Higher orders and structure of perturbation theory series for screened Coulomb potential

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(Submitted 12 September 1981)
Zh. Eksp. Teor. Fiz. 82, 1070–1078 (April 1982)

An effective method is developed for calculating the higher orders of perturbation theory for potentials of polynomial type. The method is based on a transition to the perturbation theory problem for a Fock operator with purely discrete spectrum. In this case, allowance for the dynamical symmetry of the unperturbed operator makes it possible to express the corrections of any order in perturbation theory as polynomials with rational coefficients. The method is used to calculate the bound states of the Schrödinger equation with screened Coulomb potential. The analytic properties of the solutions are investigated. By means of the Padé method, the exact values of the energy are obtained in a wide range of variation of the screening parameter. The real and imaginary parts of the energies of quasistationary states are calculated.

PACS numbers: 03.65.Ge, 03.65.Db

1. INTRODUCTION

In connection with the solution of a number of fundamental problems of quantum mechanics and field theory, there has recently been a considerable increase in interest in the calculation of the higher orders of perturbation theory.[1-4] The best known quantum-mechanical problems for which the analytic properties and structure of the perturbation series have been investigated in detail are the anharmonic oscillator[4-8] and the hydrogen atom in an external field.[9-12]

In the present paper, we discuss various aspects of the use of Rayleigh–Schrödinger perturbation theory to find the energies of the bound states of a particle in the screened Coulomb potential

$$V(r)=-Ze^{-\alpha r}/r.$$

This problem is of interest because it has numerous physical applications in nuclear theory, plasma physics, solid-state physics, and scattering theory.[13,14]

After separation of the angular variables and the scale transformation $r\to Zr$, the problem reduces to the radial Schrödinger equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}-\frac{e^{-\varepsilon r}}{r}-E\right]P(r)=0, \tag{1}$$

where $\varepsilon=\alpha/Z$. The energy E^Z_{nl} of the particle is related to the eigenvalue $E=E_{nl}$ of Eq. (1) by $E^Z_{nl}=Z^2E_{nl}$.

It is well known that Eq. (1) cannot be integrated exactly, so that approximate methods must be used to solve it. One usually employs either numerical integration[15] or perturbation theory in the parameter ε.[3,16-20] It is not always convenient to use numerical methods, since they involve lengthy calculations for each set of parameter ε, n, and l separately. In addition, the possibilities for investigating the functional properties of the solutions are very limited in such an approach.

For small values of the parameter ε, the perturbing potential $U(r)$ can be expanded in powers of ε:

$$U(r)\equiv r^{-1}(1-e^{-\varepsilon r})=\varepsilon\sum_{k=1}^{\infty}\frac{1}{k!}(-\varepsilon r)^{k-1}. \tag{2}$$

In each order in ε, it has the form of a polynomial in powers of r. The methods of perturbation theory in the parameter ε make it possible to find approximate solutions in the form

$$E_{nl}(\varepsilon)=\sum_{N=0}^{\infty}E^{(N)}_{nl}\varepsilon^N. \tag{3}$$

It is not difficult to find the energy to third order in powers of ε, since the wave function depends on ε only in the second order. The finding of the following coefficients is a rather difficult problem.

To calculate the corrections of higher order in quantum-mechanical problems, wide use is currently made of the method based on transition from the Schrödinger equation to a Riccati equation for the logarithmic derivative of the wave function.[6,16,21,22] In the case of the screened Coulomb potential, this method was used in Ref. 16 to calculate correctly five orders, and the recently published Ref. 23 reports the calculation of ~100 perturbation orders for the ground level and summation of the perturbation theory series. In Ref. 17, four orders were found for an arbitrary state[1)] with $n=l-1$. However, the use of this method encounters considerable difficulties in the case of excited states, when the radial wave function has nodes.[12,22] Therefore, it is not possible to obtain general expressions for the corrections of higher order in the perturbation theory for arbitrary n and l in such an approach.

