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PERTURBATION THEORY WITHOUT A COMPLETE SET

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It is shown how to develop a perturbation theory for the eigenvalues of Schrödinger equation without defining a complete set of eigenfunctions. The coefficients are entirely dependent on the state which is being perturbed. This is achieved by replacing the eigenvalue problem by an algebraic equation.

1. Introduction

When seeking the approximate solution of the eigenvalue problem for Schrödinger equation, one usually starts by expanding the wave function in a power series of conveniently chosen perturbation. If the potential is defined as

$$V = V_0 + \varepsilon V' \tag{1.1}$$

then the eigenfunction ψ_n is represented as

$$\psi_n = \psi_n^0 + \varepsilon \psi_n^1 + \dots \tag{1.2}$$

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The eigenvalue, corresponding to ψ_n, is

$$E_n = E_n^0 + \varepsilon E_n^1 + \dots . \tag{1.3}$$

Obtaining the corrections E_n^k to E_n^0 is the prime interest of the perturbation theory. To achieve this it is assumed that the set of eigenfunctions ψ_n, including the continuum, form a complete set, whence the coefficients E_n^k are found[1]. Thus the first order correction is

$$E_n^1 = \int_0^\infty \psi_n^0 V' \psi_n^0 \, \mathrm{d}\tau \equiv < n \mid V' \mid n > \tag{1.4}$$

and the second order

$$E_n^2 = \sum_{m \neq n} \frac{\mid < n \mid V' \mid m > \mid^2}{E_n^0 - E_m^0} \tag{1.5}$$

where the sum extends over the complete set, including the continuum. Similarly, higher order terms are obtained.

There are several objections to such a procedure. The most obvious one is how to correctly obtain the second order correction E_n^2 if only few bound states are present. Defining and integrating the continuum states is often not easy thing to do. The other difficulty with such procedure becomes evident when trying to extend the method to the resonance states i.e. the complex eigenvalues of Schrödinger equation. Such states have similar properties as the bound states except that they have finite lifetime. The perturbation procedure, as outlined above, is not directly applicable to such a case.

In this article we show that there is an alternative definition of the perturbation series (1.3), which does not require the use of a complete set of eigenfunctions. The essential idea is to note that the eigenvalues of Schrödinger equation appear as the poles of the S-matrix[2] or if one talks in terms of the Jost functions[3], then the eigenvalues are the roots of one of the Jost functions. Since the Jost function appropriate to (1.1) is ε dependent, so will be the roots of it. The idea is of the perturbation method to expand this roots in a power series of ε. As it will be shown, the coefficients of such expansion depend only on the wave function and its derivatives of this particular eigenvalue. The method easily covers all possible eigenvalues, both real and complex, and to all orders, without making use of the eigenstates for different eigenvalues. We will show the advantages of such a method on few examples.

2. *The theory*

Schrödinger equation for the l-th partial wave of a two particle system is

$$\psi'' = \left[V(r) + \frac{l(l+1)}{r^2} - k^2 \right] \psi . \tag{2.1}$$

The regular solution of (2.1) is zero for $r \to 0$, but for $r \to \infty$ it is a linear combination of two plane waves: incoming and outgoing

$$\psi \sim j^{+}(k)\, e^{ikr} + j\,(k)\, e^{-ikr}. \tag{2.2}$$

The coefficients of (2.2) are the Jost functions. The eigenvalue k_n for (2.1) is defined as the one for which the outgoing component of ψ is zero. This is satisfied for those k_n for which

$$j\,(k_n) = 0. \tag{2.3}$$

It can be shown that the roots of (2.3) are either imaginary or complex in the lower half of k-plane[2]. There are no other zeros. For a positive imaginary root $k = \mathrm{i}\, k_0$, the regular wave function ψ for $r \to \infty$, is

$$\psi \sim e^{-k_0 r} \tag{2.4}$$

therefore it is square integrable. Furthermore, $k^2 = -\, k_0^2 < 0$, hence the wave function is the eigenfunction of a bound state with the eigenvalue $-\, k_0^2$.

Similarly, the resonance poles are represented by the complex values of k in the lower half plane, but their corresponding eigenfunctions are not square integrable.

