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Solution of Schrödinger Equation for a Particle Bound to More Than One Spherical Potential*

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We consider the quantum-mechanical problem of a particle bound to a configuration of spherical potentials, each of finite range. If the Schrödinger equation can be solved for each potential by itself, then it is shown how to solve it for the configuration, provided the potentials do not overlap. The energy levels are the zeros of a determinant of formally infinite order, but in practice this is always well approximated by a finite determinant and often by one of small order. As illustrative examples we consider some states of a particle bound to three square wells with the configuration of an equilateral triangle, and to two truncated Coulomb potentials. The possibility of extending an approximate version of the method to overlapping potentials is pointed out.

I. INTRODUCTION

IN a recent paper[1] we have treated the problem of the scattering of a wave from several scatterers, under the assumption that one could solve the problem of the scattering from each taken separately. It is more or less obvious from this work that the same point of view can be used to solve the problem of a particle bound to more than one potential, providing that the potentials do not overlap and that one can solve the bound-state problem for each of the potentials taken separately. In the present paper we spell this out in some detail.

II. THE GENERAL FORMULAS

In this section we write down an infinite secular determinant, whose roots give the energy levels of the particle.

To begin, we suppose that we have N spherically symmetric potentials fixed in space, in some definite configuration. The potentials need not all have the same shape, i.e., some may be square wells, and others cutoff Coulomb potentials, etc., but we assume that they all have finite radius, the ith potential having radius a_i, and that they do not overlap. For each potential we set up a spherical coordinate system with origin at the center of the potential and for the ith potential, coordinates r_i, θ_i, ϕ_i. These coordinate systems need not have the same orientation; in general, the most convenient orientation will be dictated by the specific problem.

We then write the general solution to the Schrödinger equation inside each of the spherical regions $1,2,\cdots N$ as follows[2]:

$$\begin{aligned}\Psi^{(1)} &= \sum_{m,l} A_{ml}^{(1)}\Phi_l^{(1)}(r_1)Y_{ml}(\theta_1,\phi_1),\\ &\vdots \\ \Psi^{(N)} &= \sum_{m,l} A_{ml}^{(N)}\Phi_l^{(N)}(r_N)Y_{ml}(\theta_N,\phi_N).\end{aligned}\tag{1}$$

In these equations the $A_{ml}^{(i)}$ are arbitrary constants. The functions $\Phi_l^{(i)}(r)$ are assumed to be known. They depend, of course, on the energy E which we are trying to find. For a square well, for example, Φ_l is just $j_l(\kappa r)$ where $\kappa=[(2m/\hbar^2)(V_0-|E|)]^{\frac{1}{2}}$, and j_l is a spherical Bessel function.

Now we write a general solution of the wave equation for the region of space *outside* all the potentials, i.e., for $r_i > a_i$, for all i. Exactly as in the problem of multiple scattering,[1] we can take the field Ψ_e (subscript e for external), in the region external to all the potentials, to be the sum of the fields produced by the individual potentials, i.e.,

$$\Psi_e=\Psi_e^{(1)}+\cdots\Psi_e^{(N)},$$

where

$$\begin{aligned}\Psi_e^{(1)} &= \sum_{m,l} B_{ml}^{(1)}h_l(ikr_1)Y_{ml}(\theta_1,\phi_1),\\ &\vdots \\ \Psi_e^{(N)} &= \sum_{m,l} B_{ml}^{(N)}h_l(ikr_N)Y_{ml}(\theta_N,\phi_N).\end{aligned}\tag{2}$$

This expression for Ψ_e is certainly a possible solution of the free space wave equation, since it is simply a linear combination of such solutions. In these equations the B_{ml} are arbitrary coefficients, the functions h_l are spherical Hankel functions of imaginary argument, and $k=(2m|E|/\hbar^2)^{\frac{1}{2}}$.

Now we require that the wave function and its radial derivative be continuous at each of the boundaries $r_1=a_1, \cdots r_N=a_N$. For matching at $r_i=a_i$, say, the internal solution $\Psi^{(i)}$ is in suitable r_i, θ_i, ϕ_i coordinates. But of the total exterior wave function Ψ_e, only $\Psi_e^{(i)}$ is in r_i, θ_i, ϕ_i coordinates, so to apply the matching conditions we must express all the other $\Psi_e^{(j)}$, $j\neq i$, in these coordinates. The basic formula for these transformations is, referring to Fig. 1, that for expressing the solution $h_l(ikr')Y_{ml}(\theta',\phi)$ in terms of new variables r, θ, ϕ, which are spherical coordinates in a coordinate system with the origin a distance d from the first but

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[1] L. Eyges, Ann. phys. **2**, 101 (1957).

