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BOUND STATE PERTURBATION THEORY : A NEW APPROACH

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A B S T R A C T

New formulae are derived for the n -th order coefficients in the perturbation expansion of a bound state energy in non-relativistic quantum mechanics. These formulae involve only the unperturbed wave-function and unperturbed energy, and not a sum over all the unperturbed states, as in the usual expressions. Explicit conditions for the convergence of the perturbation series are given, involving only the potentials, and the unperturbed wave-functions. These conditions include bounds on truncation errors, so that one can compute in advance how many terms must be taken for a pre-assigned accuracy.

1. - INTRODUCTION

One of the practical disadvantages of the usual perturbation theory for the calculation of bound-state energies is that one needs to know the complete spectrum of eigenvalues and eigenstates of the unperturbed Hamiltonian, if one is to proceed beyond first order. There are cases where one only knows the ground state of the unperturbed Hamiltonian, and here the usual theory only permits one to calculate the first-order change in the energy level. It is the purpose of this paper to provide an alternative method for the calculation of higher order perturbations, given only the unperturbed energy and the corresponding eigenstate wave-function.

Generally speaking, even if the complete set of unperturbed eigenfunctions is at hand, it is still a considerable computational problem to calculate higher-order coefficients, unless there are special simplifying circumstances. Moreover, alternative methods are available for the evaluation of perturbed energy levels, for example the variational method ¹⁾ or, for the many-electron atom, the Hartree-Fock ¹⁾ technique. Compared with these methods, perturbation theory often converges very slowly, and in some cases not at all. Nevertheless, even when the perturbation series diverges, it may have value as an asymptotic series, and it may be possible to resum it by means of some algorithm that gives convergence when the simple series diverges, and which considerably speeds convergence in cases where the series converges in the first place. Such a summation procedure is the method of Padé approximants, which has recently been shown to provide good convergence for the anharmonic oscillator problem ²⁾.

The paper is laid out as follows. In Section 2, a heuristic derivation of the second-order perturbation term is given, using only classical differential equation techniques. After a résumé of the usual Green's function formulation of perturbation theory ¹⁾ in Section 3, a new Green's function is introduced in Section 4, and a new form of the perturbation series is obtained, in which each term only involves the unperturbed eigenfunction and eigenvalue, and not the infinite sum over all the eigenstates of the unperturbed Hamiltonian, as in the usual

formulae. For simplicity, it is assumed throughout that the unperturbed eigenvalue is not degenerate, otherwise one would have the usual diagonalization problem in the subspace of the eigenfunctions belonging to the unperturbed eigenvalue. For definiteness, the radial Schrödinger equation is treated, but of course the formulae apply equally well to the odd solutions of a one-dimensional problem with a symmetric potential. For the even solutions, in which the derivative of the wave-function, rather than the wave-function itself, vanishes at the origin, the formulae are a little different. It is shown that the second-order term agrees with the formula obtained in the heuristic treatment of Section 2. It is suggested that, instead of expanding the perturbed energy as a power series in the perturbation, in which the high-order terms are somewhat unwieldy (as is also the case for the usual perturbation expression), it would be better to define the perturbed energy as the limit of a sequence of rational fractions in the perturbation. A compact and usable expression is given for this sequence.

In Section 5, lower bounds are given for the radius of convergence of the perturbation series. These formulae involve only the two potentials, and the unperturbed eigenfunction. In order to cover all potentials of physical interest, it is necessary to work in a Banach space more general than a Hilbert space. An inner product is defined as in L^2 Hilbert space, but the norm is no longer constrained to be the L^2 norm. In Section 6, it is shown that the general formulae of Section 5 can be specialized to L^2 Hilbert space itself, in the case that the potential diverges monotonically to $+\infty$, as $r \rightarrow \infty$, faster than $r^{2/3}$. Certain technical assumptions of smoothness, expressed as asymptotic conditions on the first two derivatives of the potential, are needed. In Section 7, a point-norm is introduced, which allows the treatment of potentials which vanish, as $r \rightarrow \infty$, faster than $1/r$. The known exponential asymptotic behaviour of the wave-function is exploited in the definition of this norm. In Section 8, a generalization of the point-norm of Section 7 is used, and this allows the potential to have any asymptotic behaviour, less than exponential, as $r \rightarrow \infty$. For cases of physical interest, this general norm should suffice. However, it does not, in principle, supersede the L^2 norm of Section 6 for a potential that diverges faster than $r^{2/3}$, in that the L^2 norm allows worse local singularities than does the point-norm.

It is assumed throughout that the radial Schrödinger equation is for an S wave, and that the potential does not diverge as badly as $1/r^2$, as $r \rightarrow 0$. However, this is purely for simplicity, and there is no doubt that singular, repulsive cores could be handled as usual ³⁾.

2. - HEURISTIC TREATMENT

Suppose that $\psi(r; E_0)$ is a real eigensolution of the radial Schrödinger equation,

$$\left[-\left(\frac{d}{dr}\right)^2 + V(r) - E_0\right]\psi(r; E_0) = 0, \quad (2.1)$$

that satisfies the usual bound-state condition at infinity,

$$\psi(r; E_0) \xrightarrow{r \rightarrow \infty} 0, \quad (2.2)$$

the normalization condition

$$\int_0^\infty dr \psi^2(r; E_0) = 1, \quad (2.3)$$

and the eigensolution condition

$$\psi(r; E_0) \xrightarrow{r \rightarrow 0} 0. \quad (2.4)$$

Let the Hamiltonian be perturbed now by an additional potential $\lambda U(r)$, and suppose that $\varphi(r; E, \lambda)$ is the solution of the equation

$$\left[-\left(\frac{d}{dr}\right)^2 + V(r) + \lambda U(r) - E\right] \varphi(r; E, \lambda) = 0 \quad (2.5)$$

that satisfies

$$\varphi(r; E, \lambda) \xrightarrow{r \rightarrow \infty} 0, \quad (2.6)$$

and

$$\int_0^\infty dr \varphi^2(r; E, \lambda) = 1. \quad (2.7)$$

Then it is required to find the eigenvalue, $E = E(\lambda)$, for which

$$\varphi(r; E, \lambda) \xrightarrow{r \rightarrow 0} 0, \quad (2.8)$$

$$\varphi(r; E, \lambda) \xrightarrow{\lambda \rightarrow 0} \psi(r; E_0), \quad (2.9)$$

$$E(\lambda) \xrightarrow{\lambda \rightarrow 0} E_0. \quad (2.10)$$

It is assumed that E_0 is a simple eigenvalue of the unperturbed Hamiltonian.

Consider the problem of calculating $E(\lambda)$ to first order in λ . For the moment, let us pretend that we know $\varphi(r; E, \lambda)$, as a function of r, E, λ , where the conditions (2.6) and (2.7) are explicitly satisfied. In practice, of course, we do not really know $\varphi(r; E, \lambda)$,

but only $\psi(r; E_0)$, but this will turn out to be enough. One can consider E to be an implicit function of λ by virtue of the eigenvalue condition (2.8), i.e. :

$$\varphi(0; E, \lambda) = 0, \quad (2.11)$$

for then

$$\frac{\partial}{\partial \lambda} \varphi(0; E, \lambda) + \frac{dE}{d\lambda} \frac{\partial}{\partial E} \varphi(0; E, \lambda) = 0, \quad (2.12)$$

so that

$$E = E_0 - \lambda \left[\frac{\frac{\partial}{\partial \lambda} \varphi(0; E, \lambda)}{\frac{\partial}{\partial E} \varphi(0; E, \lambda)} \right]_{\lambda=0} + O(\lambda^2). \quad (2.13)$$

Evidently, one does not need $\varphi(r; E, \lambda)$ completely, but only its partial derivatives with respect to E and λ , at $r = 0$ and $\lambda = 0$. The problem, then, is to evaluate these partial derivatives.

By differentiation of Eq. (2.5), one has

$$\begin{aligned} [-(\frac{\partial}{\partial r})^2 + V(r) + \lambda U(r) - E] \frac{\partial}{\partial E} \varphi(r; E, \lambda) \\ = \varphi(r; E, \lambda), \end{aligned} \quad (2.14)$$

and

$$\begin{aligned} [-(\frac{\partial}{\partial r})^2 + V(r) + \lambda U(r) - E] \frac{\partial}{\partial \lambda} \varphi(r; E, \lambda) \\ = -U(r) \varphi(r; E, \lambda). \end{aligned} \quad (2.15)$$

One can regard Eq. (2.14) as a differential equation for $\partial\varphi/\partial E$, with the known inhomogeneous term, φ . But since one already has at hand one solution of the corresponding homogeneous equation, namely φ itself, one can work out the general solution of Eq. (2.14), by the method of variation of parameters. This gives

$$A\varphi(r;E,\lambda) + B\varphi(r;E,\lambda)\int_0^r ds \varphi^{-2}(s;E,\lambda) + \varphi(r;E,\lambda)\int_0^r ds \varphi^{-2}(s;E,\lambda)\int_s^\infty dt \varphi^2(t;E,\lambda), \quad (2.16)$$

where A and B are arbitrary constants. In order to evaluate $\partial\varphi/\partial E$, one must calculate A and B . Now $\varphi(r;E,\lambda)$ vanishes at least as quickly as an exponential as $r \rightarrow \infty$, so $\partial\varphi/\partial E$ will also vanish in this limit. The first and third terms of (2.16) do vanish asymptotically, but the second blows up, roughly like φ^{-1} . Thus one must impose $B = 0$. The constant A can be most easily determined by differentiating the normalization condition (2.7) :

$$\int_0^\infty d\tau \varphi(\tau;E,\lambda) \frac{\partial}{\partial E} \varphi(\tau;E,\lambda) = 0. \quad (2.17)$$

Thus one obtains

$$\begin{aligned} \frac{\partial\varphi(r)}{\partial E} = & \varphi(r) \int_0^\infty dq \varphi^2(q) \int_0^{\min(r,q)} dt \varphi^{-2}(t) - \\ & - \varphi(r) \int_0^\infty dq \varphi^2(q) \int_0^\infty ds \varphi^2(s) \int_0^{\min(q,s)} dt \varphi^{-2}(t), \end{aligned} \quad (2.18)$$

where the variables E and λ have been suppressed, for brevity.

