2P_{1\frac{1}{2}}$ has been noted by H. N. Russell [Mt. Wilson Contract No. 344 (1927) page 30 (unpublished)]. Except for the $z\,^2P_{1\frac{1}{2}}$ g-value (it is not Landé and was probably not assumed), all g-values given for the levels of $y\,^2D$, $z\,^2P$, and $y\,^2F$ terms of Ti II are assumed Landé values (used to calculate other g-values that are given without colons).

[12] A discussion of this variation and a partial tabulation of values of H_2 is given in Sec. 6 of A. In Sc II and Ti III it is estimated that $H_2=200\pm 20$. The parameters B and C of calculation (2) of Table II were corrected slightly for this effect but no allowance is made for it in calculations A, B, or C of Table I.

[13] The notation for these parameters is that used by N. Rosenzweig [Phys. Rev. 88, 580 (1952)]. G. Racah [Phys. Rev. 62, 523 (1942)] has given an evaluation of these parameters in Sc I ($R_d=-3063$ and $R_e=950$) but his calculation neglects polarization effects which are expected to be large. If his interaction parameters are used in Sc II the value of the $z\,^3P-y\,^3P$ interaction element is very large (-4013 K). Since the observed separation of these terms is 9443 K it would be attributed almost entirely to configuration interaction.

PHYSICAL REVIEW VOLUME 97, NUMBER 3 FEBRUARY 1, 1955

Electromagnetic Spectrum of Am^{241}

PAUL P. DAY
Chemistry Division, Argonne National Laboratory, Lemont, Illinois
(Received October 18, 1954)

The electromagnetic spectrum of Am^{241} has been studied with a ten-inch bent-crystal spectrometer and a sodium iodide scintillation counter. Twelve gamma rays, sixteen Np L x-rays, and eight Am L x-rays have been measured. The gamma rays in Np have energies of 26.363, 33.199, 43.463, 59.568, 103, 113, 130, 159, 210, 270, 328, and 370 kev. The x-ray energies establish the validity of the Mosley extrapolations in this region of the periodic table. Details of the spectrometer operation and calibration are given.

INTRODUCTION

AMERICIUM-241 is a complex alpha emitter which decays with a 470-year half-life[1] to Np^{237}. A transmission type, bent-crystal spectrometer and a 20-channel scintillation counter have been used to analyze the electromagnetic spectrum emitted during the decay of this isotope. The results are reported herein.

The alpha spectrum has been measured by Asaro *et al.*[2] with a magnetic spectrometer. Six alpha groups were reported with energies of 5.546, 5.535, 5.503, 5.476, 5.433, and 5.379 Mev with relative intensities of 0.23 percent, 0.34 percent, 0.21 percent, 84.2 percent, 13.6 percent, and 1.42 percent, respectively. Later,[3] the 5.546-Mev alpha "peak" was ascribed to scattering from one of the baffles in the spectrometer.

[1] B. G. Harvey, Phys. Rev. 85, 482 (1952).

[2] Asaro, Reynolds, and Perlman, Phys. Rev. 87, 277 (1952).

[3] F. Asaro (unpublished data, September, 1953).