upper curve of Fig. 13 yields $S^r = 32.1/\text{sec}^{1/2}$. Table III yields a value of $\tau_c = 6\times10^{-6}$ sec, from which the computed value of $\tilde{C}^r$ is 7.12×10^{-38} cm^6/sec for $B_1 = 24$ G. The computed value of N_p is $1.6\times10^{19}/\text{cm}^3$, as compared to the value of $2.85\times10^{19}/\text{cm}^3$ supplied by the manufacturer of the crystal.[11] If this effective value of N_p were used to calculate D in Sec. IIIA, instead of the value supplied by the manufacturer of the crystal, the computed value of D would have been larger by a factor of 2.18 than those given in Table III, and in closer agreement with the value calculated in Ref. 16.

IV. CONCLUSIONS

The results of these experiments give quantitative support to current theories of nuclear spin relaxation via paramagnetic centers where spin diffusion plays a part. In particular, the measured value for the spin-diffusion constant in CaF_2 agrees reasonably well with its current theoretical value. The spin-diffusion vanishing case, predicted in LT, has been found, and the dependence of T_1 upon the magnetic field, τ_c and N_p, has been verified for both this case and the diffusion-limited case. In these experiments, the technique of studying relaxation in the rotating reference frame has been extremely useful, for it has allowed us to find T_1 and thus estimate τ_c. It has also allowed us to work in regions where the direct spin-lattice relaxation rate is very rapid without having an extremely high concentration of paramagnetic centers. This in turn has allowed us to verify Blumberg's prediction of how the nuclear spin system should relax when there is zero magnetization gradient in the sample.

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Random-Walk Models of Photoemission*

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An exact solution in closed form is given for the photoyield in the isotropic random-walk model of photoemission. The proof makes use of a theorem of importance in the theory of queues and ladder-point variables. The effect of reflection of the photoelectrons at the interface is also treated. A recursion relation for the probability of emission on the nth step P_n is derived from the expression for the photoyield. Numerical values of the photoyield and the P_n's are tabulated for numerous values of the relevant parameters, and these numbers are compared with the results of approximate expressions. The exact photoyield values are in good correspondence to a slightly modified version of a formula derived by Kane. A simple approximation is also given for the values of the P_n's.

I. INTRODUCTION

PHOTOELECTRIC emission is a two-step process, involving the creation of a free electron in the interior of the solid and the eventual escape of this electron through the surface into the vacuum. The transport part of the problem has been treated as a random-walk phenomenon and both Monte Carlo results[1,2] and approximate analytical formulas[3–6] have been given for the photoemission. However, as this paper shows, an exact closed-form expression can be obtained for the photoyield in the random-walk model. In addition, a formula for the probability of escape after exactly n collisions P_n is expressed in a form suitable for machine calculation, and the first twelve P_n's have been calculated for numerous values of the absorption and scattering parameters. These probabilities are compared to the results of the approximate calculations, and it is shown that some rather simple formulas give very good approximations to the exact results.

II. RANDOM-WALK MODEL

The model considers an electron, created at (x, y, z) in the solid, that undergoes an isotropic random walk. The problem is to compute the probability that the electron will pass through the plane $x=0$ before its energy has been reduced to the point where it is impossible for the electron to escape. This energy loss usually occurs suddenly due to pair creation, electron-hole recombination, or the ionization of an impurity in the lattice. We will call the energy-loss event "absorption"

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[1] R. Stuart, F. Wooten, and W. E. Spicer, Phys. Rev. **135**, A495 (1964).
[2] R. Stuart and F. Wooten, Phys. Rev. **156**, 364 (1967).
[3] S. Duckett and P. Metzger, Phys. Rev. **137**, A953 (1965).
[4] E. O. Kane, Phys. Rev. **147**, 335 (1966).
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[6] P. J. Roberts, Phys. Rev. Letters **18**, 823 (1967).

of the walker. If there is no reflection of the electron at the $x=0$ interface, the problem can be reduced to a one-dimensional one, where we consider only the walk generated by the projection of the three-dimensional walk on the x axis. We will consider the effects of electron reflection later.