The expression (2.18) can only be considered as a formal result, since the integrals over $\varphi^{-2}(t)$ may diverge, if $\varphi(t)$ has zeros. However, the divergences cancel between the two terms of

Eq. (2.18). In particular, since $\varphi(t; E, \lambda)$ vanishes at $t = 0$, when E is an eigenenergy of the Hamiltonian, it is convenient to replace (2.18) by

$$\begin{aligned} \frac{\partial \varphi(r)}{\partial E} = & \varphi(r) \int_0^\infty dq \varphi^2(q) \int_R^{\min(r, q)} dt \varphi^{-2}(t) - \\ & - \varphi(r) \int_0^\infty dq \varphi^2(q) \int_0^\infty ds \varphi^2(s) \int_R^{\min(q, s)} dt \varphi^{-2}(t), \end{aligned} \quad (2.19)$$

where R is arbitrary. This is because (again formally)

$$\begin{aligned} \int_0^\infty dq \varphi^2(q) \int_0^R dt \varphi^{-2}(t) = \\ = \int_0^\infty dq \varphi^2(q) \int_0^\infty ds \varphi^2(s) \int_0^R dt \varphi^{-2}(t). \end{aligned} \quad (2.20)$$

It is required now to evaluate $\partial \varphi(r; E, \lambda) / \partial E$ in the limit $\lambda \rightarrow 0$, $E \rightarrow E_0$, $r \rightarrow 0$. According to Eq. (2.9), one has $\varphi(r) \rightarrow \psi(r)$. But since

$$\psi(r) \xrightarrow{r \rightarrow 0} 0, \quad (2.21)$$

it follows from Eq. (2.19) that

$$\left. \frac{\partial \varphi(0)}{\partial E} \right|_{\lambda=0} = - \lim_{r \rightarrow 0} \left\{ \psi(r) \int_r^R dt \psi^{-2}(t) \right\} \equiv -A. \quad (2.22)$$

In a similar way, it may be shown from Eq. (2.15) that

$$\begin{aligned} \frac{\partial \varphi}{\partial \lambda} = & -\varphi(r) \int_0^\infty dq U(q) \varphi^2(q) \int_R^{\min(r, q)} dt \varphi^{-2}(t) + \\ & + \varphi(r) \int_0^\infty dq \varphi^2(q) \int_0^\infty ds U(s) \varphi^2(s) \int_R^{\min(q, s)} dt \varphi^{-2}(t), \end{aligned} \quad (2.23)$$

and then (2.21) leads to

$$\left. \frac{\partial \varphi(0)}{\partial \lambda} \right|_{\lambda=0} = A \int_0^\infty dq \, u(q) \psi^2(q). \quad (2.24)$$

According to Eqs. (2.13), (2.22) and (2.24), one has

$$E = E_0 + \lambda \int_0^\infty dq \, u(q) \psi^2(q) + O(\lambda^2), \quad (2.25)$$

which of course is a well-known result.

Consider now the more complicated situation of second order perturbations. One has

$$E = E_0 + \lambda \left(\frac{dE}{d\lambda} \right)_{\lambda=0} + \frac{1}{2} \lambda^2 \left(\frac{d^2 E}{d\lambda^2} \right)_{\lambda=0} + O(\lambda^3), \quad (2.26)$$

and, from Eq. (2.11),

$$\begin{aligned} \frac{d^2 E}{d\lambda^2} = & - \frac{\partial^2 \varphi}{\partial \lambda^2} \left(\frac{\partial \varphi}{\partial E} \right)^{-1} + 2 \frac{\partial^2 \varphi}{\partial \lambda \partial E} \frac{\partial \varphi}{\partial \lambda} \left(\frac{\partial \varphi}{\partial E} \right)^{-2} \\ & - \frac{\partial^2 \varphi}{\partial E^2} \left(\frac{\partial \varphi}{\partial \lambda} \right)^2 \left(\frac{\partial \varphi}{\partial E} \right)^{-3}. \end{aligned} \quad (2.27)$$

One already has expressions for $\partial \varphi / \partial \lambda$ and $\partial \varphi / \partial E$, namely Eqs. (2.19) and (2.23), and it is required now to evaluate $\partial^2 \varphi / \partial \lambda^2$, $\partial^2 \varphi / \partial E^2$ and $\partial^2 \varphi / \partial E \partial \lambda$. This can be done by repeated differentiations of the Schrödinger equation, Eq. (2.5). This gives a differential equation for the second order derivatives, in which the inhomogeneous term only contains first order derivatives, which have already been evaluated. Hence the second order derivatives can be calculated by the same method of variation of parameters, coupled with the boundary condition constraints.

The differential equation for the general partial derivative is

$$\begin{aligned} & \left[-\left(\frac{\partial}{\partial \tau}\right)^2 + V(\tau) + \lambda U(\tau) - E \right] \frac{\partial^{m+n} \phi}{\partial E^m \partial \lambda^n} = \\ & = m \frac{\partial^{m+n-1} \phi}{\partial E^{m-1} \partial \lambda^n} - n U(\tau) \frac{\partial^{m+n-1} \phi}{\partial E^m \partial \lambda^{n-1}}, \end{aligned} \quad (2.28)$$

$m, n = 0, 1, 2, 3, \dots$, except $m = n = 0$. All the partial derivatives can be generated successively. One can always set one of the constants in the general solution to zero, as in Eq. (2.16), and the other can be determined from the normalization condition (2.7), suitably differentiated :

$$\int_0^\infty d\tau \frac{\partial^{m+n} \phi^2(\tau)}{\partial E^m \partial \lambda^n} = 0, \quad (2.29)$$

$m, n = 0, 1, 2, 3, \dots$, except $m = n = 0$.

Finally, one has to calculate the limit $r \rightarrow 0$, as in Eqs. (2.22) and (2.24). This gives, for the second order derivatives,

$$\frac{\partial^2 \phi(0)}{\partial E^2} = 0, \quad (2.30)$$

$$\begin{aligned} \frac{\partial^2 \phi(0)}{\partial \lambda^2} = & -2A \int_0^\infty d\tau U(\tau) \phi^2(\tau) \int_0^\infty ds U(s) \phi^2(s) \int_R^{\min(\tau, s)} dt \phi^{-2}(t) + \\ & + 2A \left[\int_0^\infty d\tau U(\tau) \phi^2(\tau) \right] \int_0^\infty d\tau \phi^2(\tau) \int_0^\infty ds U(s) \phi^2(s) \cdot \\ & \cdot \int_R^{\min(\tau, s)} dt \phi^{-2}(t), \end{aligned} \quad (2.31)$$

$$\begin{aligned} \frac{\partial^2 \phi(0)}{\partial E \partial \lambda} = & A \int_0^\infty dr \mathcal{U}(r) \phi^2(r) \int_0^\infty ds \phi^2(s) \int_R^{\min(r,s)} dt \phi^{-2}(t) - \\ & - A \left[\int_0^\infty dp \mathcal{U}(p) \phi^2(p) \right] \int_0^\infty dr \phi^2(r) \int_0^\infty ds \phi^2(s) \cdot \\ & \cdot \int_R^{\min(r,s)} dt \phi^{-2}(t). \end{aligned} \quad (2.32)$$

As in Eqs. (2.19) and (2.23), the expressions do not depend on R , which should be chosen such that $\phi(R) \neq 0$. The integrals $\int_R^{\min(r,s)}$ are to be understood normally, in particular, they do not vanish when $\min(r,s) < R$: the integration range is merely described in the negative sense in such a case.

On combining Eqs. (2.26), (2.27), (2.30)-(2.32), one finds

$$\begin{aligned} E = & E_0 + \lambda \int_0^\infty dq \mathcal{U}(q) \psi^2(q) + \\ & + \lambda^2 \left\{ - \int_0^\infty dp \mathcal{U}(p) \psi^2(p) \int_0^\infty dq \mathcal{U}(q) \psi^2(q) \int_R^{\min(p,q)} dr \psi^{-2}(r) + \right. \\ & + 2 \left[\int_0^\infty ds \mathcal{U}(s) \psi^2(s) \right] \int_0^\infty dp \mathcal{U}(p) \psi^2(p) \int_0^\infty dq \psi^2(q) \cdot \\ & \cdot \int_R^{\min(p,q)} dr \psi^{-2}(r) \\ & - \left[\int_0^\infty ds \mathcal{U}(s) \psi^2(s) \right]^2 \int_0^\infty dp \psi^2(p) \int_0^\infty dq \psi^2(q) \cdot \\ & \cdot \int_R^{\min(p,q)} dr \psi^{-2}(r) \left. \right\} \\ & + O(\lambda^3). \end{aligned} \quad (2.33)$$

As promised, the second order term only involves the ground-state wave-function (or more generally the wave-function for the state that is to be perturbed), and not the infinite set of eigenstates, as in the usual formula. Moreover, it should be clear that higher-order terms can be calculated in the same way, although the complexity increases

severely. In the next two sections, the connection between the new formula and the usual text-book expression will be clarified, and this will permit an equation of the type (2.33) to be written down for the n -th order expansion coefficient.

Before this is done, and by way of an exercise to convince the author and the reader that Eq. (2.33) is correct, consider the square-well potential

$$\begin{aligned} V(r) &= 0, & 0 \leq r < 2, \\ &= \infty, & r \geq 2, \end{aligned} \tag{2.34}$$

with the perturbation

$$\begin{aligned} \lambda U(r) &= 0, & 0 \leq r < 1, \\ &= \lambda, & 1 \leq r < 2, \\ &= \infty, & r \geq 2. \end{aligned} \tag{2.35}$$

In this simple case one can do all the integrals in Eq. (2.33) for the ground-state unperturbed wave-function, which is

$$\psi(r) = \sin [\pi r/2], \tag{2.36}$$

for $0 \leq r \leq 2$. One finds

$$E = \frac{\pi^2}{4} + \frac{\lambda}{2} - \frac{\lambda^2}{4\pi^2} + O(\lambda^3). \tag{2.37}$$

One can also solve the problem exactly, and expand in powers of λ , and the result agrees with Eq. (2.37).

3. - THE USUAL FORMULATION

The relation of the new formula to the usual one can best be brought out by a review of the Green's function, or resolvent formalism. The function $G(r,t;E)$ is defined to vanish as $r \rightarrow 0$ and as $r \rightarrow \infty$, to be a symmetric function of r and t , and to satisfy

$$\left[-\left(\frac{d}{dr}\right)^2 + V(r) - E\right] G(r,t;E) = \delta(r-t). \quad (3.1)$$

This Green's function is well defined except on the spectrum of the (unperturbed) Hamiltonian, H_0 , which has the configuration representation

$$\langle r | H_0 | \Psi \rangle \equiv \left[-\left(\frac{d}{dr}\right)^2 + V(r)\right] \langle r | \Psi \rangle. \quad (3.2)$$

Let $\psi(r;E)$ be the function that satisfies the homogeneous equation

$$\left[-\left(\frac{d}{dr}\right)^2 + V(r) - E\right] \psi(r;E) = 0, \quad (3.3)$$

and which obeys the following asymptotic and normalization conditions :

$$\psi(r;E) \xrightarrow{r \rightarrow \infty} 0, \quad (3.4)$$

$$\int_0^\infty dr \psi^2(r;E) = 1. \quad (3.5)$$

The function $\psi(r; E)$ is uniquely defined for all values of E for which condition (3.4) is possible, the precise domain being determined by $V(r)$. The discrete eigenvalues of H_0 are those values $E = E_i$, $i = 0, 1, 2, \dots$, for which

$$\psi(0; E_i) = 0. \quad (3.6)$$

It is easy to see that the Green's function may be written in terms of $\psi(r; E)$ as

$$G(\tau, t; E) = \psi(\tau; E) \psi(t; E) \int_0^{\min(\tau, t)} ds \psi^{-2}(s; E), \quad (3.7)$$

for those values of E for which Eq. (3.4) is possible. The integral fails to exist precisely when the eigenvalue condition (3.6) is satisfied.