[2] We use the notation of P. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953). The real spherical harmonics they define are divided into two classes, the even ones Y_{ml}^e and the odd ones Y_{ml}^o. For the general development it is convenient not to put in the superscripts and to leave it understood that Y_{ml} refers to either an even or odd harmonic to which there corresponds coefficients $A_{ml}^{(i)e}$ and $A_{ml}^{(i)o}$.

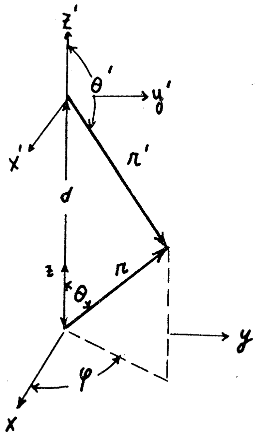

FIG. 1. Illustrating the geometry involved in expressing solutions of the wave equation $h_l(ikr')Y_{ml}(\theta',\phi)$ in terms of functions of the unprimed variables r, θ, and ϕ.

with the same orientation as the first. This formula is,[1] for $r<d$:

$$h_l(ikr')Y_{ml}(\theta',\phi)$$

$$=D(l)\sum_{n=0}^{\infty}\sum_{s=0}^{l}(n+l+\tfrac{1}{2})$$

$$C_n{}^{l+\frac{1}{2}}(\cos\theta)\frac{j_{l+n}(ikr)}{(ikr)^l}h_{l+n}(ikd)$$

$$\times\frac{(-)^{l-s}(l+m)!}{(l-s)!(m+s)!}\left(\frac{r}{d}\right)^s Y_{ms}(\theta,\phi),\quad(3)$$

where $D(l)=2^{l+\frac{1}{2}}(2/\pi)^{\frac{1}{2}}\Gamma(l+\frac{1}{2})$, $\Gamma(l)$ is the gamma function, and $C_n{}^{l+\frac{1}{2}}$ is a Gegenbauer[3] polynomial. This is expressible completely in terms of spherical harmonics $Y_{m's'}(\theta,\phi)$ if we write

$$C_n{}^{l+\frac{1}{2}}(\cos\theta)Y_{ms}(\theta,\phi)=\textstyle\sum_{m's'}D_{nl,\,ms,\,m's'}Y_{m's'}(\theta,\phi),\quad(4)$$

and get the coefficients $D_{nl,\,ms,\,m's'}$ by the orthogonality of the $Y_{m's'}$. By the addition theorem for spherical harmonics, we can always reduce the problem of transformation for two arbitrary coordinate systems to that for two coordinate systems with the same orientation, and for which Eq. (3) applies. Thus we can always transform from the jth to the ith coordinate system in a way which we can write symbolically as

$$h_{l'}(ikr_j)Y_{m'l'}(\theta_j,\phi_j)$$
$$=\textstyle\sum_{ml}F_{ml,\,m'l',\,ij}(r_i,R_{ij})Y_{ml}(\theta_i,\phi_i),\quad r_i<R_{ij},\quad(5)$$

where R_{ij} is the distance between potentials i and j, and where the $F_{ml,\,m'l',\,ij}$ are functions of the relative orientations and separations of the two coordinate systems, and are calculable once these are prescribed. Although one could write a specific expression in the general case of N potentials for these functions, it is too clumsy to be instructive. In any particular case they can be worked out.

Now, the condition that the wave function be continuous at $r_i=a_i$ can be written

$$\sum_{m,l}A_{ml}{}^{(i)}\Phi_l{}^{(i)}(a_i)Y_{ml}(\theta_i,\phi_i)$$

$$=\sum_{m,l}B_{ml}{}^{(i)}h_l(ika_i)Y_{ml}(\theta_i,\phi_i)$$

$$+\sum_{\substack{m,l,m',l',j\\ j\neq i}}B_{m'l'}{}^{(j)}F_{ml,\,m'l',\,ij}(a_i,R_{ij})Y_{ml}(\theta_i,\phi_i).\quad(6a)$$