If we let $1-S$ be the probability of absorption at each hop, the probability of escape on the nth hop of a walker starting at x is of the form $p_n(x)S^{n-1}$, where $p_n(x)$ is the probability of passing through $x=0$ for the first time in the absence of absorption processes. This expression is derived in more detail in Sec. III. The distribution of x is given by $f(x)=\alpha e^{-\alpha x}$, where α is the absorption coefficient of the light. Thus the fractional number of electrons escaping after n hops is

$$P_n=\alpha\int_0^\infty e^{-\alpha x}p_n(x)S^{n-1}dx\equiv\alpha\hat{p}_n(\alpha)S^{n-1}, \quad (1)$$

where the circumflex denotes "Laplace transform of." The quantum yield Y is given by the sum of the P_n's:

$$Y=\alpha\sum_{n=1}^{\infty}\hat{p}_n(\alpha)S^{n-1}. \quad (2)$$

We note that Y is α/S times the Laplace transform of the generating function of p_n.

To calculate this quantity we proceed as follows. Let $U_n(u)$ be the probability that u is the maximum excursion in the course of n steps of a walker starting at the origin. The total fraction of walkers that started at the origin and penetrated the plane $u=x$ sometime during n steps is thus

$$\int_x^\infty U_n(u)\,du;$$

the number entering the region $u\geq x$ for the first time on the nth step is

$$\int_x^\infty U_n(u)\,du-\int_x^\infty U_{n-1}(u)\,du\equiv p_n(x). \quad (3)$$

Hence,

$$\hat{p}_n(\alpha)\equiv\int_0^\infty e^{-\alpha x}p_n(x)\,dx=-\alpha^{-1}\hat{U}_n(\alpha)+\alpha^{-1}\hat{U}_{n-1}(\alpha). \quad (4)$$

Thus,

$$Y=\sum_{n=1}^{\infty}[\hat{U}_{n-1}(\alpha)-\hat{U}_n(\alpha)]S^{n-1}$$
$$=\{\sum_{j=0}^{\infty}\hat{U}_j(\alpha)S^j-S^{-1}[\sum_{j=0}^{\infty}\hat{U}_j(\alpha)S^j-1]\}$$
$$=S^{-1}[1-(1-S)\sum_{j=0}^{\infty}\hat{U}_j(\alpha)S^j]. \quad (5)$$

The U_j are related to the "ladder variables," which are well known in probability theory. Feller[7] shows that

$$\sum_{j=0}^{\infty}\hat{U}_j(\alpha)S^j=(1-S)^{-1}\times\exp\left(\sum_{n=1}^{\infty}\frac{S^n}{n}\int_0^\infty(e^{-\alpha x}-1)f_n(x)\,dx\right), \quad (6)$$

where f_n is the probability density of the positions of the walkers after n steps in the case that the walkers start at the origin with no restrictions on their excursions. Thus

$$Y=S^{-1}\left\{1-\exp\left[\sum_{n=1}^{\infty}\frac{S^n}{n}\int_0^\infty(e^{-\alpha x}-1)f_n(x)\,dx\right]\right\}. \quad (7)$$

Since $f_1(x)$ is assumed symmetric in x, we have

$$\int_0^\infty f_n(x)\,dx=\tfrac{1}{2}, \qquad \text{for all } n.$$

Also,

$$f_n(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-ix\theta)\varphi^n(\theta)\,d\theta=\pi^{-1}\int_0^\infty\cos\theta x\varphi^n(\theta)\,d\theta,$$

where $\varphi(\theta)$ is the characteristic function of $f_1(x)$. Accordingly

$$\int_0^\infty e^{-\alpha x}f_n(x)\,dx=\frac{2}{2\pi}\int_0^\infty\varphi^n(\theta)\int_0^\infty e^{-\alpha x}\cos\theta x\,dx$$
$$=\pi^{-1}\int_0^\infty\varphi^n(\theta)\frac{\alpha}{\alpha^2+\theta^2}\,d\theta. \quad (8)$$

Finally, we use the expansion

$$\ln(1-x)=-\sum_{n=1}^{\infty}\frac{x^n}{n}$$

to obtain

$$Y(\alpha,S)=S^{-1}\left(1-(1-S)^{1/2}\times\exp\left\{-\pi^{-1}\int_0^\infty\ln[1-S\varphi(\theta)]\frac{\alpha}{\alpha^2+\theta^2}\,d\theta\right\}\right). \quad (9)$$

This is the general expression for the photoyield. Notice that Eq. (2), which formally contains an infinite number of truncated convolution integrals, has been expressed in a form containing only one integral. The correct expression to use for $\varphi(\theta)$ in the photoemission case will be considered in Sec. III.