It is usual to expand the Green's function over the complete set of eigenfunctions, $\psi(r; E_i)$, of H_0 , giving

$$G(\tau, t; E) = \sum_{i=0}^{\infty} \frac{\psi(\tau; E_i) \psi(t; E_i)}{E_i - E}, \quad (3.8)$$

where multiple terms are to be understood in the case of degenerate eigenvalues, where an integration is understood for any continuous portion of the spectrum, and where, in general, one only has convergence in the mean.

The function $\phi(r; E, \lambda)$ that satisfies the perturbed Schrödinger equation (2.5) can be written in terms of the Green's function as

$$\phi(\tau; E, \lambda) = -\lambda \int_0^{\infty} G(\tau, t; E) dt U(t) \phi(t; E, \lambda). \quad (3.9)$$

This is a homogeneous linear integral equation for φ ; and, for a given value of λ , it only has solutions for exceptional values of E , namely the eigenvalues of the perturbed Hamiltonian. To isolate the specific eigenfunction that tends to $\psi(r; E_0)$ as $\lambda \rightarrow 0$, one can use the expansion (3.8) to rewrite Eq. (3.9) as

$$\varphi(r; E, \lambda) = \psi(r; E_0) + \lambda \int_0^\infty dt \sum_{i=1}^{\infty} \frac{\psi(r; E_i) \psi(t; E_i)}{E - E_i} U(t) \varphi(t; E, \lambda) \quad (3.10)$$

where the coefficient of $\psi(r; E_0)$ has been chosen to be unity, which implies

$$E = E_0 + \lambda \int_0^\infty dt \psi(t; E_0) U(t) \varphi(t; E, \lambda). \quad (3.11)$$

The equations (3.10) and (3.11) can be written in operator notation as

$$|\varphi\rangle = |\psi_0\rangle + \lambda \sum_{i \neq 0} \frac{|\psi_i\rangle \langle \psi_i| U |\varphi\rangle}{E - E_i}, \quad (3.12)$$

$$E = E_0 + \lambda \langle \psi_0 | U | \varphi \rangle. \quad (3.13)$$

Repeated iteration of these equations gives the following expansion for E :

$$\begin{aligned} E = & E_0 + \lambda \langle \psi_0 | U | \psi_0 \rangle + \\ & + \lambda^2 \sum_{i \neq 0} \frac{\langle \psi_0 | U | \psi_i \rangle \langle \psi_i | U | \psi_0 \rangle}{E - E_i} + \\ & + \lambda^3 \sum_{i \neq 0} \sum_{j \neq 0} \frac{\langle \psi_0 | U | \psi_i \rangle \langle \psi_i | U | \psi_j \rangle \langle \psi_j | U | \psi_0 \rangle}{(E - E_i)(E - E_j)} + \dots \end{aligned} \quad (3.14)$$

This is not yet an explicit expression for E , but the perturbation expansion,

$$E = E_0 + \sum_{n=1}^{\infty} \lambda^n \varepsilon_n, \quad (3.15)$$

may be obtained from (3.14) by repeated expansions of the denominators in powers of λ . One finds

$$\varepsilon_1 = \langle \psi_0 | U | \psi_0 \rangle, \quad (3.16)$$

$$\varepsilon_2 = \sum_{i \neq 0} \frac{\langle \psi_0 | U | \psi_i \rangle \langle \psi_i | U | \psi_0 \rangle}{E_0 - E_i}, \quad (3.17)$$

$$\begin{aligned} \varepsilon_3 = & \sum_{i \neq 0} \sum_{j \neq 0} \frac{\langle \psi_0 | U | \psi_i \rangle \langle \psi_i | U | \psi_j \rangle \langle \psi_j | U | \psi_0 \rangle}{(E_0 - E_i)(E_0 - E_j)} - \\ & - \langle \psi_0 | U | \psi_0 \rangle \sum_{i \neq 0} \frac{\langle \psi_0 | U | \psi_i \rangle \langle \psi_i | U | \psi_0 \rangle}{(E_0 - E_i)^2}. \end{aligned} \quad (3.18)$$

4. - GREEN'S FUNCTION FORMULATION OF THE NEW METHOD

The purpose of this section is to repeat the work of the previous section, but using a different Green's function, and avoiding the expansion over the infinite set of intermediate states ^{*}). Instead of Eq. (3.7), define a new Green's function

^{*}) The Green's function formulation has been independently obtained by Dr. E. Brézin (private communication).

$$F(r, t; E) = \psi(r; E) \psi(t; E) \int_R^{\min(r, t)} ds \psi^{-2}(s; E), \quad (4.1)$$

where R is some fixed point, $R \neq 0$, for which $\psi(R; E_0)$ does not vanish. Then F is well defined at $E = E_0$, whereas G does not exist at this point. The Green's function, F , satisfies the same differential equation (3.1) as G , and it vanishes as $r \rightarrow \infty$, at fixed t . However, it is not zero in general for $r = 0$.

The equation (2.5) for $\varphi(r; E, \lambda)$ will be solved now using $F(r, t; E_0)$ alone. Since Eq. (2.5) can be rewritten

$$\left[-\left(\frac{d}{dr}\right)^2 + V(r) - E_0\right] \varphi(r; E, \lambda) = [E - E_0 - \lambda U(r)] \varphi(r; E, \lambda), \quad (4.2)$$

it follows that

$$\begin{aligned} \varphi(r; E, \lambda) = & A \psi(r; E_0) + \\ & + \int_0^\infty dt F(r, t; E_0) [E - E_0 - \lambda U(t)] \varphi(t; E, \lambda), \end{aligned} \quad (4.3)$$

where a multiple of $\psi(r; E_0)$, a solution of the homogeneous equation [the left-hand side of Eq. (4.2) equal to zero] has been added. No other solution of the homogeneous equation can be tolerated by the boundary condition at infinity, and the coefficient A in Eq. (4.3) is determined by normalization. In fact, since the integral term vanishes in the limit $\lambda \rightarrow 0$, and one wants $\varphi(r; E_0, 0) = \psi(r; E_0)$, it is convenient to set $A = 1$. The eigenvalue condition,

$$\varphi(0; E, \lambda) = 0, \quad (4.4)$$

prescribes the vanishing of the integral term in Eq. (4.3) at $r = 0$, i.e.,

$$\int_0^\infty dt \psi(t; E_0) [E - E_0 - \lambda u(t)] \varphi(t; E, \lambda) = 0, \quad (4.5)$$

or

$$E = E_0 + \lambda \frac{\int_0^\infty dt \psi(t; E_0) u(t) \varphi(t; E, \lambda)}{\int_0^\infty dt \psi(t; E_0) \varphi(t; E, \lambda)}. \quad (4.6)$$

In operator notation, Eqs. (4.3) and (4.6) read

$$|\varphi\rangle = |\psi_0\rangle + F_0(E - E_0 - \lambda u) |\varphi\rangle, \quad (4.7)$$

$$E = E_0 + \lambda \frac{\langle \psi_0 | u | \varphi \rangle}{\langle \psi_0 | \varphi \rangle}. \quad (4.8)$$

These equations are similar to Eqs. (3.12)-(3.13), but with the important difference that the operator F_0 is known explicitly in terms of $\psi(r; E_0)$, whereas in Eq. (3.12) one has an infinite sum over states. Since $E - E_0$ is of order λ , it is convenient to write

$$E - E_0 = \lambda \varepsilon, \quad (4.9)$$

so that Eq. (4.7) becomes

$$|\varphi\rangle = |\psi_0\rangle + \lambda F_0(\varepsilon - u) |\varphi\rangle, \quad (4.10)$$

and this can be iterated to give

$$|\phi\rangle = |\psi_0\rangle + \sum_{n=1}^{\infty} \lambda^n [F_0(\epsilon - \mathcal{U})]^n |\psi_0\rangle. \quad (4.11)$$

Hence the eigenvalue equation (4.8) becomes

$$\epsilon = \frac{\sum_{n=0}^{\infty} \lambda^n \langle \psi_0 | \mathcal{U} [F_0(\epsilon - \mathcal{U})]^n | \psi_0 \rangle}{\sum_{n=0}^{\infty} \lambda^n \langle \psi_0 | [F_0(\epsilon - \mathcal{U})]^n | \psi_0 \rangle}. \quad (4.12)$$

This expansion is not explicit, in that ϵ occurs on the right. In this respect it resembles the implicit expansion (3.14). The explicit series

$$\epsilon = \sum_{n=1}^{\infty} \epsilon_n \lambda^{n-1} \quad (4.13)$$

may be obtained from (4.12) by collecting powers of λ . One finds

$$\epsilon_1 = \langle \psi_0 | \mathcal{U} | \psi_0 \rangle, \quad (4.14)$$

and

$$\epsilon_2 = -\langle \psi_0 | (\mathcal{U} - \epsilon_1) F_0(\mathcal{U} - \epsilon_1) | \psi_0 \rangle. \quad (4.15)$$

The last equation may be rewritten

$$\begin{aligned} \mathcal{E}_2 = & -\langle \psi_0 | U F_0 U | \psi_0 \rangle + 2\langle \psi_0 | U | \psi_0 \rangle \langle \psi_0 | U F_0 | \psi_0 \rangle - \\ & - [\langle \psi_0 | U | \psi_0 \rangle]^2 \langle \psi_0 | F_0 | \psi_0 \rangle, \end{aligned} \quad (4.16)$$

and it will be recognized that the second order term in Eq. (2.33) is just the configuration space representation of this quantity. The third-order term is

$$\begin{aligned} \mathcal{E}_3 = & \langle \psi_0 | (U - \mathcal{E}_1) F_0 (U - \mathcal{E}_1) F_0 (U - \mathcal{E}_1) | \psi_0 \rangle + \\ & + 2\mathcal{E}_2 \langle \psi_0 | (U - \mathcal{E}_1) F_0 | \psi_0 \rangle. \end{aligned} \quad (4.17)$$

There is no reason why Eq. (4.12) should be expanded as a straightforward power series. Its form would suggest a rational function approximant. Thus, define a sequence $\{ \mathcal{E}^{(p)} \}$, with

$$\mathcal{E}^{(1)} = \langle \psi_0 | U | \psi_0 \rangle, \quad (4.18)$$

and

$$\mathcal{E}^{(p+1)} = \frac{\sum_{n=0}^p \lambda^n \langle \psi_0 | U [F_0 (\mathcal{E}^{(p)} - U)]^n | \psi_0 \rangle}{\sum_{n=0}^p \lambda^n \langle \psi_0 | [F_0 (\mathcal{E}^{(p)} - U)]^n | \psi_0 \rangle}, \quad (4.19)$$

for $p = 1, 2, 3, \dots$. It is to be expected that in some cases the sequence converges, $\mathcal{E}^{(p)} \xrightarrow[p \rightarrow \infty]{} \mathcal{E}$, when the series (4.13) diverges. However, in the next section, rather conservative convergence conditions will be given,

which will ensure not only the convergence of (4.19), but also that of the power series (4.13). Nevertheless, the form (4.19) would probably be the most convenient to use in practice, since one could in principle write a computer program for a calculation of arbitrary order, whereas this is more difficult with the power series (4.13), since high-order terms are very cumbersome in form.