By defining the perturbation V' in (1.1), we notice that the Jost function j is also a function of ε, hence the roots of j are also ε dependent. For small ε we can develop the n-th root in a power series

$$k_n = k_n^0 + \varepsilon\, k_n^1 + \frac{\varepsilon^2}{2}\, k_n^2 + \dots . \tag{2.5}$$

where the coefficients are given by

$$k_n^0 = k_n\,(\varepsilon = 0);\; k_n^1 = \frac{\mathrm{d}\, k_n^1}{\mathrm{d}\, \varepsilon}\,(\varepsilon = 0);\; k_n^2 = \frac{\mathrm{d}^2\, k_n}{\mathrm{d}\, \varepsilon^2}\,(\varepsilon = 0). \tag{26}$$

The derivatives of k_n with respect to ε can be obtained from (2.3), thus giving for k_n^1

$$k_n^1 = -\frac{\partial j}{\partial \varepsilon} \bigg/ \frac{\partial j}{\partial k_n} \equiv -\frac{\overset{0}{j}}{j'}. \tag{2.7}$$

Similarly, for k_n^2 we get

$$k_n^2 = -\frac{1}{j'}\,(\overset{00}{j} + 2\, k_n^1 \overset{0\prime}{j} - (k_n^1)^2\, j''). \tag{2.8}$$

where the derivatives in (2.7) and (2.8) are assumed taken for $\varepsilon = 0$.

The problem is now to find the relationship of (2.7) and (2.8) to the perturbation potential V'. This task is solved by knowing the Jost function j as a function of ε. To find such a relationship, let us define the integral representation of the equation (2.1).

Given the unperturbed solution ψ_0 of (2.1), the exact regular solution of (2.1) is obtained from[2]

$$\psi = \psi_0 - \frac{\varepsilon}{2ik} \int_0^r K(r, r')\, V'(r')\, \psi(r')\, dr' \tag{2.9}$$

where $K(r, r')$ is the Green's function

$$K(r, r') = f_0^+(r) f_0^-(r') - f_0^+(r') f_0^-(r) \tag{2.10}$$

where

$$f_0^{\pm}(r) \sim e^{\mp ikr};\ r \to \infty. \tag{2.11}$$

The Jost function j is now obtained from (2.9) and (2.2)

$$j = j_0 - \frac{\varepsilon}{2ik} \int_0^\infty f_0^-\, V'\, \psi\, dr. \tag{2.12}$$

The equation (2.9) has a solution for all ε if the integral

$$\int_0^\infty \mathrm{d}r\, r\, |V'(r)|\, \exp(r(|\nu| \pm \nu)) \tag{2.13}$$

is finite[2], where $\nu = Im(k)$. The restriction (2.13) is k-dependent and would imply that the calculation, hence developing a perturbation method for the resonances, is not possible. Namely, the resonances are the complex zeros of j with $Im(k) < 0$, and since the Jost function is obtained from (2.12), the solution $f_0^-(r)$ is required. Since f_0^- is a function which exponentially increases as $\exp(-Im(k)\, r)$, the equation (2.12) does not have a solution for $Im(k) < 0$ unless $V(r)$ is a function which goes to zero for $r \to \infty$ faster then $\exp(-2|\nu| r)$. Generally speaking, such potentials are of rather special type, therefore in general it would appear that j does not exist. One way out of difficulty is to continue the potential into the complex coordinate plane and get f_0^- along the ray $z = r \exp(i\varphi)$; $\varphi > 0$ and for $Im(k) > 0$[4]. This is equivalent to calculating f_0^- with $k \to k \exp(i\varphi)$ and $V \to \exp(2i\varphi)(V(r \exp(i\varphi))$. The condition (2.13) now reads with $\nu = Im(k \exp(i\varphi))$ and the solution for j exists even for $Im(k) < 0$, provided $|\arg(k)| < \varphi$. The analyticity region of j is now extended to $Im(k) < 0$ with the restriction $|\arg(k)| \leqslant \varphi$, and the resonances are the roots of (2.3), evaluated on the ray $z = r \exp(i\varphi)$.

One is very often using the potentials which do not have analytic continuation into the coordinate plane e. g. square well. In such a case it is enough if for $r > R$ the potential is analytic. The equation (2.9) is now solved on a broken ray going along the real axis till $r = R$ and then into the complex plane for $r > R$. In other words, the solution of (2.9) is asymptotically on the ray $z = r \exp(i\varphi)$.