It was shown earlier in Ref. 24 that if one uses the method of Sturm expansions the perturbation theory corrections to the wave functions and energies of hydrogen-like atoms can be obtained in a closed analytic form for a large class of perturbing potentials. The corrections have a particularly simple form in the case of potentials of polynomial type. In this case, the calculation of the higher-order corrections reduces to the use of a simple recursion procedure, and this is equally convenient for the ground state and the excited states. In Ref. 3, this method was used to find exact expressions for the first six perturbation-theory corrections to the energy E_{nl} of an arbitrary bound state. Later,[19] the same number of corrections was obtained using

0038-5646/82/040625-05$04.00

hypervirial relations and the Gell-Mann–Feynman theorem.

In Sec. 2 of the present paper, we take into account the dynamical symmetry of the Fock operator and develop further the method proposed in Ref. 3. We obtain in analytic form 13 orders of the perturbation theory for arbitrary n and l and in numerical form more than 70 orders for the ground state and 50 orders for all excited states with $n=2,3$. We investigate the behavior of the coefficients of the series (3) for large N. In Sec. 3, we investigate the applicability of the method of Padé approximants for finding the exact values $E_{nl}(\varepsilon)$ in a wide range of variation of ε and we determine the critical value ε^*_{nl} $(E^*_{nl}(\varepsilon^*_{nl})=0)$ of the screening parameter. We establish rapid convergence of the approximants. We investigate quasistationary states when $\varepsilon<0$ and $\varepsilon>\varepsilon^*_{nl}$ for $l\neq 0$.

2. CALCULATION OF THE HIGHER ORDERS OF PERTURBATION THEORY

To solve Eq. (1), we use expansions with respect to a complete system of square integrable functions associated with the unperturbed Schrödinger equation. Making transformations of the unknown function, $P(r)\to y(r)=r^{-1/2}P(r)$, and the independent variable, $r\to x=(-8E_0)^{1/2}r$, we arrive at the equation

$$(M_1-n)y=Wy, \tag{4}$$

where $E_0=-1/2n^2$ is the unperturbed energy, and

$$M_1=-\frac{d}{dx}x\frac{d}{dx}+\frac{s^2}{4x}+\frac{x}{4}, \tag{5}$$

the Fock operator for a particle in the Coulomb field, has a purely discrete spectrum of equidistant eigenvalues

$$\lambda_p=p+(s+1)/2,\quad s=2l+1,\quad p=0,1,2,\ldots.$$

Thus, we have gone over from the perturbation theory problem for the Schrödinger operator for a particle in the Coulomb field to the equivalent problem for the Fock operator M_1. The term on the right-hand side of the equation, which is due to the presence of the perturbation, has the form

$$W={}^1/_2n^2x\delta E-V(x), \tag{6}$$

where

$$V(x)=n(1-e^{-\varepsilon nx/2})=-n\sum_{k=1}^{\infty}\frac{(-\varepsilon nx)^k}{2^k k!} \tag{7}$$

is the perturbing operator, and $\delta E=E-E_0$.

Besides M_1, we introduce the operators

$$M_2=M_1-\frac{x}{2},\quad M_3=i\left(x\frac{d}{dx}+\frac{1}{2}\right), \tag{8}$$

which have a purely continuous spectrum of eigenvalues. It was shown earlier in Refs. 25 and 26 that the self-adjoint operators M_i $(i=1,2,3)$ satisfy the commutation relations

$$[M_2,M_1]=iM_3,\quad [M_1,M_3]=iM_2,\quad [M_3,M_2]=-iM_1 \tag{9}$$

and, therefore, are elements of the Lie algebra of the noncompact group $O(2,1)$. The quadratic form

$$Q=M_1^2-M_2^2-M_3^2$$

is a Casimir operator of the group. Since

$$Q=(s^2-1)/4=l(l+1),$$

the complete set $\{y_n^s\}$ of eigenfunctions of the operator M_1 for fixed s realizes the basis of a unitary irreducible representation of $O(2,1)$.

It is convenient to introduce the operators $M_\pm=M_2\pm iM_3$, which satisfy the commutation relations

$$[M_1,M_\pm]=\pm M_\pm,\quad [M_-,M_+]=2M_1, \tag{9a}$$

from which it follows directly that

$$\langle n|M_+|m\rangle=\langle m|M_-|n\rangle=[(n+l)(m-l)]^{1/2}\delta_{m,n-1}, \tag{10}$$

$$\langle n|\hat{A}|m\rangle\equiv\int_0^\infty y_n^s(x)\hat{A}y_m^s(x)\,dx.$$

Bearing in mind that $x=2(M_1-M_2)=2M_1-M_+-M_-$, we obtain

$$\langle n|x|m\rangle=2n\delta_{nm}-[(n+l)(m-l)]^{1/2}\delta_{m,n-1}-[(m+l)(n-l)]^{1/2}\delta_{m,n+1}. \tag{11}$$

The relation (11) was obtained by a different method in Ref. 26, in which it is also noted that there is an analogy between the Sturm problem for the hydrogen atom and the harmonic oscillator problem.