Certain asymptotic forms of Eq. (9) can be noted. If α is very large

$$Y\sim(1/S)[1-(1-S)^{1/2}] \quad (10)$$

independently of the form of $f_1(x)$. To find the behavior

[7] W. Feller, *An Introduction to Probability Theory and Its Applications* (John Wiley & Sons, Inc., New York, 1966), Vol. II, p. 573.

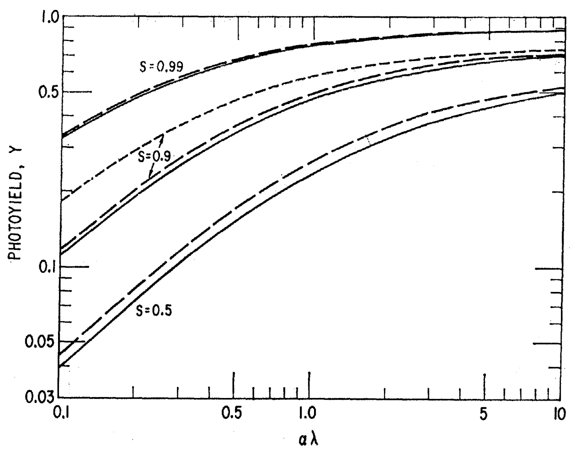

FIG. 1. Photoyield Y versus $\alpha\lambda$ for the case $R=0$. The solid curves are from the exact calculation; the short-dashed curve is from Kane's formula; the long-dashed curves are from Kane's formula, slightly modified as described in the text.

for small α we rewrite the integral in Eq. (9) as

$$\int_0^\infty \ln[1-S\varphi(\alpha y)]\frac{dy}{1+y^2}.$$

For symmetric $f_1(x)$ the first two terms of the expansion $\varphi(\alpha y)$ are $1-(1/2)\sigma^2\alpha^2y^2$, where σ^2 is the variance of $f_1(x)$. For small $\alpha\sigma$ we get

$$\pi^{-1}\int_0^\infty \ln[1-S\varphi(\alpha y)]\frac{dy}{1+y^2}$$

$$\approx\pi^{-1}\int_0^\infty \ln\{1-S[1-(1/2)\sigma^2\alpha^2y^2]\}\frac{dy}{1+y^2}$$

$$=\ln[\alpha\sigma(S/2)^{1/2}+(1-S)^{1/2}].$$

Thus for small $\alpha\sigma$

$$Y\approx S^{-1}\left(\frac{\alpha\sigma[S/2(1-S)]^{1/2}}{1+\alpha\sigma[S/2(1-S)]^{1/2}}\right). \tag{11}$$

We next derive an expression for the $p_n(\alpha)$. From Eqs. (2) and (7) we obtain

$$\sum_{n=1}^{\infty}p_n(\alpha)\,S^n=\alpha^{-1}\{1-\exp[-\sum_{n=1}^{\infty}a_n(S^n/n)]\}, \tag{12}$$

where

$$a_n=\int_0^\infty[1-e^{-\alpha x}]f_n(x)\,dx.$$

We take the derivative of Eq. (12) with respect to S and equate powers of S to obtain

$$p_n(\alpha)=\frac{a_n}{\alpha n}-n^{-1}\sum_{j=1}^{n-1}a_jp_{n-j}(\alpha). \tag{13}$$

III. THE SCATTERING FUNCTION

We now specialize the general formulas (9) and (13) to the scattering function $f_1(x)$ that we expect for electron scattering. We assume that the probability per unit pathlength of lastice or quasi-elastic isotropic scattering is λ_s^{-1}; the corresponding probability for absorption is λ_a^{-1}. In 3-space, the scattering density, which is the probability of an "alive" walker stepping to the point R, is

$$f(R)=e^{-R/\lambda}/4\pi R^2\lambda_s,$$

where we have defined $\lambda^{-1}\equiv\lambda_s^{-1}+\lambda_a^{-1}$.