We are now in position to calculate (2.7) and (2.8) in terms of $V'(r)$. Thus we obtain for k_n^1

$$k_n^1 = \frac{1}{j_0'} \frac{1}{2i\,k_n^0} \int_0^\infty f_0^- \, V' \, \psi_0 \, \mathrm{d}r \tag{2.14}$$

and k_n^2

$$k_n^2 = -\frac{1}{j_0'} \left[(k_n^1)^2 j_0'' - \frac{k_n^1}{i\,k_n^0} \frac{\partial}{\partial k} \left(\int_0^\infty f_0^- \, \psi_0 \, V' \, \mathrm{d}r \right) - \right.$$
$$\left. - \frac{1}{2\,(k_n^0)^2} \int_0^\infty f_0^- \, V' \, \mathrm{d}r \int_0^r K(r, r') V'(r') \, \psi_0(r') \, \mathrm{d}r' \right]. \tag{2.15}$$

In both cases we get the coefficients in a closed form, without refering to a complete set of functions. However, in the relationship for k_n^2 we have to find the derivatives of matrix element (2.14) with respect to k.

If we make the use of relationship[2]

$$i\,j'\,j^+ = \int_0^\infty (\psi_n)^2 \, \mathrm{d}r \tag{2.16}$$

the coefficient (2.14) assumes more familiar form

$$k_n^1 = \frac{1}{2k_n^0} \frac{\int_0^\infty \psi_0 \, V' \, \psi_0 \, \mathrm{d}r}{\int_0^\infty (\psi_0)^2 \, \mathrm{d}r.}. \tag{2.17}$$

3. Discussion of the perturbation series

Let us compare this method to a more conventional one, the Rayleigh-Shrödinger method. Firstly, the *R-S* method uses the complete set[1], which in this approach is not necessary. This fact may be of advantage for the systems with few bound states, since the second order coefficient in the *R-S*, given by

$$E_n^2 = \sum_{m \neq n} \frac{|\langle n |\, V' \,| m \rangle|^2}{E_n - E_m} \tag{3.1}$$

may not have accurate value if the sum includes only the bound states. Otherwise one has to form a complete set out of the bound and unbound states, which is often a difficult thing to do.

When there are many bound states, so that they form approximate complete set, one would still have to calculate most of the bound states to get reasonable convergence in (3.1). The R-S method also fails for highly excited states because the number of the states higher in energy, and which contribute to (3.1), are fewer in number and they again are far from being a complete set. Furthermore, in the framework of the R-S method, the perturbation for the resonances has not been developed.

In this approach there is no concept of a complete set. The perturbation on a single bound state requires the knowledge of the solution of (2.1) in a small neighbourhood of that state (because of the derivative of Jost and wave function with respect to k). Furthermore, the resonances are treated on an equal footing with the bound states except that care should taken to evaluate the integrals along the broken ray, as discussed earlier.

There is also a difference in the variable which is being treated for perturbation expansion. In the R-S method one developes the energy variable (i.e. k_n^2) in a power series, while in this method one developes the wave number (i.e. k_n). To obtain the relationship between the two sets of coefficients, we take the square of

$$k_n = k_n^0 + \varepsilon\, k_n^1 + \frac{\varepsilon^2}{2}\, k_n^2 + \dots . \tag{3.2}$$

and compare with

$$k_n^2 = (k_n^2)^0 + \varepsilon\, (k_n^2)^1 + \frac{\varepsilon^2}{2} (k_n^2)^2 + \dots . \tag{3.3}$$

We get

$$(k_n^2)^2 = (k_n^0)^2;\ (k_n^2)^1 = 2\, k_n^0\, k_n^1;\ (k_n^2) = (k_n^1)^2 + k_n^0\, k_n^2. \tag{3.4}$$

Therefore, given the expansion coefficients of $k_n(\varepsilon)$ we obtain the coefficients for $k_n^2(\varepsilon)$ by using (3.4). In particular (3.1) is

$$(k_n^2)^2 = \sum_{m \neq n} \frac{|<n|\, V' \,|m>|^2}{(k_n^2)^0 - (k_m^2)^0} = (k_n^1)^2 + k_n^0\, k_n^2 \tag{3.5}$$

where k_n^1 and k_n^2 are given by (2.17) and (2.15), respectively.