5. - CONVERGENCE OF PERTURBATION SERIES

In this section, conditions for the convergence of the perturbation series will be given. These conditions differ from those of Kato ⁴⁾, because use will only be made of the unperturbed eigenfunction, $\psi(r; E_0)$, whereas Kato needs to introduce the concept of the "isolation distance" of E_0 from the rest of the spectrum, in order to derive a lower bound for the radius of convergence.

The formulae will be given for a general Banach space in which an inner product, $\langle \psi | \phi \rangle$, is defined, but for which the norm of $|\psi\rangle$ does not in general need to be $\langle \psi | \psi \rangle^{\frac{1}{2}}$, as in a Hilbert space. However, it is required of the norm that

$$|\langle \psi | \phi \rangle| \leq \|\psi\| \cdot \|\phi\|. \quad (5.1)$$

The proof of convergence will be given in sufficient detail to enable upper bounds on the errors involved in truncating the system (4.19) at the p-th stage to be written down.

In Section 6, the formulae will be specialized to the case of L^2 Hilbert space ; but in Sections 7 and 8 more general Banach spaces will be used, and these will enable most physically interesting potentials to be handled.

Let $\mathcal{B}$ be some Banach space, containing $|\psi_0\rangle$, on which the linear operators F_0 and $F_0 U$ are bounded. Define f_0 and f_1 by

$$\|F_0\| = f_0, \quad (5.2)$$

$$\|F_0 U\| = f_0 f_1. \quad (5.3)$$

Although U itself need not be bounded on the whole space, it is supposed that $U|\psi_0\rangle$ has finite norm. Define

$$\|U|\psi_0\rangle\| = u_1. \quad (5.4)$$

Note that, because of Eq. (5.1),

$$\epsilon_1 = \epsilon^{(1)} = \langle \psi_0 | U | \psi_0 \rangle \leq u_1. \quad (5.5)$$

It will be shown that, if f_0 , f_1 and u_1 exist, and if λ is small enough, then the exact equations (4.7) and (4.8) have a unique solution, and that the rational approximant (4.19) tends to this solution as $p \rightarrow \infty$.

It is convenient to break up Eq. (4.19) into two pieces,

$$\epsilon^{(p+1)} = \frac{\langle \psi_0 | U | \varphi^{(p)} \rangle}{\langle \psi_0 | \varphi^{(p)} \rangle}, \quad (5.6)$$

for $p = 1, 2, 3, \dots$, where

$$|\varphi^{(p)}\rangle = |\psi_0\rangle + \sum_{n=1}^p \lambda^n [F_0(\varepsilon^{(p)} - u)]^n |\psi_0\rangle, \quad (5.7)$$

and where $\varepsilon^{(1)}$ was defined in Eq. (4.18). It will first be shown that, if suitable bounds are placed on λ , then $\varepsilon^{(p)}$ and $\|\varphi^{(p)}\|$ are uniformly bounded for all p .

From Eq. (5.7)

$$\begin{aligned} \|\varphi^{(p)} - \psi_0\| &\leq \sum_{n=1}^p [\lambda f_0(|\varepsilon^{(p)}| + f_1)]^n \\ &\leq \frac{\lambda f_0(|\varepsilon^{(p)}| + f_1)}{1 - \lambda f_0(|\varepsilon^{(p)}| + f_1)}, \end{aligned} \quad (5.8)$$

provided that

$$\lambda f_0(|\varepsilon^{(p)}| + f_1) < 1. \quad (5.9)$$

From Eq. (5.6), on the other hand,

$$\begin{aligned} |\varepsilon^{(p+1)}| &\leq \frac{|\langle \psi_0 | u | \psi_0 \rangle| + |\langle \psi_0 | u | \varphi^{(p)} - \psi_0 \rangle|}{1 - |\langle \psi_0 | \varphi^{(p)} - \psi_0 \rangle|} \\ &\leq \frac{1 + \|\varphi^{(p)} - \psi_0\|}{1 - \|\varphi^{(p)} - \psi_0\|} u_1. \end{aligned} \quad (5.10)$$

Upon combining (5.8) and (5.10), one finds

$$|\varepsilon^{(p+1)}| \leq \frac{u_1}{1 - 2\lambda f_0(|\varepsilon^{(p)}| + f_1)}. \quad (5.11)$$

Suppose now that λ satisfies the inequality

$$\lambda \leq [2Nf_0(\frac{Nu_1}{N-1} + f_1)]^{-1}, \quad (5.12)$$

where N is some number, greater than unity, that will be chosen later. It will be proved by induction that

$$|\varepsilon^{(p)}| \leq \frac{N}{N-1} u_1, \quad (5.13)$$

for all p . For (5.13) is certainly true for $p = 1$ [see Eq. (5.5)]. Suppose now that (5.13) holds for a particular p . Then, from Eq. (5.11),

$$\begin{aligned} |\varepsilon^{(p+1)}| &\leq \frac{u_1}{1 - 2\lambda f_0(\frac{N}{N-1} u_1 + f_1)} \\ &\leq \frac{N}{N-1} u_1, \end{aligned} \quad (5.14)$$

by (5.12). This completes the induction. From Eqs. (5.8), (5.12) and (5.13),

$$\begin{aligned} \|\varphi^{(p)} - \psi_0\| &\leq \frac{\lambda f_0(\frac{N}{N-1} u_1 + f_1)}{1 - \lambda f_0(\frac{N}{N-1} u_1 + f_1)} \\ &\leq \frac{1}{2N-1}. \end{aligned} \quad (5.15)$$

Thus $|\varepsilon^{(p)}|$ and $\|\varphi^{(p)}\|$ are uniformly bounded.

It will now be shown that, if λ satisfies inequality (5.12) for a suitable value of N , then $\{\varepsilon^{(p)}\}$ is a Cauchy sequence. From Eq. (5.6), one sees that

$$\varepsilon^{(p+n+1)} - \varepsilon^{(p+1)} = \frac{\langle \psi_0 | u | \varphi^{(p+n)} \rangle \langle \psi_0 | \varphi^{(p)} - \varphi^{(p+n)} \rangle + \langle \psi_0 | \varphi^{(p+n)} - \varphi^{(p)} \rangle \langle \psi_0 | \varphi^{(p+n)} \rangle}{\langle \psi_0 | \varphi^{(p+n)} \rangle \langle \psi_0 | \varphi^{(p)} \rangle}, \quad (5.16)$$

where $p, n \geq 1$. Hence, from Eq. (5.15),

$$|\varepsilon^{(p+n+1)} - \varepsilon^{(p+1)}| \leq \frac{N(2N-1)}{(N-1)^2} u, \|\varphi^{(p+n)} - \varphi^{(p)}\|. \quad (5.17)$$

One needs now to obtain an upper bound on $\|\varphi^{(p+n)} - \varphi^{(p)}\|$ from Eq. (5.7). It is easiest to define first the auxiliary function, $|\bar{\varphi}^{(p)}\rangle$, as the solution of the integral equation

$$|\bar{\varphi}^{(p)}\rangle = |\psi_0\rangle + \lambda F_0(\varepsilon^{(p)} - u) |\bar{\varphi}^{(p)}\rangle. \quad (5.18)$$

So long as λ satisfies Eq. (5.12), one can show, by the contraction mapping theorem, that (5.18) has a unique solution in $\mathcal{B}$, that may be expressed as the strongly convergent series

$$|\bar{\varphi}^{(p)}\rangle = |\psi_0\rangle + \sum_{n=1}^{\infty} \lambda^n [F_0(\varepsilon^{(p)} - u)]^n |\psi_0\rangle. \quad (5.19)$$

On comparing Eqs. (5.7) and (5.19), one sees that

$$|\bar{\varphi}^{(p)} - \varphi^{(p)}\rangle = \sum_{n=p+1}^{\infty} \lambda^n [F_0(\varepsilon^{(p)} - u)]^n |\psi_0\rangle, \quad (5.20)$$

so that

$$\begin{aligned} \|\bar{\varphi}^{(p)} - \varphi^{(p)}\| &\leq \sum_{n=p+1}^{\infty} [\lambda f_0 (|\varepsilon^{(p)}| + f_1)]^n \\ &\leq \left(\frac{1}{2N}\right)^p \frac{1}{2N-1} \end{aligned} \quad (5.21)$$

where Eqs. (5.12) and (5.13) have been used. From Eq. (5.18), on the other hand, one can write

$$\begin{aligned} |\bar{\varphi}^{(p+n)} - \bar{\varphi}^{(p)}\rangle &= \lambda F_0 (\varepsilon^{(p+n)} - \mathcal{U}) |\bar{\varphi}^{(p+n)} - \bar{\varphi}^{(p)}\rangle + \\ &+ \lambda (\varepsilon^{(p+n)} - \varepsilon^{(p)}) F_0 |\bar{\varphi}^{(p)}\rangle, \end{aligned} \quad (5.22)$$

so that

$$\begin{aligned} \|\bar{\varphi}^{(p+n)} - \bar{\varphi}^{(p)}\| &\leq \frac{1}{2N} \|\bar{\varphi}^{(p+n)} - \bar{\varphi}^{(p)}\| + \lambda f_0 \frac{2N}{2N-1} |\varepsilon^{(p+n)} - \varepsilon^{(p)}| \\ &\leq \left(\frac{2N}{2N-1}\right)^2 \lambda f_0 |\varepsilon^{(p+n)} - \varepsilon^{(p)}|. \end{aligned} \quad (5.23)$$

On combining Eqs. (5.21) and (5.23), one finds

$$\begin{aligned} \|\varphi^{(p+n)} - \varphi^{(p)}\| &\leq \|\varphi^{(p+n)} - \bar{\varphi}^{(p+n)}\| + \|\bar{\varphi}^{(p+n)} - \bar{\varphi}^{(p)}\| + \\ &+ \|\bar{\varphi}^{(p)} - \varphi^{(p)}\| \\ &\leq \frac{2}{2N-1} \left(\frac{1}{2N}\right)^p + \lambda f_0 \left(\frac{2N}{2N-1}\right)^2 |\varepsilon^{(p+n)} - \varepsilon^{(p)}|. \end{aligned} \quad (5.24)$$

From Eqs. (5.17) and (5.24),

$$|\varepsilon^{(p+n+1)} - \varepsilon^{(p+1)}| \leq \frac{u_1}{(N-1)^2 (2N)^{p-1}} + \lambda f_0 u_1 \frac{4N^3}{(N-1)^2 (2N-1)} |\varepsilon^{(p+n)} - \varepsilon^{(p)}|. \quad (5.25)$$

This inequality can be iterated to give

$$|\varepsilon^{(p+n+1)} - \varepsilon^{(p+1)}| \leq \left[\frac{2N}{(N-1)(2N-1)} \right]^p \left[\frac{2N-1}{N^2-1} u_1 + |\varepsilon^{(n+1)} - \varepsilon^{(n)}| \right] \quad (5.26)$$