The projection of this on the x axis is

$$f_1(x)=(2\lambda_s)^{-1}\int_{|x|}^\infty\frac{\exp(-y/\lambda)}{y}\,dy. \tag{14}$$

The probability density as written is defective (does not sum to unity); we can write Eq. (14) in terms of the nondefective density

$$f_1(x)=S(2\lambda)^{-1}\int_{|x|}^\infty\frac{\exp-(y/\lambda)}{y}\,dy, \tag{15}$$

where

$$S=\lambda/\lambda_s=[1+(\lambda_s/\lambda_a)]^{-1}. \tag{16}$$

The characteristic function of the exponential integral density is

$$\varphi_{(\theta)}=(\tan^{-1}\lambda\theta)/\lambda\theta.$$

The total photoyield thus becomes

$$Y(\alpha,\lambda_s,\lambda_a)=S^{-1}\Bigg[1-(1-S)^{1/2}$$

$$\times\exp\left(-\frac{\alpha}{\pi}\int_0^\infty\frac{\ln\{1-[S(\tan^{-1}\lambda\theta)/\lambda\theta]\}d\theta}{\alpha^2+\theta^2}\right)\Bigg], \tag{17}$$

with S given by Eq. (16). A trivial rearrangement of the integral in Eq. (17) yields a somewhat more useful form,

$$Y(\alpha\lambda,S)=S^{-1}\Bigg[1-(1-S)^{1/2}$$

$$\times\exp\left(-\pi^{-1}\int_0^\infty\frac{\ln\{1-[S(\tan^{-1}\alpha\lambda y)/\alpha\lambda y]\}dy}{1+y^2}\right)\Bigg]. \tag{18}$$

So far we have not considered the possibility of electron reflection at the interface. We assume the reflection is diffuse, since surface irregularities will probably be of the order of the electron wavelength (~10 Å). Suppose a fraction R of the electrons approaching the surface is reflected. A certain fraction F of these will again approach the surface. Since the number of previous hops has no effect on the future scattering,

$$F=2S[Y(\infty,S)-(1/2)]=[1-(1-S)^{1/2}]^2. \tag{19}$$

A fraction R of these one-reflected electrons may, of

TABLE I. Values of the photoyield for numerous values of S and $\alpha\lambda$ for the case $R=0$.

$\alpha\lambda$	S = 0.5	0.75	0.9	0.95	0.975	0.99	0.995	0.998	0.999
0.1	0.0392	0.0629	0.1101	0.1600	0.2232	0.3255	0.4132	0.5340	0.6221
0.2	0.0726	0.1136	0.1903	0.2653	0.3520	0.4765	0.5702	0.6832	0.7557
0.4	0.1266	0.1908	0.3002	0.3959	0.4954	0.6209	0.7043	0.7944	0.8470
0.6	0.1687	0.2470	0.3720	0.4740	0.5737	0.6911	0.7645	0.8402	0.8827
0.8	0.2025	0.2900	0.4230	0.5262	0.6231	0.7327	0.7989	0.8653	0.9018
1.0	0.2305	0.3240	0.4611	0.5637	0.6574	0.7603	0.8212	0.8811	0.9138
1.5	0.2831	0.3848	0.5247	0.6236	0.7099	0.8010	0.8532	0.9034	0.9303
2.0	0.3203	0.4255	0.5644	0.6591	0.7399	0.8234	0.8704	0.9152	0.9390
4.0	0.4024	0.5088	0.6391	0.7229	0.7917	0.8603	0.8984	0.9340	0.9527
10.0	0.4834	0.5831	0.6993	0.7713	0.8292	0.8864	0.9175	0.9465	0.9617

course, be reflected again. The quantum yield is thus

$$Y(\alpha\lambda, S, R)=(1-R)\,Y(\alpha\lambda, S)\sum_{n=0}^{\infty}(RF)^n$$

$$=\frac{1-R}{1-R[1-(1-S)^{1/2}]^2}\,Y(\alpha\lambda, S). \quad (20)$$

Finally we reduce Eq. (13) for the individual probabilities of emission after n steps (in the absence of reflection) to a form suitable for machine calculation. The probability of emission on the nth step is

$$P_n=\alpha\hat{p}_n(\alpha)\,S^{n-1}=S^{-1}\left(\frac{a_nS^n}{n}-n^{-1}\sum_{j=1}^{n-1}a_jS^jP_{n-j}\right). \quad (21)$$