The condition that the radial derivative be continuous is

$$\sum_{m,l}A_{ml}{}^{(i)}\left(\frac{\partial}{\partial r_i}\Phi_l{}^{(i)}(a_i)\right)Y_{ml}(\theta_i,\phi_i)$$

$$=\sum_{m,l}B_{ml}{}^{(i)}\left(\frac{\partial}{\partial r_i}h_l(ika_i)\right)Y_{ml}(\theta_i,\phi_i)$$

$$+\sum_{\substack{m,l,m',l',j\\ j\neq i}}B_{m'l'}{}^{(j)}\left(\frac{\partial}{\partial r_i}F_{ml,\,m'l',\,ij}(a_i,R_{ij})\right)$$

$$\times Y_{ml}(\theta_i,\phi_i),\quad(6b)$$

where, e.g., $(\partial/\partial r_i)\Phi_l(a_i)$ means, of course,

$$\left.\frac{\partial}{\partial r_i}\Phi_l(r_i)\right|_{r_i=a_i}.$$

For each of the N potentials we have an equation like (6a) and one like (6b), $2N$ equations in all. In each of these $2N$ equations we equate to zero the coefficients of spherical harmonics. This gives the following infinite set of homogeneous linear equations which hold for all i, m, and l, for the amplitudes $A_{ml}{}^{(i)}$ and $B_{ml}{}^{(i)}$:

$$A_{ml}{}^{(i)}\Phi_l{}^{(i)}(a_i)-B_{ml}{}^{(i)}h_l(ika_i)$$
$$-\sum_{\substack{m'l'j\\ j\neq i}}B_{m'l'}{}^{(j)}F_{ml,\,m'l',\,ij}(a_i,R_{ij})=0,\quad(7a)$$

$$A_{ml}{}^{(i)}\left(\frac{\partial}{\partial r_i}\Phi_l{}^{(i)}(a_i)\right)-B_{ml}{}^{(i)}\left(\frac{\partial}{\partial r_i}(h_l(ika_i)\right)$$

$$-\sum_{\substack{m'l'j\\ j\neq i}}B_{m'l'}{}^{(j)}\frac{\partial}{\partial r_i}F_{ml,\,m'l',\,ij}(a_i,R_{ij})=0.\quad(7b)$$

We then equate the determinant of this set of equations to zero and the energy levels we seek are the roots of this secular equation. The rows of this determinant are labeled by the sequence[2]

$$Y_{00}(1),\quad Y_{00}(1')\cdots Y_{00}(N),\quad Y_{00}(N');$$
$$Y_{01}{}^e(1)\cdots Y_{01}{}^e(N');\quad Y_{01}{}^o(1)\cdots Y_{01}{}^o(N');\ \cdots,$$

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[3] These are defined in different ways by different authors. We use the definition given by A. Erdelyi in *Higher Transcendental Functions*, edited by Bateman Project (McGraw-Hill Book Company, Inc., New York, 1954), Vol. 2.

where $Y_{ml}(i)$ refers to the equation got by equating to zero the coefficients of Y_{ml} in the ith one of Eqs. (6a) (function continuous) and $Y_{ml}(i')$ to the corresponding equation of Eqs. (6b) (derivative continuous). The columns of the determinant are labelled by the sequence

$$A_{00}{}^{(1)},\quad B_{00}{}^{(1)}\cdots A_{00}{}^{(N)},\quad B_{00}{}^{(N)};$$
$$A_{01}{}^{(1)e}\cdots B_{01}{}^{(N)e};\quad A_{01}{}^{(1)o}\cdots B_{01}{}^{(N)o};\ \cdots.$$

This labeling is arbitrary, of course. One can interchange the rows and columns of the determinant at will. The most advantageous labeling will be determined by the properties of the state functions that one is looking for. If in particular examples, one knows something about these properties in advance, e.g., from group theory, then one can use this information to advantage in labelling the determinant. It is hard to indicate how this is to be done in general. But this question is closely connected with the question of how in practice the infinite determinant breaks down to a finite one, and this is discussed in the next section.

III. QUESTIONS OF CONVERGENCE

The infinite secular determinant we have described is not useful unless it is accurately approximated by a reasonably small finite determinant. This is so, in many practical examples. The basic reason is the behavior for large order $l+n$ of the Bessel functions j_{l+n} that occur in the transformation equation (3). In the argument ikr of these functions, k is real and r is always set equal to some radius a, so we have to deal with functions $j_{l+n}(ika)$. Now these functions become very small for $l+n \gg ka$, and hence the terms in (3) for which this condition is satisfied can be neglected. This has a consequence that the determinantal equation does not involve spherical harmonics of high order, and is to a good approximation a finite one. The question of just how much greater $l+n$ must be than ka in order to make the approximation we have indicated is one that cannot be answered in general. It depends of course not only on the value of ka but on the accuracy that one seeks and on the value of kd. The dependence on kd is usually weak, however, and it is the numerical value of ka that dominates the series.