To find the corrections to the energy in accordance with perturbation theory, we proceed from the identity

$$\langle n|W(1-Q_nW)^{-1}|n\rangle=0, \tag{12}$$

where $Q_n=(M_1-n)^{-1}P_n$, and P_n is the projection operator onto the subspace orthogonal to $|n\rangle$.

TABLE I. Coefficients of analytic expressions for perturbation theory corrections.

N	q	p	$C_{pq}^{(N)}$	N	q	p	$C_{pq}^{(N)}$	N	q	p	$C_{pq}^{(N)}$
0	−1	0	−1/2	7	6	0	−22763/126	10	5	0	−550099/6300
1	0	0	−2	8	3	1	1/4			1	160259/84
2	0	1	1			2	145/48			2	623447/270
	1	0	−3			3	557/48			3	1369049/1080
3	1	0	−2/3			4	2767/192			4	399751/1440
		1	2		4	0	−17799/560		6	0	−772114291/45360
	2	0	−10/3			1	21681/80			1	11701261/360
4	1	1	1/2			2	6779/32			2	329953/48
		2	5/4			3	829/16			3	38207/72
	2	0	−55/12		5	0	−914375/576		7	0	−2414775527/21600
		1	5/2			1	10131/8			1	44513
	3	0	−77/12			2	10241/96			2	981737/720
5	2	0	−2/5		6	0	−5051449/1440		8	0	−721750181/7560
		1	5			1	27469/80			1	15580619/2520
		2	9/2		7	0	−885551/1344		9	0	−909259231/90720
	3	0	−49/2	9	4	0	−2/9	11	5	0	−2/11
		1	7			1	4409/90			1	1991/14
	4	0	−171/10			2	31129/216			2	772521/1400
6	2	1	1/3			3	38353/216			3	315091/300
		2	41/18			4	22469/288			4	166389/160
		3	34/9		5	0	−613085/648			5	927271/2400
	3	0	−1057/90			1	232991/72		6	0	−7870603/1400
		1	98/3			2	545567/432			1	17009603/420
		2	21/2			3	35893/216			2	1940341/80
	4	0	−386/3		6	0	−60252829/4320			3	1692431/240
		1	23			1	1362907/180			4	148967/160
	5	0	−4763/90			2	18109/48		7	0	−37705747/160
7	3	0	−2/7		7	0	−7905637/432			1	46796821/160
		1	49/3			1	103247/72			2	4254371/120
		2	61/2		8	0	−32694383/12960			3	409591/240
		3	103/6	10	4	1	1/5		8	0	−6053053711/7200
	4	0	−937/6			2	359/100			1	434135783/1680
		1	415/2			3	20563/900			2	8396419/1680
		2	65/2			4	44773/720		9	0	−5021064583/10080
	5	0	−6050/9			5	55561/900			1	91789969/3360
		1	517/6						10	0	−216473573/5280

Note. The coefficients $C_{0,n-1}^{(2n)}$ for $n=1,2,\ldots,6$ are equal to zero and are not given in the table.

We seek the correction δE to the energy in the form of the expansion (3) in powers of ε using the formal expansion that follows from (12):

$$\langle n|x\sum_{k=0}^{\infty}(Q_nW)^k|n\rangle\delta E=\frac{2}{n^2}\langle n|V\sum_{k=0}^{\infty}(Q_nW)^k|n\rangle. \tag{13}$$

Substituting in (13) the expansion (7) for V and equating to zero the coefficients of the different powers of ε, we can express $E^{(N)}$ in terms of corrections of lower order and in terms of the matrix elements of the products of several operators x and Q_n.