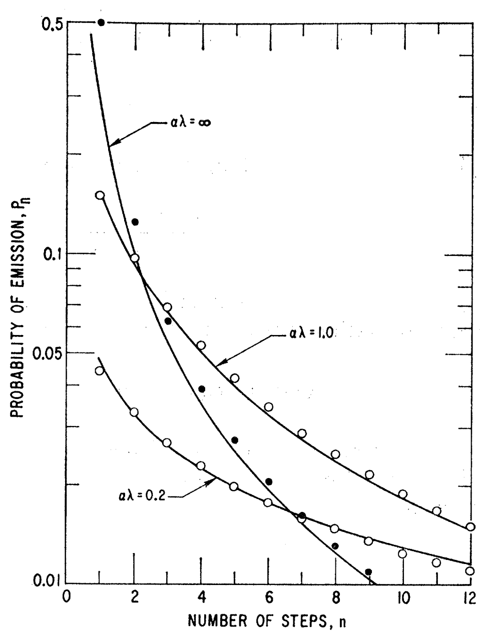

FIG. 2. Fractional emission on the nth step, P_n, versus n for the case $S=1$, $R=0$. The points are from the exact calculation; the curves are taken from the approximate expression described in the text.

The a_nS^n are given by

$$a_nS^n=\int_0^{\infty}[1-e^{-\alpha x}]S^nf_n(x)\,dx$$

$$=\tfrac{1}{2}S^n-\int_0^{\infty}e^{-\alpha x}\frac{S^n}{\pi}\int_0^{\infty}\cos\theta x\varphi^n(\theta)\,d\theta dx$$

$$=\frac{S^n}{\pi}\int_0^{\infty}\left[1-\left(\frac{\tan^{-1}\alpha\lambda y}{\alpha\lambda y}\right)^n\right]\frac{dy}{1+y^2}.$$

Thus

$$P_n(\alpha\lambda, S)$$

$$=(nS)^{-1}\left(\left\{\frac{S^n}{\pi}\int_0^{\infty}\left[1-\left(\frac{\tan^{-1}\alpha\lambda y}{\alpha\lambda y}\right)^n\right]\frac{dy}{1+y^2}\right\}\right.$$

$$\left.-\sum_{j=1}^{n-1}\frac{S^j}{\pi}\left\{P_{n-j}\int_0^{\infty}\left[1-\left(\frac{\tan^{-1}\alpha\lambda y}{\alpha\lambda y}\right)^j\right]\frac{dy}{1+y^2}\right\}\right). \quad (22)$$

IV. NUMERICAL RESULTS AND DISCUSSION

The photoyield $Y(\alpha\lambda, S)$ (Eq. 18) is tabulated in Table I for different values of $\alpha\lambda$ and S. The first 12 values of $P_n(\alpha\lambda, 1)$ are found in Table II. $P_n(\alpha\lambda, S)$ is, of course, equal to $P_n(\alpha\lambda, 1)\,S^{n-1}$.

The approximate expressions for the photoyields have been compared with the results of the exact calculation. A modification of the formula derived by Kane[4] has been found to give the best fit. The approximation of Duckett and Metzger[3] is more cumbersome and not as accurate. The results of Beckman[5] and of Roberts[6] require numerical integration; although very accurate, they are not exact, because these authors have used in their proofs the assumption that the angular distribution of walkers passing through an imaginary plane is isotropic, whereas the real distribution is biased toward small angles because electrons traveling normal to any given plane are much more likely to intersect it before being scattered.

Some of the Monte Carlo calculations by Stuart and Wooten[2] cover the range of parameters for which we have evaluated Eq. (18), and the results agree to better

TABLE II. Values of the fractional emission on the nth step, P_n, for the case $S=1$, $R=0$; the numbers for other values of S are obtained multiplying the P_n's by S^{n-1}.

$\alpha\lambda$	N: 1	2	3	4	5	6	7	8	9	10	11	12
0.1	0.0234	0.0181	0.0150	0.0130	0.0116	0.0105	0.0096	0.0089	0.0083	0.0078	0.0073	0.0069
0.2	0.0442	0.0331	0.0269	0.0228	0.0199	0.0177	0.0160	0.0146	0.0135	0.0125	0.0116	0.0109
0.4	0.0794	0.0566	0.0441	0.0361	0.0306	0.0265	0.0233	0.0208	0.0188	0.0170	0.0156	0.0144
0.6	0.1083	0.0738	0.0556	0.0443	0.0366	0.0310	0.0268	0.0235	0.0208	0.0187	0.0169	0.0154
0.8	0.1326	0.0870	0.0636	0.0494	0.0400	0.0333	0.0283	0.0245	0.0215	0.0191	0.0171	0.0154
1.0	0.1534	0.0973	0.0692	0.0527	0.0419	0.0344	0.0289	0.0248	0.0215	0.0189	0.0168	0.0151
1.5	0.1946	0.1149	0.0776	0.0567	0.0437	0.0349	0.0287	0.0242	0.0207	0.0179	0.0158	0.0140
2.0	0.2253	0.1256	0.0815	0.0578	0.0436	0.0342	0.0278	0.0231	0.0196	0.0169	0.0147	0.0130
4.0	0.2988	0.1429	0.0841	0.0559	0.0403	0.0307	0.0244	0.0199	0.0167	0.0142	0.0123	0.0108
10.0	0.3801	0.1479	0.0786	0.0496	0.0347	0.0260	0.0204	0.0166	0.0138	0.0117	0.0101	0.0088