The fact that only a finite number of Bessel functions need be taken into account is closely related to the fact that the scattering of plane waves of wave number k from an object of size a involves to good accuracy only the first ka partial waves. The reason for this is, of course, that the transformation formula we use is very similar to the formula for expanding a plane wave in spherical coordinates. For example, Eq. (3) for $l=0$ is the expansion of a point source in a spherical coordinate system a distance d from the source, and it is easy to see that when d approaches infinity it becomes the expansion for a plane wave. Of course, for the scattering problem the argument of the Bessel functions is real, and for the bound-state problem it is imaginary, but this does not make an essential difference.

TABLE I. Illustration of the convergence of the expansion of Eq. (3) for $l=0$. $h_0(ikr')=\Sigma_{n=0}\,A_nP_n(\cos\theta)$, where $A_n=(2n+1)\times j_n(ikr)h_n(ikd)$.

	$kd=3.0$		
n	$A_n/A_0,\quad kr=0.5$	$A_n/A_0,\quad kr=1.0$	$A_n/A_0,\quad kr=1.5$
0	1.000	1.000	1.000
1	0.478	1.252	1.168
2	0.138	0.710	1.441
3	0.0308	0.313	0.980
4	0.00651	0.123	0.546
5	0.00114	0.0454	0.300
6		0.00164	0.161

The size of the secular determinant is determined then by the convergence of the series in Eq. (3). To illustrate the kind of convergence to be expected in practical problems we give in Table I the coefficients in the expansion of $h_0(ikr')$ for some representative values of the parameters. ka is often of the order of unity for practical problems.

Even though one has an idea of the convergence of (3) for various values of the parameters, an important question remains: how can one determine *in advance* where to cut off the secular equation? There is a circularity that must be cut through. That is, the effective size of the secular equation is determined by the energy, that is to say by ka. On the other hand, the energy is not given *a priori* but is determined by the secular equation. Where does one start?

Effectively, the answer is that one must make a guess from the physics of the specific situation and then see if this guess is consistent. It is, of course, impossible to describe how to do this in general; each case is different. Some light is thrown on this question in Sec. IV, where we treat some specific examples. It is worth noting that this method is in some respects easier to apply in finding excited states of the system since ka gets smaller and smaller for higher and higher excited states. This is an unusual result in that ordinarily the ground state is easiest to treat in most approximation methods.

IV. SOME ILLUSTRATIVE EXAMPLES

a. Three Square Wells: *S* Waves Only

We now consider some illustrative examples. We begin by considering some states of a particle bound to three identical square wells whose centers form an equilateral triangle of side d. The potential energy V in each well is $V=-V_0$ for $r<a$, and is zero for $r>a$. We assume $d>2a$.

For comparison, we first state the well-known results for a single square well. For this we define the internal wave number $k_i=[(2m/\hbar^2)(V_0-|E|)]^{\frac{1}{2}}$ and the external wave number $k_e=[(2m/\hbar^2)|E|]^{\frac{1}{2}}$, where E is, of course, negative for a bound state. We also define the parameters $\xi=k_ia$, $\eta=k_ea$. Then the internal solution for a spherically symmetric state is $j_0(k_i r)$ and the external solution is $h_0(ik_e r)$. The condition that the wave function and its derivative be continuous at $r=a$ leads to the pair of equations

$$\xi \cot\xi = -\eta, \tag{8a}$$

$$\xi^2+\eta^2=\lambda^2, \tag{8b}$$

where

$$\lambda^2 = V_0 a^2 2m/\hbar^2.$$

The properties of the solutions of this set of equations depend of course on the value of λ.

Now we come back to the three square wells. For the sake of a simple example, let us suppose that λ is such that for a *single* well there is a spherically symmetric state which is very weakly bound, i.e., one for which η is small compared to unity. This is always possible for an appropriate choice of λ. If the three potentials are very far apart there are states of this kind corresponding to a particle localized around, i.e., bound to, any of these three wells. And there is, of course, a state of the same energy which corresponds to a linear combination of these localized states. If now the wells are brought together the energy of this state will become lower, and it is this we shall calculate. We also expect that if the energy remains sufficiently small, the wave function remains spherically symmetric inside each of the three potentials.