From Eq. (5.13), it is evident that

$$|\varepsilon^{(n+1)} - \varepsilon^{(n)}| \leq |\varepsilon^{(n+1)}| + |\varepsilon^{(n)}| \leq \frac{2N}{N-1} u_1 \quad (5.27)$$

so that finally

$$|\varepsilon^{(p+n+1)} - \varepsilon^{(p+1)}| \leq \frac{2N^2 + 4N - 1}{N^2 - 1} u_1 \left[\frac{2N}{(N-1)(2N-1)} \right]^p \quad (5.28)$$

It is clear that, if N is chosen so that

$$\frac{2N}{(N-1)(2N-1)} < 1, \quad (5.29)$$

then the right-hand side of (5.28) can be made as small as one likes, by choosing p large enough. Under these conditions, $\{\varepsilon^{(p)}\}$ is a Cauchy sequence, and so $\varepsilon^{(p)}$ converges to a limit

$$\varepsilon^{(p)} \xrightarrow{p \rightarrow \infty} \varepsilon. \quad (5.30)$$

The restriction (5.29) implies

$$N > \frac{5 + (17)^{1/2}}{4} \approx 2.3. \quad (5.31)$$

The above formulae will be rewritten for the special choice $N = 3$, for convenience. The condition (5.12) becomes

$$\lambda \leq [3f_0(3u_1 + 2f_1)]^{-1}, \quad (5.32)$$

formula (5.13) is

$$|\varepsilon^{(p)}| \leq \frac{3}{2} u_1, \quad (5.33)$$

and (5.15) reads

$$\|\varphi^{(p)} - \psi_0\| \leq \frac{1}{5}. \quad (5.34)$$

In view of Eq. (5.30), one also has

$$|\varepsilon| \leq \frac{3}{2} u_1. \quad (5.35)$$

By replacing p by $p-1$ in Eq. (5.28), taking $n \rightarrow \infty$, and setting $N = 3$, one finds

$$|\varepsilon^{(p)} - \varepsilon| \leq \frac{29}{8} \left(\frac{3}{5}\right)^{p-1} u_1. \quad (5.36)$$

This gives an upper bound on the error committed by truncating the iteration (4.19) at the p -th stage.

From Eq. (5.24), one finds

$$\| \varphi^{(p+n)} - \varphi^{(p)} \| \leq \frac{2}{5} \left(\frac{1}{6} \right)^p + \frac{29}{8} \left(\frac{3}{5} \right)^p, \quad (5.37)$$

so $\{ \varphi^{(p)} \}$ is a Cauchy sequence in the complete space $\mathcal{B}$, and so has a unique strong limit in $\mathcal{B}$,

$$\varphi^{(p)} \xrightarrow{p \rightarrow \infty} \varphi. \quad (5.38)$$

The right-hand side of (5.37) serves also to bound $\| \varphi^{(p)} - \varphi \|$. Of course, by choosing λ still smaller than the bound (5.32), one can speed the convergence (5.36) and (5.37).

It is easy to see that the limit functions $\mathcal{E}$ and φ satisfy the exact equations (4.7) and (4.8). This can be shown formally by writing the equations as a mapping $(\mathcal{E}, \varphi) \rightarrow (\mathcal{E}', \varphi')$ according to

$$|\varphi'\rangle = |\psi_0\rangle + \lambda F_0 (\mathcal{E} - \mathcal{U}) |\varphi\rangle, \quad (5.39)$$

$$\mathcal{E}' = \frac{\langle \psi_0 | \mathcal{U} | \varphi \rangle}{\langle \psi_0 | \varphi \rangle}. \quad (5.40)$$

The work of this section amounts to a demonstration that this is a contraction when condition (5.32) is satisfied, so that the limit functions $\mathcal{E}, \varphi$ defined by Eqs. (5.30) and (5.38) do indeed satisfy the exact equations.

Finally, it should be pointed out that condition (5.32) guarantees not only the convergence of the sequence $\{\mathcal{E}^{(p)}\}$, but also that of the perturbation series (4.13) itself. For it can be proved, by induction, that $\mathcal{E}^{(p)}$ is holomorphic in the circle about $\lambda = 0$ defined by Eq. (5.12), in much the same way as $\mathcal{E}^{(p)}$ was shown to be uniformly bounded, Eq. (5.13). Moreover, it has already been shown that $\mathcal{E}^{(p)} \rightarrow \mathcal{E}$ uniformly with respect to λ , so long as Eq. (5.12) is satisfied [Eq. (5.36)]. Hence, by the Vitali theorem, $\mathcal{E}$ is itself analytic in the circle (5.12), and hence the perturbation series converges in this domain.

6. - UNBOUNDED POTENTIALS

The most familiar Banach space is real L^2 Hilbert space, in which the norm is defined, for real $|\psi\rangle$, by

$$\|\psi\|^2 \equiv \langle \psi | \psi \rangle = \int_0^\infty d\tau \psi^2(\tau). \quad (6.1)$$

In this space, the norm of $F(r, t; E_0)$ may be written

$$\begin{aligned} \|F_0\|^2 &= \int_0^\infty d\tau \int_0^\infty dt \psi^2(\tau; E_0) \psi^2(t; E_0) \left[\int_R^{\min(\tau, t)} ds \psi^{-2}(s; E_0) \right]^2 \\ &= 2 \int_0^\infty d\tau \int_0^\tau dt \psi^2(\tau; E_0) \psi^2(t; E_0) \left[\int_R^t ds \psi^{-2}(s; E_0) \right]^2. \end{aligned} \quad (6.2)$$

In the case that $r^{1+\epsilon} V(r) \xrightarrow{r \rightarrow \infty} 0$, one has, in the bound state region $E_0 < 0$,

$$\psi(\tau; E_0) \underset{\tau \rightarrow \infty}{\sim} \exp[-(-E_0)^{1/2} \tau], \quad (6.3)$$

and it is easy to see that the quantity (6.2) is divergent ^{*}). Hence for this class of potentials, in which there is a continuum, as well as a discrete part of the spectrum, one cannot use L^2 , but must consider some other space for the analysis of Section 5.

It will now be shown that the norm (6.2) exists if $V(r)$ satisfies the following conditions :

$$r^{-\frac{2}{3}-\varepsilon} V(r) \xrightarrow{r \rightarrow \infty} +\infty, \quad (6.4)$$

with $\varepsilon > 0$; there exist R and K such that

$$V(r) - E_0 \geq K > 0, \quad (6.5)$$

for $r \geq R$; there exist constants C_1 and C_2 such that

$$|r V'(r)| \leq C_1 [V(r) - E_0], \quad (6.6)$$

for $r \geq R$, and

$$|r^2 V''(r)| \leq C_2 [V(r) - E_0], \quad (6.7)$$

for $r \geq R$. Conditions (6.6) and (6.7) say essentially that $V(r)$ must be a non-pathological function of order zero (i.e., with less than exponential growth at infinity). These conditions could be somewhat

^{*}) A more precise statement of the asymptotics of ψ when $V \rightarrow 0$ will be given in Sections 7 and 8.

relaxed, with extra work, and in particular it should not be difficult to handle potentials with exponential growth at infinity. It is also assumed that $V(r)$ is bounded for $r < R$, except possibly at $r = 0$, where a singularity not worse than $r^{-2+\epsilon}$, $\epsilon > 0$, may be tolerated. It is well known that more singular potentials can be handled, so long as $V(r)$ diverges monotonically to $+\infty$ as $r \rightarrow 0+$, and it would be possible to allow such a behaviour here, but the behaviour at the origin is essentially extraneous to the problems of interest in this paper, and so this refinement will be omitted.

In the Appendix, it is shown that constants, C_3, C_4 exist such that

$$C_3 f_-(r) \leq |\psi(r; E_0)| \leq C_4 f_-(r), \quad (6.8)$$

for $r \geq R$, where

$$f_-(r) = [V(r) - E_0]^{-1/4} \exp \left\{ - \int_R^r ds [V(s) - E_0]^{1/2} \right\}. \quad (6.9)$$

This will be recognized as the WKB ansatz. The task now is to use the double inequality (6.8) to demonstrate the convergence of (6.2). With the assumptions on $V(r)$, the only doubtful region is that in which the integration variables tend toward infinity. Accordingly, it will be enough to show that

$$\int_R^\infty dr \int_R^r dt \psi^2(r; E_0) \psi^2(t; E_0) \left[\int_R^t ds \psi^{-2}(s; E_0) \right]^2 \quad (6.10)$$

is finite. On using Eq. (6.8) one finds that this is bounded by

$$\left(\frac{C_4}{C_3} \right)^4 \int_R^\infty dr \int_R^r dt f_-^2(r) f_-^2(t) \left[\int_R^t ds f_-^{-2}(s) \right]^2. \quad (6.11)$$

Now

$$\begin{aligned} \int_R^t ds f_-^{-2}(s) &= \int_R^t ds [V(s) - E_0]^{1/2} \exp \left\{ 2 \int_R^s dw [V(w) - E_0]^{1/2} \right\} \\ &\leq \frac{1}{2} \exp \left\{ 2 \int_R^t dw [V(w) - E_0]^{1/2} \right\}. \end{aligned} \quad (6.12)$$

Hence (6.11) is not greater than

$$\frac{1}{4} \left(\frac{C_4}{C_3} \right)^4 \int_R^\infty d\tau f_-^2(\tau) \int_R^\tau dt [V(t) - E_0]^{1/2} \exp \left\{ \int_R^t ds [V(s) - E_0]^{1/2} \right\} \mu(t) \quad (6.13)$$

where

$$\mu(t) = [V(t) - E_0]^{-1} \exp \left\{ \int_R^t ds [V(s) - E_0]^{1/2} \right\}. \quad (6.14)$$

Now R can be chosen so large that $\mu(t)$ is monotonic increasing for $t \geq R$, so (6.13) can be majorized by replacing $\mu(t)$ by $\mu(r)$, and the integrand that remains can be integrated exactly. One finds that (6.13) is majorized by

$$\frac{1}{4} \left(\frac{C_4}{C_3} \right)^4 \int_R^\infty \frac{d\tau}{[V(\tau) - E_0]^{3/2}}, \quad (6.15)$$

and since Eq. (6.4) is satisfied, this integral converges.

It is also necessary for $\|F_0 U\|$ to exist. In L^2 this may be expressed

$$\|F_0 U\|^2 = 2 \int_0^\infty d\tau \int_0^\tau dt U^2(\tau) \Psi^2(\tau; E_0) \Psi^2(t; E_0) \left[\int_R^t ds \Psi^{-2}(s; E_0) \right]^2 \quad (6.16)$$

It is required, then, that

$$\int_R^\infty \frac{dr \, U^2(r)}{[V(r) - E_0]^{3/2}} \quad (6.17)$$

converge. Clearly, if $U(r)$ is bounded as $r \rightarrow \infty$, then (6.17) will exist, but this is not necessary. For example, if

$$V(r) \underset{r \rightarrow \infty}{\sim} r^n, \quad (6.18)$$

and

$$U(r) \underset{r \rightarrow \infty}{\sim} r^m, \quad (6.19)$$

then, for convergence of (6.17) one needs

$$m < \frac{3}{4}n - \frac{1}{2}. \quad (6.20)$$

Thus $n = 4$ and $m = 2$ is allowed. The quantity u_1 [Eq. (5.4)] exists also, of course.