The reduced Green's operator Q_n of the unperturbed problem can be represented in the form of an expansion in the eigenfunctions y_m^s of the operator M_1:

$$Q_n=\sum_{m\neq n}\frac{|m\rangle\langle m|}{m-n}. \tag{14}$$

In the case of a polynomial perturbing potential of the type (2) or (7), all the sum over the intermediate states $|m\rangle$ in the relation (13) terminate at finite m. Indeed, by virtue of the "sum rule" (11) for integral $q\geqslant 0$ we have $\langle m|x^q|n\rangle=0$ when $|m-n|>q$. Thus, the corrections of any perturbation order can be expressed as simple analytic expressions containing polynomials in n and l with rational coefficients. Using this method, we have found in explicit form the corrections to the energy up to 13 orders in ε for all n and l. They have the form

$$E_{nl}^{(N)}=\left(\frac{-1}{2}\right)^N\sum_{p=0}^{k}\sum_{q=N-k-1}^{N-p-1}C_{pq}^{(N)}\Lambda^p n^{2q}, \tag{15}$$

where $\Lambda=l(l+1)$, and k is the integral part of the number $N/2$. The coefficients $C_{pq}^{(N)}$ are rational numbers. Their values are given in Table I.

Note that the proposed method is fairly universal and free of the difficulties that arise, for example, in the calculation of the excited states using methods based on the Riccati equation.[12,22]

In Fig. 1, the quantities $(-1)^N E_{nl}^{(N)}$ are plotted against N in a semilogarithmic scale for the $1s, 2s, 2p, 3s, 3p$, $3d$ states. To within the accuracy of the figure, the curves for states with the same n practically coincide. For the ground state, the obtained dependence can be well approximated by the function $f(N)=(N/e\ln N)^N$ in a wide range of N.

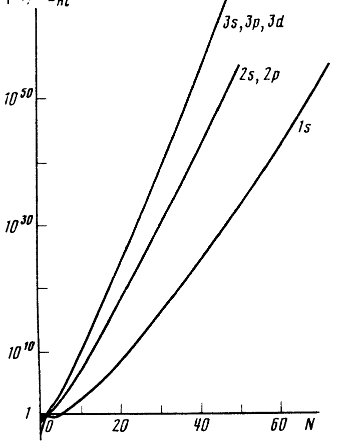

FIG. 1. Coefficients of the expansion of the energy in powers of ε.

3. USE OF THE METHOD OF PADÉ APPROXIMANTS

As was shown in Ref. 3, the asymptotic nature of the series (3) means that direct summation of them does not give satisfactory results already when $\varepsilon\gtrsim 0.3\varepsilon_{nl}^*$, where ε_{nl}^* is the critical value of the screening parameter at which a level enters the continuum. Thus, the calculation of the higher perturbation orders in this case is of no value. However, the use of generalized methods of summation of formally divergent series[27] makes it possible to use the information contained in the expansion coefficients to find the required function in a fairly wide range of ε. The effectiveness of such methods depends in the first place on the number of terms of the expansion that can be taken into account with sufficient accuracy. Therefore, if these methods are to be used, the calculation of the higher perturbation orders is important.

Various methods of generalized summation of perturbation series in problems of quantum mechanics and field theory have been used recently.[23,28-31] In the case of the screened Coulomb potential, it was shown in Ref. 3 that when a comparatively small number ($N=6, 7$) of expansion terms are taken into account the Euler, Hölder, and Hutton methods makes it possible to obtain satisfactory results (to accuracy 10^{-3}) in the region $0\leqslant\varepsilon\leqslant 0.7\varepsilon_{nl}^*$. However, to obtain reliable results in the complete range of ε up to ε_{nl}^* it is necessary to know considerably more expansion terms. One of the most effective methods in this case is the method of Padé approximants,[32,33] which makes it possible to take into account approximately the presence of poles of the unknown function and, thus, approximate this function in a region that extends far beyond the limits of convergence of the Taylor series. The advantages of the Padé method are manifested when there are sufficiently many exact coefficients of the original series.