As a consequence of the symmetrical geometry, and the assumed symmetry of the state, we can confine ourselves to matching the wave function at only one boundary, say $r_1=a_1$. Hence we write, with the assumption of S waves only,

$$\Psi^{(1)} = A j_0(k_i r_1).$$

This is of course a special case of the general Eqs. (1); Eqs. (2), for the solution in the region of space outside all the potentials become, using only the lowest order spherical harmonic,

$$\Psi_e = B[h_0(ik_e r_1)+h_0(ik_e r_2)+h_0(ik_e r_3)].$$

For satisying the continuity conditions at $r_1=a$ we put $h_0(ikr_2)$ and $h_0(ikr_3)$ into r_1 coordinates, using only the first term in the expansion (3) for $l=0$; i.e., near $r_1=a$ we use $h_0(ik_e r_2)\approx j_0(ik_e r_1)\, h_0(ik_e d)$, and similarly for $h_0(ikr_3)$.

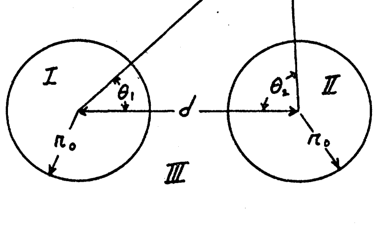

FIG. 2. Geometry for a particle bound to two truncated Coulomb potentials. In region I the potential is $-e^2/r_1$; in region II it is $-e^2/r_2$, and in region III it is zero.

With these simplifying assumptions the infinite determinant becomes the following transcendental equation determining the energy

$$\frac{\xi j_0'(\xi)}{j_0(\xi)} = i\eta \frac{h_0'(i\eta)}{h_0(i\eta)} \left\{ \frac{1+2j_0'(i\eta)h_0(ik_e d)/h_0'(i\eta)}{1+2j_0(i\eta)h_0(ik_e d)/h_0(i\eta)} \right\}.$$

If we express the Bessel functions in terms of trigonometric functions and exponentials we get

$$\xi\cot\xi = 1-(1+\eta) \times \left\{ \frac{1+[e^{2\eta}(1-\eta)-(1+\eta)e^{-\gamma\eta}]/[\gamma\eta(\eta+1)]}{1+(e^{2\eta}-1)e^{-\gamma\eta}/\gamma\eta} \right\}, \tag{9}$$

where γ is the ratio of the separation of the potential wells to their radius, i.e., $\gamma=d/a$. For $\gamma\rightarrow\infty$, we see that the expression in the curly brackets in (9) becomes unity and we get back the transcendental equation (8a) corresponding to a particle bound to a single well.

Since we have assumed η small, we can consistently expand the expression in the curly bracket in (9) in powers of it; in lowest order this expression is independent of η and is just equal to $(1+2/\gamma)^{-1}$. In this approximation the transcendental equation becomes

$$\xi\cot\xi = \frac{-\eta+(2/\gamma)}{1+(2/\gamma)}.$$

We can get a specific expression for the new energy by expanding this equation about its value when γ is infinite. That is, we assume $\xi=\xi_0+\xi'$, $\eta=\eta_0+\eta'$, where now we use ξ_0 and η_0 to mean the solution of Eq. (8). We get to first order in η_0

$$\eta = \eta_0 + \frac{2}{\gamma}(1+\eta_0).$$

This result shows that η (which is proportional to the square root of the energy) remains small only if γ is very large. Thus, even though η_0 is small, i.e., even though a *single* well has a very weakly bound level, this will not be the case for three wells when they are at all close together. Physically this is not surprising. If a particle is bound to a well with very small binding energy, this energy is small because the mean kinetic energy is very nearly equal to the mean potential energy; there is almost an exact balance. If now the shape of the potential energy contour is changed, e.g., by bringing up a second (and third) well from infinity there is no reason in general why this balance should not be upset and why the binding energy should not become appreciable.