The conclusion is that, if the integrals (6.15) and (6.17) converge, then the perturbation series converges inside a non-vanishing circle about $\lambda = 0$. In particular, if $V(r) = r^4$ and $\lambda U(r) = \lambda r^2$, then the perturbation series converges if λ satisfies the corresponding inequality (5.13).

However, the restriction (6.20) should not be taken seriously, because in Section 8, with the help of another Banach space, it will be shown that all one really needs is

$$m \leq n. \quad (6.21)$$

7. - BOUNDED POTENTIALS

In this section, the case in which the potential vanishes asymptotically faster than r^{-1} , i.e. :

$$r^{1+\varepsilon} V(r) \xrightarrow{r \rightarrow \infty} 0 \quad (7.1)$$

with $\varepsilon > 0$, will be treated. The Hamiltonian has a continuum spectrum for $E > 0$, corresponding to the scattering states, and can have a discrete spectrum for $E < 0$, corresponding to bound states. Consider, as before, a non-degenerate eigenvalue $E_0 < 0$, with eigenfunction $\psi(r; E_0)$.

Write $K_0 = +(-E_0)^{\frac{1}{2}}$, and suppose that $V(r)$ satisfies the following conditions : R exists such that

$$\frac{|V'(r)|}{V(r) + K_0^2} \leq \frac{C_1}{r}, \quad (7.2)$$

for all $r \geq R$, and

$$\frac{|V''(r)|}{V(r) + K_0^2} \leq \frac{C_2}{r^2} \quad (7.3)$$

for all $r \geq R$.

According to the results of the Appendix, these conditions [for condition (A.2) follows from (7.1) and the fact that E_0 is negative] imply that C_3 and C_4 exist, such that

$$C_3 f_-(r) \leq |\psi(r; E_0)| \leq C_4 f_-(r) \quad (7.4)$$

for all $r \geq R$, where $f_-(r)$ was defined in Eq. (6.9), just as in Section 6. However, in this case

$$\exp \left\{ - \int_R^r ds [V(s) + K_0^2]^{1/2} \right\} = e^{-K_0(r-R)} \cdot \exp \left\{ - \int_R^r \frac{ds V(s)}{K_0 [V(s) + K_0^2]^{1/2}} \right\}, \quad (7.5)$$

and, because of Eq. (7.1), the integral in the second factor on the right of (7.5) remains bounded as $r \rightarrow \infty$. Hence it follows that one can replace Eq. (7.4) by

$$C_3 e^{-K_0 r} \leq |\psi(r; E_0)| \leq C_4 e^{-K_0 r}, \quad (7.6)$$

for all $r \geq R$, by suitably redefining C_3 and C_4 . Notice that this is not possible if $V(r)$ goes to zero more slowly than is indicated by Eq. (7.1). In particular, in the Coulomb case, $V \sim 1/r$, it is well known that the Laguerre functions depart from exponential behaviour to the extent of a multiplicative polynomial in r .

For potentials obeying (7.1), it is no longer possible to analyze the integral equation (4.10) in L^2 Hilbert space. Instead, use a Banach space, $\mathcal{B}_M$, in which the norm is defined by ^{*})

$$\|\phi\| \equiv (2\alpha)^{-1/2} \sup_{0 \leq r < \infty} [e^{\alpha r} \phi(r)], \quad (7.7)$$

where α is a constant that satisfies

$$0 < \alpha < K_0. \quad (7.8)$$

^{*}) I would like to thank Dr. A. Martin for having suggested this norm.

Clearly $\psi(r)$ possesses a norm of this kind, because it is bounded for $0 \leq r \leq R$, and it satisfies Eq. (7.6) for $r \geq R$. The space of all continuous functions that possess a norm (7.7) is complete. Moreover, if ψ and ϕ belong to the space, then

$$\begin{aligned} |\langle \psi | \phi \rangle| &= \left| \int_0^\infty dr \psi(r) \phi(r) \right| \\ &\leq 2\alpha \|\psi\| \cdot \|\phi\| \int_0^\infty dr e^{-2\alpha r} \\ &= \|\psi\| \cdot \|\phi\|, \end{aligned} \quad (7.9)$$

which is a property that was required in the general analysis of Section 5.

It has to be shown that $\|F_0\|$ exists with this norm. From the definition (4.1), and the bounds (7.6), one finds that

$$|F(\tau, t; E_0)| \leq \left(\frac{C_4}{C_3} \right)^2 \frac{\exp \{ 2K_0 \min(\tau, t) - K_0\tau - K_0t \}}{2K_0}, \quad (7.10)$$

for $r, t \geq R$. Let $\phi(t)$ be any function that belongs to the Banach space. Then

$$\begin{aligned} & \left| \int_R^\infty dt F(\tau, t; E_0) \phi(t) \right| \\ & \leq \left(\frac{C_4}{C_3} \right)^2 \frac{1}{2K_0} \left\{ e^{-K_0\tau} \int_R^\tau dt e^{K_0t} |\phi(t)| \right. \\ & \quad \left. + e^{K_0\tau} \int_\tau^\infty dt e^{-K_0t} |\phi(t)| \right\} \\ & \leq \left(\frac{C_4}{C_3} \right)^2 \frac{(2\alpha)^{1/2}}{2K_0} \|\phi\| \left\{ e^{-K_0\tau} \int_R^\tau dt e^{(K_0-\alpha)t} \right. \\ & \quad \left. + e^{K_0\tau} \int_\tau^\infty dt e^{-(K_0+\alpha)t} \right\} \\ & \leq \left(\frac{C_4}{C_3} \right)^2 \frac{(2\alpha)^{1/2}}{K_0^2 - \alpha^2} \|\phi\| e^{-\alpha\tau}, \end{aligned} \quad (7.11)$$

for $r \geq R$. Now, by definition,

$$f_0 = \|F_0\| = \sup_{\phi} \{ \|F\phi\| / \|\phi\| \}, \quad (7.12)$$

where the supremum is taken over all ϕ belonging to $\mathcal{B}_M$, except, of course, $\phi(r) \equiv 0$. From Eq. (7.11),

$$\begin{aligned} \|F_0 \phi\| / \|\phi\| &= (2\alpha)^{-1/2} \sup_{0 \leq r < \infty} \left| e^{\alpha r} \int_0^\infty dt F(r, t; E_0) \phi(t) \right| / \|\phi\| \\ &\leq \left(\frac{c_4}{c_3} \right)^2 \frac{1}{K_0^2 - \alpha^2} + \\ &\quad + \sup_{0 \leq r < R} \left| e^{\alpha r} \int_0^\infty dt F(r, t; E_0) e^{-\alpha t} \right|. \end{aligned} \quad (7.13)$$

So $\|F_0\|$ does indeed exist, since clearly the second term in (7.13) is bounded.

It was also required in Section 5 that $\|F_0 U\| = f_0 f_1$ should exist. It is evident from the analysis of Eq. (7.11) that it is enough if $U(r)$ is bounded as $r \rightarrow \infty$, which in practice will mean $U(r) \xrightarrow{r \rightarrow \infty} 0$. Note, however, that although $V(r)$ must obey Eq. (7.1) for the applicability of the foregoing analysis, $U(r)$, the perturbation, may go to zero more slowly than $V(r)$, and the perturbation series will still converge, for λ small enough. This is not too surprising, however, since such a $U(r)$ can at most change the asymptotic behaviour from $\exp[-K_0 r]$ to $\exp[-K_0 r + o(r)]$, which does not violate the norm (7.7), since $\alpha < K_0$. Clearly the constant u_1 , Eq. (5.5), also exists, so the radius of convergence of the perturbation series can be estimated from Eq. (5.32).

8. - GENERAL CASE

In Section 6, potentials were treated which grow faster than $r^{2/3}$, as $r \rightarrow \infty$, and in the last section, potentials which vanish faster than r^{-1} . Evidently there is an intermediate domain which has not yet been covered, and this includes the physically interesting case of the Coulomb potential.

In this section, a generalization of the Banach space of Section 7 will be introduced, and this will permit the treatment of any potential that vanishes as $r \rightarrow \infty$, or that grows less quickly than an exponential. In particular, it works in the intermediate domain r^{-1} to $r^{2/3}$. The potential is subjected to the three requirements (A.2)-(A.4), so that one has the double bound (A.5).

The more general Banach space, which will be called $\mathcal{B}$, is the complete space of all continuous functions, $\phi(r)$, for which the following norm exists :

$$\begin{aligned} \|\phi\| = N \sup_{0 \leq r < R} |\phi(r)| + \\ + N \sup_{R \leq r < \infty} \left| \phi(r) [V(r) - E_0]^{-3/4} \exp \left[\alpha \int_R^r ds [V(s) - E_0]^{1/2} \right] \right| \end{aligned} \quad (8.1)$$

where α satisfies

$$0 < \alpha < 1, \quad (8.2)$$

and where the normalization constant, N , is

$$N = \left\{ R + \int_R^\infty dr [V(r) - E_0]^{3/2} \exp \left[-2\alpha \int_R^r ds (V(s) - E_0)^{1/2} \right] \right\}^{-1/2}. \quad (8.3)$$

The term $[\bar{V}(r) - E_0]^{-3/4}$ supplies a convenient integrating factor, in the estimation of $\|F_0\|$, and it is bounded for $r \geq R$, by Eq. (A.2). One verifies again that, if ϕ and ψ belong to $\mathcal{B}$, then

$$|\langle \phi | \psi \rangle| \leq \|\phi\| \cdot \|\psi\|. \quad (8.4)$$

It will now be shown that $f_0 = \|F_0\|$ exists. From Eqs. (4.1) and (A.5), one has

$$\begin{aligned} |F(\tau, t; E_0)| &\leq \left(\frac{C_4}{C_3}\right)^2 f_-(\tau) f_-(t) \int_R^{\min(\tau, t)} ds f_-^{-2}(s) \\ &\leq \frac{1}{2} \left(\frac{C_4}{C_3}\right)^2 \left\{ f_-(\tau) f_+(t) \theta(\tau - t) + f_+(\tau) f_-(t) \theta(t - \tau) \right\} \end{aligned} \quad (8.5)$$

for $r, t \geq R$. Hence, if $\phi(t)$ belongs to $\mathcal{B}$,

$$\begin{aligned} &\left| \int_R^\infty dt F(\tau, t; E_0) \phi(t) \right| \\ &\leq \left(\frac{C_4}{C_3}\right)^2 \frac{\|\phi\|}{2N} \left\{ f_-(\tau) \int_R^\tau dt [V(t) - E_0]^{1/2} \exp \left[-(1-\alpha) \int_R^t ds (V(s) - E_0)^{1/2} \right] + \right. \\ &\quad \left. + f_+(\tau) \int_\tau^\infty dt [V(t) - E_0]^{1/2} \exp \left[-(1+\alpha) \int_R^t ds (V(s) - E_0)^{1/2} \right] \right\} \quad (8.6) \\ &\leq \left(\frac{C_4}{C_3}\right)^2 \frac{\|\phi\|}{N(1-\alpha^2)} [V(\tau) - E_0]^{-1/4} \exp \left\{ -\alpha \int_R^\tau ds (V(s) - E_0)^{1/2} \right\}, \end{aligned}$$

for $r \geq R$. The norm of $\|F_0\|$ can be broken up into four pieces :

$$\begin{aligned} &\frac{N}{\|\phi\|} \sup_{R \leq \tau < \infty} \left| [V(\tau) - E_0]^{-1/4} \exp \left\{ -\alpha \int_R^\tau ds [V(s) - E_0]^{1/2} \right\} \int_R^\infty dt F(\tau, t; E_0) \phi(t) \right| \\ &\leq \left(\frac{C_4}{C_3}\right)^2 \frac{1}{1-\alpha^2} \sup_{R \leq \tau < \infty} \left[\frac{1}{V(\tau) - E_0} \right]. \end{aligned} \quad (8.7)$$