The Padé approximants $[M/L]$ to the function $f(z)$ are defined[32,33] as the ratio of two polynomials $P_M(z)$ and $Q_L(z)$ of degrees M and L, respectively, this ratio having the same first $M+L+1$ coefficients of its Taylor expansion as $f(z)$:

$$f^{[M/L]}(z)\equiv P_M(z)/Q_L(z)=f(z)+O(z^{M+L+1}). \tag{16}$$

In Ref. 31, 13 coefficients of the expansion (3) were found numerically and used to construct the Padé approximants [6/6] and [7/6], these making it possible to approximate the energy in the region $\varepsilon<\varepsilon_{nl}^*$ to an accuracy of three of four decimal places. The large number of expansion coefficients obtained in Ref. 23 for the $1s$ ground state made it possible to investigate the convergence of the diagonal Padé approximants to the energy, $E_{10}^{[N/N]}$, up to $N=18$. It was shown that in this case the Padé approximants beginning with [10/10] give a good approximation to the energy in the range $0<\varepsilon<\varepsilon_{10}^*$. In the present work, we have found 73 terms of the expansion (3) for the ground state and 50 terms for the series for the excited states. This number of coefficients is entirely adequate for investigating the convergence of the Padé approximants in a wide range of ε, including ε^*_{nl}, and also to consider the case of quasistationary states.

Table II demonstrates the convergence of the diagonal Padé approximants for the states 1*s* and 2*p* for different values of ε. The calculations show that for $l=0$ the Padé approximants converge rapidly for $0 \leqslant \varepsilon \leqslant \varepsilon^*_{n0}$, and for the ground state even up to $\varepsilon \approx 5\varepsilon^*_{10}$; moreover, as one would expect, the limit function has a vanishing derivative at $\varepsilon = \varepsilon^*_{n0}$. The states with $l \neq 0$, the Padé approximant converges somewhat more slowly.

Since the graphs of the functions $E_{n0}(\varepsilon)$ touch the abscissa, to determine the critical screening parameter it is convenient to approximate the functions $[-E_{n0}(\varepsilon)]^{1/2}$ and find their roots. The roots of the Padé approximants to the function $[-E_{n0}(\varepsilon)]^{1/2}$, which are the approximate values of ε^*_{n0}, are given in Table III and compared with the more accurate values of ε^*_{n0} (last row of the table) obtained earlier in Refs. 15 and 34. The deviation of the roots of the Padé approximants from ε^*_{n0} characterizes the accuracy of the calculation of the energy in the least favorable case when $\varepsilon = \varepsilon^*_{n0}$. The table demonstrates the rapid convergence of the roots. For the states 2*s* and 3*s*, the quantity ε^*_{n0}, defined as the limiting value of the roots of the Padé approximants, is calculated to an accuracy two orders of magnitude greater than the value obtained by numerical integration in Ref, 15, while for the ground state it is calculated with the same accuracy as was achieved by the analytic method considered in Ref. 34 and to an accuracy an order of magnitude greater than the value $\varepsilon^*_{10} = 1.190612$ obtained in Ref. 23.

In the case $l \neq 0$, there is a nonvanishing derivative, $dE_{nl}/d\varepsilon \neq 0$, at $\varepsilon = \varepsilon^*_{nl}$, and the values of ε^*_{nl} are determined by the points of intersection of the curves of $E_{nl}(\varepsilon)$ with the abscissa. Bearing in mind that the convergence of the Padé approximants in the region of $\varepsilon \sim \varepsilon^*_{nl}$ is slower than in the case of the *s* states, the numerical values of ε^*_{nl} for $l \neq 0$ were found as the roots of the diagonal Padé approximants, $E^{[N,N]}_{nl}$, for $N = 12$–14 to three decimal places:

$$\varepsilon_{21}^* = 0.220; \quad \varepsilon_{31}^* = 0.112; \quad \varepsilon_{32}^* = 0.0913.$$

On the intervals $(\varepsilon^*_{nl}, \infty)$ when $l \neq 0$ many poles of the Padé approximants accumulate, and the sequence of approximants becomes divergent. Such an arrangement of the poles is characteristic when the function has cuts[32] and reflects the circumstance that in the given case we are dealing with quasistationary states, and function $E_{nl}(\varepsilon)$ is no longer a single-valued function of the complex variable ε. For $l \neq 0$ and $\varepsilon > \varepsilon^*_{nl}$, quasistationary states arise because of the presence of a centrifugal potential barrier.

TABLE II. Convergence of the diagonal Padé approximants.