It goes without saying that this simple example far from exhausts a complete description of the states of this system. In general, however, calculation of the energies can only be done numerically, for definite prescribed values of the parameters λ and d. This is true even for a particle bound to a single well, and the system we discuss is very much more complicated. This example is meant only to be pedagogical and to illustrate the general result of Sec. II in a simple way.

b. Two Truncated Coulomb Potentials: *S* and *P* Waves

As a second illustrative example we take the problem of a particle bound to two truncated Coulomb potentials. We refer to Fig. 2. The potential within region I is proportional to $-1/r_1$ for $r_1 < r_0$. It is convenient to get into familiar units by taking the constant of proportionality to be e^2, where e is the electron charge. Thus, within I the potential is $-e^2/r_1$ for $r_1 < r_0$, and similarly within II. The potential in region III is zero. To begin, we write down the known results for the solution of the Schrödinger equation for a region of space in which there is a Coulomb potential. We use atomic units: radial distances r are measured in units of the Bohr radius a_0; energies E in units of rydbergs, $e^2/2a_0$. Then the solution $C_l(\epsilon,x)$ of the radial Schrödinger equation for an attractive Coulomb potential, for E negative, and for angular momentum l, is[4]

$$C_l(\epsilon,x) = x^l e^{-x/2} F_l(\epsilon,x),$$

where

$$\epsilon = 1 - 1/(|E|)^{\frac{1}{2}}, \quad x = 2(|E|)^{\frac{1}{2}} r,$$

and $F_l(\epsilon,x)$ is a hypergeometric function defined by the series

$$F_l(\epsilon,x) = 1 + \frac{2l+\epsilon}{2l+2}x + \frac{(2l+\epsilon)(2l+\epsilon+1)x^2}{2!(2l+2)(2l+3)} + \frac{(2l+\epsilon)(2l+\epsilon+1)(2l+\epsilon+2)}{3!(2l+2)(2l+3)(2l+4)}x^3 + \cdots.$$

For reference in what follows we write the transcendental equation determining the ground-state energy for a "cutoff hydrogen atom," i.e., one for which the potential is Coulomb for $r < r_0$ and zero for $r > r_0$. For such a system the interior solution for $l=0$ is

$$\Psi_{\text{in}} = e^{-x/2} F_0(\epsilon,x),$$

and the exterior solution is

$$\Psi_e = \frac{e^{-x/2}}{x/2}.$$

Continuity of the logarithmic derivative at $x_0 = 2(|E|)^{\frac{1}{2}} r_0$ gives an equation for the energy,

$$F_0'(\epsilon,x_0)/F_0(\epsilon,x_0) = -1/x_0, \tag{10}$$

where a prime means differentiation with respect to the variable x and then setting x equal to x_0.

Now we return to the problem of the ground state of a particle bound to *two* truncated Coulomb wells. We assume that it is sufficient to take only the first two spherical harmonics in the expansion of the wave function inside region I; this will be adequate if r_0 is not too large, since the parameter that determines the convergence is $x_0 = 2(|E|)^{\frac{1}{2}} r_0$ and when r_0 decreases, E also decreases, and as a consequence so does x_0. Of course, this is not the way that problems usually present themselves in practice. Ordinarily a quantity such as r_0 would be prescribed in advance, and then we would be faced with the problem mentioned before, of determining where to cut off the secular equation. But for the sake of illustration we can invert this procedure and assume that we know that r_0 is small enough to justify our keeping only S and P waves. With this simplification the solution inside region I is

$$\Psi^{(1)} = A_0 e^{-x_1/2} F_0(\epsilon,x_1) + A_1 e^{-x_1/2} x_1 F_1(\epsilon,x_1) P_1(\cos\theta_1)$$

and because of the symmetry of the ground state we can take a similar solution, with x_1 and θ_1 replaced by x_2 and θ_2, inside region II.

We then take for the solution in region III

$$\Psi_e = B_0 h_0(ix_1/2) + B_1 h_1(ix_1/2) P_1(\cos\theta_1) + B_0 h_0(ix_2/2) + B_1 h_1(ix_2/2) P_1(\cos\theta_2),$$

and it suffices, by the symmetry of the problem to match the wave function and its derivative at $r_1 = r_0$.

To do this, we express Ψ_e completely in x_1 coordinates using Eq. (3). Since we have taken only S and P waves inside region I, we need include only terms through $P_1(\cos\theta_1)$ in these formulas. We get for $r < d$, with $y_0 = kd$,

$$\begin{aligned}\Psi_e = {} & B_0[h_0(ix_1/2) + j_0(ix_1/2) h_0(iy_0) + 3j_1(ix_1/2) h_1(iy_0) P_1(\cos\theta_1)] \\ & + B_1\Big[h_1(ix_1/2) P_1(\cos\theta_1) + \frac{3j_1(ix_1/2)}{ix_1/2} h_1(iy_0) + \frac{15 j_2(ix_1/2)}{ix_1/2} h_2(iy_0) P_1(\cos\theta_1) \\ & \qquad - 3j_1(ix_1/2) \frac{h_1(iy_0)}{iy_0} P_1(\cos\theta_1)\Big].\end{aligned}$$