Secondly,

$$\begin{aligned} & \frac{N}{\|\phi\|} \sup_{R \leq \tau < \infty} \left| [V(\tau) - E_0]^{-1/4} \exp\left\{-\alpha \int_R^\tau ds [V(s) - E_0]^{1/2}\right\} \int_0^R dt F(\tau, t; E_0) \phi(t) \right| \\ & \leq C_4 \sup_{R \leq \tau < \infty} \left[[V(\tau) - E_0]^{-1/2} \exp\left\{-(1+\alpha) \int_R^\tau ds [V(s) - E_0]^{1/2}\right\} \int_0^R dt \left| \psi(t; E_0) \int_t^R \frac{dw}{\psi^2(w; E_0)} \right| \right] \end{aligned} \quad (8.8)$$

Thirdly,

$$\begin{aligned} & \frac{N}{\|\phi\|} \sup_{0 \leq \tau < R} \left| \int_R^\infty dt F(\tau, t; E_0) \phi(t) \right| \\ & \leq \frac{C_4}{1+\alpha} \sup_{0 \leq \tau < R} \left| \psi(\tau; E_0) \int_\tau^R \frac{dw}{\psi^2(w; E_0)} \right|. \end{aligned} \quad (8.9)$$

Lastly,

$$\begin{aligned} & \frac{N}{\|\phi\|} \sup_{0 \leq \tau < R} \left| \int_0^R dt F(\tau, t; E_0) \phi(t) \right| \\ & \leq \sup_{0 \leq \tau < R} \int_0^R dt |F(\tau, t; E_0)|. \end{aligned} \quad (8.10)$$

The four terms (8.7)-(8.10) are bounded, so that $\|F_0\|$, which is certainly not greater than their sum, exists.

It has to be checked now that $\|F_0 U\|$ exists. Clearly, if $U(r)$ is bounded everywhere, there is no trouble. However, it is of some interest to see under what circumstances one can allow $U(r) \rightarrow \infty$ as $r \rightarrow \infty$, and still have a convergent perturbation series. It will also prove useful, in Section 9, to allow $U(r)$ to have singularities at finite values of r . For simplicity, it is assumed that $U(r)$ has a finite number of singularities for $r < R$, none of which is worse than a simple pole. That is, there exists some integer, ν , such that

$$r^{2-\varepsilon} (r-r_1)(r-r_2) \dots (r-r_\nu) U(r) \quad (8.11)$$

remains bounded for $0 \leq r \leq R$, where $0 < r_1 < r_2 < \dots < r_\nu < R$.

Consider each of the four terms (8.7)-(8.10) in turn, but now with an extra $U(t)$ under the integrals. It is not difficult to see that (8.7) can be majorized by a constant multiple of

$$\sup_{R \leq r < \infty} \left[\frac{|U(r)|}{V(r) - E_0} \right] \quad (8.12)$$

in the case that $V(r) \rightarrow \infty$ as $r \rightarrow \infty$, and by a term proportional to

$$\sup_{R \leq r < \infty} \left[\frac{1}{V(r) - E_0} \right] \cdot \sup_{R \leq r < \infty} |U(r)| \quad (8.13)$$

when $V(r) \rightarrow 0$ as $r \rightarrow \infty$. Thus, for this term to be bounded, it suffices for $|U(r)|/V(r)$ to be asymptotically bounded if $V(r)$ diverges, and for $|U(r)|$ to be asymptotically bounded if $V(r)$ does not diverge. For the term (8.9), one can similarly extract the factor (8.12) or (8.13), depending on the case, and what is left is a constant factor times the right-hand side of (8.9).

For the remaining terms (8.8) and (8.10), with an extra factor $U(t)$, one sees that, because $\psi(t; E_0)$ and $\phi(t)$ are continuous, the pole singularities, (8.11), that $U(t)$ can have, will be integrated away, so that (8.8) and (8.10) will remain bounded.

It is of interest to compare the above conditions for the existence of a non-vanishing radius of convergence of the perturbation series, that is, for holomorphy in a neighbourhood of $\lambda = 0$, with

the conditions of Kato ⁴⁾. It seems that the two sets of conditions are not the same, but that, for a certain class of potentials, they are equivalent. Kato's condition is that, if $|x\rangle$ is any vector that belongs to the domain, $\mathcal{D}$ (of L^2 Hilbert space), of the unperturbed Hamiltonian, $p^2 + V$, where $p = -i(d/dr)$ in the configuration representation, then there is a non-vanishing radius of convergence if constants a and b exist such that

$$\|Ux\| \leq a \|(p^2 + V)x\| + b \|x\|. \quad (8.14)$$

In the case that $\mathcal{D}$ is no larger than the common domain on which p^2 and V are separately bounded, it follows that (8.14) will certainly be guaranteed if

$$\|Ux\| \leq a \|Vx\| + b \|x\|. \quad (8.15)$$

For this case, the condition agrees with Eqs. (8.12) and (8.13), so far as the asymptotics are concerned. That is, if $V(r)$ diverges, $|U(r)|/V(r)$ must be bounded, whereas if $V(r) \rightarrow 0$, it suffices for $|U(r)|$ to remain bounded asymptotically.

9. - CONSTRUCTION OF EIGENFUNCTION AND EIGENVALUE

In this last section, a brief survey will be made of the possibilities that are now open for the systematic perturbative construction of an eigenfunction and eigenvalue for a given potential, $V(r)$.

Suppose that, for a given $V(r)$, one can find a real number, E_0 , such that, for all $r \geq 0$,

$$V(r) - E_0 \geq K > 0, \quad (9.1)$$

$$\frac{|V'(r)|}{V(r) - E_0} \leq \frac{C_1}{r}, \quad (9.2)$$

$$\frac{|V''(r)|}{V(r) - E_0} \leq \frac{C_2}{r^2}, \quad (9.3)$$

where K, C_1, C_2 are positive constants.

Define $\psi_0(r)$ by

$$\psi_0(r) = N \frac{P_n(r)}{Q_n(r)} [V(r) - E_0]^{-1/4} \exp \left\{ - \int_0^r ds [V(s) - E_0]^{1/2} \right\} \quad (9.4)$$

where $P_n(r)$ and $Q_n(r)$ are polynomials of order n each, with the following properties

$$P_n(0) = 0, \quad (9.5)$$

$$Q_n(0) = 1, \quad (9.6)$$

$$Q_n(r) > 0, \quad (9.7)$$

for all $r > 0$, and $P_n(r)$ has only simple zeros,

$$P_n(r) / Q_n(r) \xrightarrow{r \rightarrow \infty} 1. \quad (9.8)$$

The normalization constant, N , is chosen so that

$$\int_0^{\infty} dr \psi_0^2(r) = 1. \quad (9.9)$$

The simplest possibility is

$$\frac{P_n(r)}{Q_n(r)} = \frac{r}{r+1}. \quad (9.10)$$

The "wave-function", $\psi_0(r)$, satisfies the equation

$$\left[-\left(\frac{d}{dr}\right)^2 + V(r) - E_0 + U(r) \right] \psi_0(r) = 0, \quad (9.11)$$

where

$$\begin{aligned} U(r) = & \frac{5}{16} \left[\frac{V'(r)}{V(r) - E_0} \right]^2 - \frac{1}{4} \left[\frac{V''(r)}{V(r) - E_0} \right] - \\ & - 2 \left\{ [V(r) - E_0]^{-1/2} + \frac{1}{4} \left[\frac{V'(r)}{V(r) - E_0} \right] \right\} \left\{ \frac{P_n'(r)}{P_n(r)} - \frac{Q_n'(r)}{Q_n(r)} \right\} + \\ & + \frac{P_n''(r)}{P_n(r)} - 2 \frac{P_n'(r) Q_n'(r)}{P_n(r) Q_n(r)} - \\ & - \frac{Q_n''(r)}{Q_n(r)} + 2 \left[\frac{Q_n'(r)}{Q_n(r)} \right]^2. \end{aligned} \quad (9.12)$$

One can now try to calculate, perturbatively, a function $\varphi(r)$, that satisfies

$$\left[-\left(\frac{d}{dr}\right)^2 + V(r) - E \right] \varphi(r) = 0, \quad (9.13)$$

$$\varphi(r) \xrightarrow{r \rightarrow \infty} 0, \quad (9.14)$$

$$\varphi(0) = 0. \quad (9.15)$$

This is done by writing

$$\left[-\left(\frac{d}{dr}\right)^2 + V(r) + U(r) - \lambda U(r) - E(\lambda) \right] \varphi(r; \lambda) = 0, \quad (9.16)$$

where $\varphi(r; \lambda)$ also satisfies the boundary conditions (9.14) and (9.15). Moreover,

$$\varphi(r; 0) = \psi_0(r), \quad (9.17)$$

$$E(0) = E_0. \quad (9.18)$$

Formally,

$$\varphi(r; 1) = \varphi(r), \quad (9.19)$$

$$E(1) = E. \quad (9.20)$$

The question is : can one continue from $\lambda = 0$ to $\lambda = 1$?

It can be seen that the "perturbing potential", $U(r)$, of Eq. (9.12), satisfies the requirements of Section 8 for the existence of a non-zero radius of convergence of the perturbation series. This is true whether $V(r) \rightarrow \infty$ or $V(r) \rightarrow 0$, as $r \rightarrow \infty$, so long as conditions (9.1)-(9.3) are satisfied. Thus one can certainly calculate $E(\lambda)$ and $\phi(r; \lambda)$ as accurately as one likes, for λ less than some λ_0 . One could first calculate $\mathcal{E} = [E(\lambda) - E_0]/\lambda$, most elegantly by the sequence (4.18), (4.19). One would then solve the integral equation (4.10), by summing the series (4.11), in order to obtain $\phi(r; \lambda)$.

In practice, of course, the series in question would have to be truncated, but formulae (5.36) and (5.37) of Section 5 give bounds on the truncation errors, so that one can compute in advance how many terms one would have to keep, for a pre-assigned accuracy.