N	$E^{[N/N]}_{10}$ (0,6)	$E^{[N/N]}_{10}$ (1,1907)	$E^{[N/N]}_{10}$ (2)	$E^{[N/N]}_{21}$ (0,2)
1	−0.086206897	0.12899328	0.300000	0.008333
2	−0.083569405	0.13406982	0.307692	0.011842
3	−0.107372719	−0.04445824	−1.276265	−0.004331
5	−0.106143442	−0.00057017	−0.171065	−0.003772
7	−0.106136003	−0.00001841	−0.162066	−0.004076
10	−0.106135907	0.00000001	−0.161572	−0.004093
14	−0.106135907	−0.00000002	−0.161572	−0.004098

TABLE III. Convergence of the roots of the Padé approximants.

N	1*s*	2*s*	3*s*
1	1.3333333	0.333333	0.148148
2	1.2080718	0.309985	0.138432
3	1.1938110	0.308729	0.138138
5	1.1907975	0.310971	0.139634
7	1.1906252	0.310223	0.139434
10	1.1906123	0.310210	0.139451
14	1.1906124	0.310209	0.139451
	1.1906124 [34]	0.3103 [15]	0.1395 [15]

To find the energies of the quasistationary states, it is necessary to approximate by means of Padé approximants a certain many-valued function. For this, we introduce a new variable t so that

$$\varepsilon = \varphi(t) = \sum_{k=1}^{\infty} \varphi_k t^k,$$

and require the function that is the inverse of $\varphi(t)$ to be many valued. After this, we calculate the Padé approximants to the function $E_{nl}(\varphi(t))$ as functions of the variable $t = \varphi^{-1}(\varepsilon)$.

We choose, for example, the function

$$\varphi(t) = a(e^t - 1), \tag{17}$$

where $a \in (-\varepsilon, 0)$. Calculations show that for this choice of $\varphi(t)$ the Padé approximants $\tilde{E}^{[M/L]}_{nl}$ to the function $E_{nl}(\varphi(t)) = \tilde{E}_{nl}(t)$ for $t = \ln(-\varepsilon/a - 1) \pm i\pi$ converge in a much wider range of ε than the Padé approximants to $E_{nl}(\varepsilon)$ [which corresponds to the case $\varphi(t) \equiv t$].

In Fig. 2, the continuous curves show the real and imaginary parts of the function $\tilde{E}^{[N/N]}_{21}$ in the region $\varepsilon \sim \varepsilon^*_{21}$ for $N = 12, 13, 14$ and $a = -0.08$. The vertical bars in the figure demonstrate the spread of values of the Padé approximants as N varies from 12 to14. In the same figure we have plotted the maximal value of the potential V_M (broken curve) and the values of the ordinary Padé approximants $E^{[12/12]}_{21}(\varepsilon)$ (chain curve). Note that $\mathrm{Im}\,\tilde{E}^{[N,N]}_{21}$ differs appreciably from zero at ε

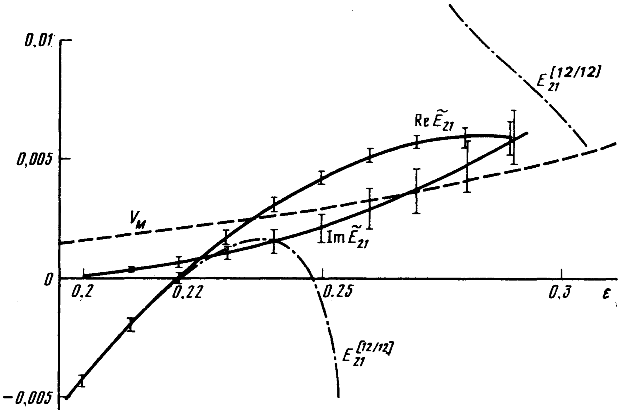

FIG. 2. Behavior of Padé approximants in the region $\varepsilon \sim \varepsilon^*_{21}$ for the state 2*p*.

values slightly less than ε_{21}^*, which can be attributed to the particular choice of the function $\varphi(t)$.

We thank M. A. Braun, Yu. Yu. Dmitriev, and L. N. Labzovskiĭ for a helpful discussion of a number of questions discussed in the paper.

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[1] The corrections of higher order given in Refs. 16 and 17 were calculated incorrectly.

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Translated by Julian B. Barbour