The determinantal equation is then as follows. Note that a prime on a function means differentiation with respect to x_0, and not with respect to the argument, which may be $ix_0/2$. This convention simplifies the

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[4] P. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 632.

formula a bit.

$$\begin{vmatrix}
e^{-x_0/2}F_0(\epsilon,x_0) & \begin{array}{l}-h_0(ix_0/2)\\ \quad -j_0(ix_0/2)h_0(iy_0)\end{array} & 0 & -\dfrac{3j_1(ix_0/2)}{ix_0/2}h_1(iy_0) \\[2ex]
\begin{array}{l}e^{-x_0/2}[F_0'(\epsilon,x_0)\\ \quad -\frac{1}{2}F_0(\epsilon,x_0)]\end{array} & \begin{array}{l}-h_0'(ix_0/2)\\ -j_0'(ix_0/2)h_0(iy_0)\end{array} & 0 & \dfrac{2}{ix_0}\left(-3j_1'(ix_0/2)+\dfrac{3j_1(ix_0)}{x_0}\right)h_1(iy_0) \\[2ex]
0 & 3j_1(ix_0/2)h_1(iy_0) & -e^{-x_0/2}x_0F_1(\epsilon,x_0) & \begin{array}{l}-\dfrac{3j_1(ix_0/2)}{ix_0/2}h_1(iy_0)\\[1ex] +\dfrac{15j_2(ix_0/2)}{ix_0/2}h_2(iy_0)+h_1(ix_0/2)\end{array} \\[2ex]
0 & 3j_1'(ix_0/2)h_1(iy_0) & \begin{array}{l}-e^{-x_0/2}(x_0/2)F_1'(\epsilon,x_0)\\ -F_1(\epsilon,x_0)e^{-x_0/2}(1-\frac{1}{2}x_0)\end{array} & \begin{array}{l}\dfrac{6}{ix_0}\left(-j_1'(ix_0/2)+\dfrac{j_1(ix_0/2)}{x_0}\right)h_1(iy_0)\\[1ex] +\dfrac{30}{ix_0}\left(j_2'(ix_0/2)-\dfrac{j_2(ix_0/2)}{x_0}\right)h_2(iy_0)\\[1ex] +h_1'(ix_0/2)\end{array}
\end{vmatrix}=0.$$

We can write this in a form that resembles Eq. (10) if we expand the determinant in minors of the first column. This gives

$$\frac{F_0'(\epsilon,x_0)}{F_0(\epsilon,x_0)}=\tfrac{1}{2}+\frac{M_{11}(\epsilon,x_0)}{M_{21}(\epsilon,x_0)}, \tag{11}$$

where M_{11} and M_{21} are the minors of the 11 and 21 elements of the determinant. When d becomes infinite, this equation becomes identical with Eq. (10). As for the preceding example this equation can only be solved numerically, once r_0 and d are prescribed. We shall not do this here. Suffice it to say that for ϵ small the right-hand side of (11) is weakly dependent on ϵ, and it is then not much more difficult to solve (11) than to solve (10).

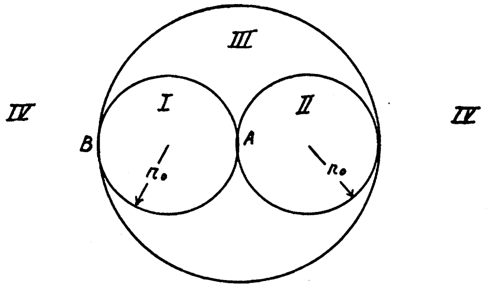

FIG. 3. Illustrating the division of space into regions appropriate for an approximate treatment of overlapping potentials.

V. OVERLAPPING POTENTIALS

One can apply an approximate version of this method to overlapping potentials, if it is possible to break space up into spherical regions, inside of each of which one can approximate the overlapping tails of the potentials by their average values. To illustrate this, consider the problem of a particle moving in two Coulomb fields, e.g., the problem of the hydrogen molecule-ion, where an electron moves in the Coulomb potentials due to two protons. We refer to Fig. 3. The potential energy for an electron moving in the field of two protons is, in atomic units, $-2(1/r_1+1/r_2)$. Now we divide space into four regions I, II, III, IV by drawing two spheres of radius r_0, one centered at each proton, and a third sphere of radius $2r_0$ with center at the origin. A possible procedure is to approximate the potentials in each of these regions, to solve this approximate problem "exactly" (in the sense of the previous sections), and then to take the difference of the true and approximate potentials into account by first-order perturbation theory.