than three places. These authors also consider cases in which the photoelectron has an "escape cone" of less than 2π sr. The yield under this restriction can be calculated to within a few percent by using in Eq. (20) an effective reflectivity, which is given by

$$R=[(2\pi-\Omega)/2\pi]^2,$$

where Ω is the value of the escape cone.

In his approximation, Kane uses the function $(S/2\lambda)\ \exp(-|x|/\lambda)$ as the step-length probability density, instead of using the function of Eq. (14), and then solves the transport integral equation exactly. The result Kane obtains for $R=0$, expressed in our notation, is

$$Y(\alpha\lambda,\ S)=\alpha\lambda/[\alpha\lambda+(1-S)^{1/2}][1+(1-S)^{1/2}]. \tag{23}$$

This function, for $S=0.9$, is plotted as the dotted curve in Fig. 1; the agreement is fair. However, it is naive to equate the λ in Kane's expression with the scattering length in 3-space. A fundamental observation of random-walk theory[8] is that the variance of the step-length density is the most important single parameter. Thus we rewrite Kane's density in the form $p(x)=(S/2\lambda_1)\ \exp(-|x|/\lambda_1)$, with λ_1 being such that the variance $\int x^2p(x)dx$ equals the variance of the density of Eq. (14). A straightforward calculation (or the comparison of the second terms of the series expansion of the respective characteristic functions) shows that $\lambda_1=\lambda/\sqrt{3}$. We thus obtain, as the approximation to use,

$$Y(\alpha\lambda,\ S)\approx\frac{\alpha\lambda/\sqrt{3}}{[(\alpha\lambda/\sqrt{3})+(1-S)^{1/2}][1+(1-S)^{1/2}]}. \tag{24}$$

[8] P. Erdös and M. Kac, Bull. Am. Math. Soc. **52**, 292 (1946).

This function is plotted as the dashed lines of Fig. 1. To correct for reflection we need to multiply Eq. (24) by $(1-R)/\{1-R[1-(1-S)^{1/2}]^2\}$ as shown in Eq. (20).

The average number of hops in the absence of any surface or absorbing barrier is $\bar{N}=S/1-S$. Equation (24) can be rewritten as

$$Y=\frac{\alpha\lambda(\bar{N}/3)^{1/2}}{[\alpha\lambda(\bar{N}/3)^{1/2}+S][1+(S/\bar{N})^{1/2}]}. \tag{25}$$

In the limit $(\bar{N})^{1/2}\gg 1$, this reduces to the expression given by diffusion theory,

$$Y_D=\frac{\alpha\lambda(\bar{N}/3)^{1/2}}{\alpha\lambda(\bar{N}/3)^{1/2}+1}. \tag{26}$$

A formula that approximates the P_n's has also been found. Kane shows that $P_n(\alpha\lambda,\ 1)\sim\alpha\lambda/2\sqrt{n}$ for $\alpha\lambda\sqrt{n}\gg 1$ in the case of no reflection. He also shows that

$$P_n\sim\frac{1+(1/\alpha\lambda)}{2(\pi n^3)^{1/2}},\quad \text{for}\quad \alpha\lambda\sqrt{n}\gg 1.$$

A simple formula that has both these limits is

$$P_n(\alpha\lambda,\ 1)\approx\frac{\gamma+1}{2(\sqrt{n})(2+\gamma^{-1}+\pi^{1/2}\gamma n)},$$

where $\gamma=\alpha\lambda/\sqrt{3}$. This approximation is plotted in Fig. 2; the approximation is poorest when $\alpha\lambda\sqrt{n}\approx 1$.

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