One has the freedom to choose P_n , Q_n and E_0 in order to maximize the radius of convergence in the λ plane, in the attempt to reach $\lambda = 1$. Note that, even if, in a particular case, one cannot manage to reach $\lambda = 1$, but only $\lambda = \lambda'_0$, say, one can then repeat the whole process, using the calculated $\phi(r; \lambda'_0)$ as a new $\psi_0(r)$. Note that errors are not cumulative in such a step-by-step continuation, because, starting with the new $\psi_0(r)$, one would calculate $\psi''_0(r)$, and then define

$$E_0 = E(\lambda'_0), \quad (9.21)$$

$$U(r) = \frac{\psi''_0(r)}{\psi_0(r)} - V(r) + E_0 \quad (9.22)$$

in the case that $r V(r) \not\rightarrow 0$ as $r \rightarrow \infty$. If $r^{1+\epsilon} V(r) \rightarrow 0$ as $r \rightarrow \infty$, it might be better to define E_0 first by

$$E_0 = \lim_{r \rightarrow \infty} \frac{\psi_0''(r)}{\psi_0(r)}, \quad (9.23)$$

instead of Eq. (9.21).

One is not forced to start the process with the ansatz (9.4). In physical problems, one often has a better way of obtaining an approximate eigenfunction, for example the variational method, or a self-consistency approach, à la Hartree. These methods, while very useful practically, are notoriously difficult to control, in so far as error estimates are concerned. The new style perturbation theory could be used to supply this deficiency, and to "tighten up" a variational approximation as much as might be desired. Note that, for the ground state, $\psi_0(r)$ has no zeros for $0 < r < \infty$, so that $U(r)$, defined by Eq. (9.22), would be bounded in this region. For other states, $\psi_0(r)$ has zeros, and so $U(r)$ would have poles. However, if one uses the norm of Section 8, and chooses R to be greater than R_0 , the position of the last finite zero of $\psi_0(r)$, all the norms in question are finite.

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- APPENDIX -

Define

$$f_{\pm}(\tau) = [V(\tau) - E_0]^{-1/4} \exp \left\{ \pm \int_R^{\tau} ds [V(s) - E_0]^{1/2} \right\}. \quad (A.1)$$

It will be supposed that $V(r)$ satisfies the following requirements :
R and K exist such that

$$V(r) - E_0 \geq K > 0, \quad (A.2)$$

for all $r \geq R$. Constants C_1 and C_2 exist such that

$$\frac{|V'(r)|}{V(r) - E_0} \leq \frac{C_1}{r}, \quad (A.3)$$

and

$$\frac{|V''(r)|}{V(r) - E_0} \leq \frac{C_2}{r^2}, \quad (A.4)$$

for all $r \geq R$.

In practice, there are two cases of interest :

(a) $V(r) \rightarrow +\infty$; (b) $V(r) \rightarrow 0$, when necessarily one must have $E_0 < 0$.

It will be shown that constants C_3 and C_4 can be found, such that

$$C_3 f_-(r) \leq |\psi(r; E_0)| \leq C_4 f_-(r), \quad (A.5)$$

for all $r \geq R$, where $\psi(r; E_0)$ satisfies Eqs. (2.1)-(2.3). It will be shown further that

$$\psi(r; E_0) / f_-(r) \xrightarrow{r \rightarrow \infty} \text{const.} \quad (A.6)$$

The demonstration may be regarded as a rigorous justification of the WKB method for the asymptotic region, when conditions (A.2)-(A.4) are satisfied.

The functions $f_{\pm}(r)$ are independent and satisfy the same differential equation

$$\left[-\left(\frac{d}{dr}\right)^2 + W(r) \right] f_{\pm}(r) = 0, \quad (A.7)$$

where

$$W(r) = V(r) - E_0 + \frac{5}{16} \left[\frac{V'(r)}{V(r) - E_0} \right]^2 - \frac{1}{4} \left[\frac{V''(r)}{V(r) - E_0} \right]. \quad (A.8)$$

The Green's function

$$\begin{aligned} \mathcal{Y}(r, t) = & f_+(r) f_-(t) \theta(t-r) + \\ & + f_-(r) f_+(t) \theta(r-t) \end{aligned} \quad (A.9)$$

satisfies

$$\left[-\left(\frac{d}{dr}\right)^2 + W(r) \right] \mathcal{Y}(r, t) = \delta(r-t). \quad (\text{A.10})$$

Since $\psi(r; E_0)$ satisfies Eq. (2.1), and the boundary conditions (2.2), it must be possible to write, for $r > R$,

$$\psi(r; E_0) = A f_-(r) + \int_R^\infty dt \mathcal{Y}(r, t) Y(t) \psi(t; E_0), \quad (\text{A.11})$$

for some constant A , where

$$Y(t) = \frac{5}{16} \left[\frac{V'(t)}{V(t) - E_0} \right]^2 - \frac{1}{4} \left[\frac{V''(t)}{V(t) - E_0} \right]. \quad (\text{A.12})$$

The reason for starting the integral only at $t = R$ is, of course, to avoid the embarrassment of zeros of $V(t) - E_0$, which would cause $Y(t)$ to become unbounded. From Eqs. (A.3) and (A.4) one has

$$|Y(t)| \leq \frac{C}{t^2}, \quad (\text{A.13})$$

for $t \geq R$, where

$$C = \frac{5}{16} C_1^2 + \frac{1}{4} C_2. \quad (\text{A.14})$$

Define

$$\mathfrak{J}(r) = r^{-\frac{1}{2}-\varepsilon} \psi(r; E_0) / f_-(r), \quad (\text{A.15})$$

with $\varepsilon > 0$. Then the integral equation (A.11) becomes

$$\mathfrak{J}(r) = A r^{-\frac{1}{2}-\varepsilon} + \int_R^\infty dt \left[r^{-\frac{1}{2}-\varepsilon} \mathcal{Y}(r, t) t^{\frac{1}{2}+\varepsilon} Y(t) f_-(t) / f_-(r) \right] \mathfrak{J}(t). \quad (\text{A.16})$$

It will be shown that the kernel of this equation is square-integrable.

In fact,

$$\begin{aligned} & \int_R^\infty dr \int_R^\infty dt r^{-1-2\varepsilon} \mathcal{Y}^2(r, t) t^{1+2\varepsilon} Y^2(t) f_-^2(t) / f_-^2(r) \\ &= 2 \int_R^\infty dr r^{-1-2\varepsilon} \int_R^r dt [V(t) - E_0]^{-1} t^{1+2\varepsilon} Y^2(t). \end{aligned} \quad (\text{A.17})$$

From Eqs. (A.2) and (A.13) one sees that this quantity is not greater than

$$\begin{aligned} & \frac{2C^2}{K} \int_R^\infty dr r^{-1-2\varepsilon} \int_R^r dt t^{-3+2\varepsilon} \\ & \leq \frac{C^2}{2K\varepsilon(1-\varepsilon)} \cdot \frac{1}{R^2} \end{aligned} \quad (\text{A.18})$$

Since the inhomogeneous term of Eq. (A.16) is also L^2 , it follows that (A.16) is a Fredholm equation. The constant R can be chosen so large that the bound (A.18) on the L^2 norm of the kernel is less than unity, so that the corresponding homogeneous equation has no non-trivial solutions, and under these conditions one knows that (A.16) has a unique square-integrable solution, $\mathfrak{J}(r)$.

From Eq. (A.16), one has

$$|r^{\frac{1}{2}+\epsilon} \zeta(r) - A| \leq \left| \int_R^r dt [V(t) - E_0]^{-\frac{1}{2}} t^{\frac{1}{2}+\epsilon} Y(t) \zeta(t) \right| + \quad (A.19)$$

$$+ \left| \int_r^\infty dt f_-^2(t) t^{\frac{1}{2}+\epsilon} Y(t) \zeta(t) \right| f_+(r) / f_-(r).$$

Using the Schwarz inequality, one sees that the first term on the right-hand side of (A.19) is bounded by

$$\left\{ \int_R^r dt [V(t) - E_0]^{-1} t^{1+2\epsilon} Y^2(t) \right\}^{\frac{1}{2}} \left\{ \int_R^r dt \zeta^2(t) \right\}^{\frac{1}{2}} \quad (A.20)$$

$$\leq \frac{C \|\zeta\|}{2 K^{\frac{1}{2}} (1-\epsilon) R^{2-2\epsilon}}.$$

This is finite, since $\|\zeta\|$ exists. In the second term on the right-hand side of (A.19), one can certainly arrange, by choosing R sufficiently large, that $f_-(t)$ is monotonic decreasing for t in the range $R \leq r \leq t < \infty$. Hence the term in question may be majorized by replacing $f_-^2(t)$ by its value at the lower limit of integration, $t = r$. This gives

$$f_+(r) f_-(r) \left| \int_r^\infty t^{\frac{1}{2}+\epsilon} Y(t) \zeta(t) dt \right| \quad (A.21)$$

$$\leq \frac{C \|\zeta\|}{2 K^{\frac{1}{2}} (1-\epsilon) R^{2-2\epsilon}}.$$

The norm $\|\zeta\|$ is proportional to the normalization parameter, A , so the sum of (A.20) and (A.21) may be written

$$\frac{\bar{C} A}{R^{2-2\epsilon}} \quad (A.22)$$

where $\bar{C}$ is constant. Choose R so large that

$$2\bar{C} \leq R^{2-2\epsilon} \quad (\text{A.23})$$

Then one has shown that

$$|r^{\frac{1}{2}+\epsilon} \mathcal{J}(r) - A| \leq \frac{1}{2}A, \quad (\text{A.24})$$

for $r \geq R$. In other words, there is an R such that

$$\frac{1}{2}A \leq |r^{\frac{1}{2}+\epsilon} \mathcal{J}(r)| \leq \frac{3}{2}A, \quad (\text{A.25})$$

for $r \geq R$. This double inequality is equivalent to Eq. (A.5), as can be seen from Eq. (A.15).

One can go further, since (A.15), (A.19) and (A.22) imply

$$A\left[1 - \frac{\bar{C}}{R^{2-2\epsilon}}\right] \leq |\psi(r; E_0) / f_-(r)| \leq A\left[1 + \frac{\bar{C}}{R^{2-2\epsilon}}\right] \quad (\text{A.26})$$

for $r \geq R$. Since one may take R as large as one likes, it follows that

$$\frac{\psi(r; E_0)}{f_-(r)} \xrightarrow{r \rightarrow \infty} A. \quad (\text{A.27})$$

Of course the normalization constant, A , will depend on R , but it must tend to a finite value as $R \rightarrow \infty$, since otherwise (A.26), which holds for all $r \geq R$, for a given fixed R , and so a fixed A , would be violated. In fact, if $A(R)$ is the normalization constant for a given value of R , it follows that

$$A(R) \left[1 - \frac{\bar{c}}{R^{2-2\epsilon}} \right] \leq A(\infty) \leq A(R) \left[1 + \frac{\bar{c}}{R^{2-2\epsilon}} \right]. \quad (\text{A.28})$$

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