We discuss some possibilities. The correct potential in region I, say, is just

$$-\left[\frac{2}{r_1}+\frac{1}{r_0}\sum_{l=0}^{\infty}\left(\frac{r_1}{2r_0}\right)^l P_l(\cos\theta_1)\right]. \tag{12}$$

If we can approximate the potential in I by taking only the first term in the series in (12), i.e., by taking the average value of potential II into account in region I, and vice versa, we are left with a soluble Schrödinger equation: the potential in I remains spherically symmetric and the extra constant term $1/r_0$ makes for no difficulty in its solution. With this, the approximate potential is $3/r_0$ at point A instead of the correct value of $4/r_0$, and at point B the approximate potential is $3/r_0$ instead of the correct value of $8/3r_0$. These are the worst cases, in the sense that the approximate potential is much less accurate at these points near the boundary of region I where r_1 is large than it is for r_1 small.

Similarly we still have an exactly soluble problem if we take into account the average value of the potential in region III, and neglect the tails of the potentials completely in region IV. For if we write the wave function in III as the sum of two wave functions, one in r_1 coordinates and the other in r_2 coordinates, we can always express this wave function in (r,θ) coordinates and match this to the free-space wave function in region IV. One sees from this point of view that although potentials like the Coulomb potential which are slowly varying have the disadvantage that they cannot be solved exactly by the method of the previous section, they have the advantage that they can be well approximated by their average values over appreciable regions of space.

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Recurrence Time of a Dynamical System

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Poincaré cycles of a many-particle system are exemplified by the motion of a linear chain. It is shown that the recurrence time increases in an approximately exponential way with the number of degrees of freedom, and as a power of the sharpness with which the recurrent state is specified. An explicit formula is given which is applicable to other separable dynamical systems as well.

INTRODUCTION

IN an interesting paper by Frisch,[1] the old questions of Poincaré cycles have been reconsidered. Besides Liouville's theorem, with which it is intimately connected, there is probably no other theorem of general dynamics so simple and so well founded as Poincaré's about the recurrence of all bounded mechanical motions. Far from creating a paradox to the mechanical theory of heat—as held by Zermelo in the famous discussion with Boltzmann—it can on the contrary be made a pillar in the foundation of statistical mechanics.

Corresponding recurrence theorems in quantum mechanics were given in a recent paper by Bocchieri and Loinger.[2] However, as was pointed out by Frisch,[1] very little is known about the actual magnitude of the recurrence times. It is the purpose of the present paper to supply an explicit calculation, albeit for a very special system, *viz.*, a linear chain. To be sure, the linear chain, like any separable mechanical system, is ergodic only in the space of the angle variables, but that does not detract from the meaning of a recurrence. For the calculation one needs only those dynamical features which are common to all separable systems, but for definiteness we shall write down the formulas appropriate to the linear chain.

1. DYNAMICAL STARTING POINT

Let the chain consist of N equal mass points, harmonically coupled neighbor to neighbor, and consider their longitudinal displacements u_k $(k=0,1,2,\cdots N-1)$. If we assume the end points of the chain to be free, the normal coordinates,

$$q_j=\sum_k C_{jk}u_k, \quad (j=0,1,\cdots N-1) \tag{1}$$

are given by

$$C_{jk}=(\epsilon_j/N)^{\frac{1}{2}}\cos[(k+\tfrac{1}{2})\pi j/N], \quad \epsilon_j=\begin{cases}2, & j\neq 0\\ 1, & j=0,\end{cases} \tag{2}$$

where the mode $j=0$, representing a free translation of the whole chain, is of no interest for our problem. The corresponding frequencies are

$$\omega_j=\omega_0\sin(\pi j/2N), \tag{3}$$

where ω_0 is a maximum frequency related to the spring constant and mass of the particles. Compounding momenta and coordinates in the complex vectors

$$Z_j=p_j+im\omega_jq_j, \tag{4}$$

the entire motion is expressed by

$$Z_j=a_je^{i\omega_jt}, \tag{5}$$

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[1] H. L. Frisch, Phys. Rev. 104, 1 (1956).

[2] P. Bocchieri and A. Loinger, Phys. Rev. 107, 337 (1957).