3. Few examples

As an example we first consider the perturbation of the ground state energy of a hydrogen like atoms when the nuclear charge is increased by N. Let V_0 is the electrostatic field of nucleus with the charge Z. The ground state energy of V^0 is then given by

$$E_0 = -\, a\, Z^2 \tag{4.1}$$

where a is a constant. Perturbation V' is

$$V' = -\frac{N e^2}{r} \tag{4.2}$$

and the matrix element (2.17) gives

$$E^{(1)} = -2a N Z. \tag{4.3}$$

The R-S method gives for the total energy[5]

$$E_{R-S} = E_0 + E^{(1)} = -a Z^2 - 2a N Z \tag{4.4}$$

while if we take the square of (3.2)

$$E = -a (N + Z)^2 \tag{4.5}$$

which is the exact result. In other words, to obtain the exact result in R-S method we must take into account the second order contribution, while in this procedure we need only the first order correction.

Let us also show one example where the R-S method does not give the second order contribution (if the continuum is excluded in the basis set).

For the potential V_0 we take the square well

$$V_0(r) = \begin{cases} -V_0; & r < r_0 \\ 0; & r \geq r_0 \end{cases} \tag{4.6}$$

for which the S-wave regular solution of (2.1) is

$$\psi_0 = \begin{cases} \sin(Kr); & r < r_0 \\ \dfrac{i}{2k}(\mathrm{j}\, \mathrm{e}^{-ikr} - j^* \mathrm{e}^{ikr}); & r \geqslant r_0 \end{cases} \tag{4.7}$$

and irregular

$$f_0^- = \begin{cases} \dfrac{1}{K}[j^* \mathrm{e}^{2ikr_0} \sin(kr) + \mathrm{j} \cos(kr)]: & r < r_0 \\ \mathrm{e}^{ikr}; & r \geqslant r_0 \end{cases} \tag{4.8}$$

where $K^2 = V_0 + k^2$. The Jost function in (4.7) and (4.8) is

$$j = -(ik \sin(K r_0) - K \cos(K r_0))\, \mathrm{e}^{ikr_0} \tag{4.9}$$

and the bound resonance states are now the roots of the equation

$$\frac{K}{ik} = \tan(K r_0). \tag{4.10}$$

The derivatives of j with respect to k are

$$\frac{\partial j}{\partial k} = (i + k\, r_0) \frac{V_0}{K^2} \sin(K r_0) \tag{4.11}$$

and

$$\frac{\partial^2 j}{\partial k^2} = \left(\frac{r_0}{1 - i k r_0} - \frac{i k}{K^2} - 2 r_0 \right) \frac{\partial j}{\partial k} \tag{4.12}$$

where we have taken into account (4.10). This completes the solution for the unperturbed system. Let us now define the perturbation V'. We take

$$V' = \mathrm{e}^{-r} \tag{4.13}$$

for which the solution of (2.1) in the region $r \geqslant r_0$ is[6)]

$$\psi = a\, \mathcal{J}_{-2ik} \left(2i \sqrt{\varepsilon z}\right) + b\, \mathcal{J}_{2ik} \left(2i \sqrt{\varepsilon z}\right) \tag{4.14}$$

where $z = \exp(-r)$ and $\mathcal{J}_\nu(x)$ is the Bessel function. The coefficients a and b are determined from the requirement that the solution (4.14) is together with its first derivative continuous across $r = r_0$. In the region $r < r_0$ the regular solution ψ is similar to (4.14) except that k is replaced by K. The coefficients a and b are such that $\psi = 0$ for $r = 0$.

The bound state energies of (4.14) are given by replacing k by ik and the equation $b = 0$ is solved. However, for complex eigenvalues one has to show that (4.14) can be analytically continued into the complex coordinate plane and that on the ray $z = r \exp(i\varphi)$, the resulting function is square integrable. For $r > r_0$ the potential $V_0 + V' \varepsilon$ is analytic for all z defined by $z = r_0 + r \exp(i\varphi)$; $|\varphi| < \frac{\pi}{2}$. Since the Bessel function can be analytically continued to complex arguments, the solution (4.14) can be continued to all z. The coefficients a and b are coordinate independent (they only depend on r_0) so that for a complex root k_0 there is a ray $z = r \exp(i\varphi)$ on which the function

$$\psi = a\, \mathcal{J}_{-2ik_0} \left(2i \sqrt{\varepsilon z}\right) \tag{4.15}$$

is square integrable. Indeed, for $r \to \infty$ the function (4.15) is $\psi \sim \exp(i k_0 z)$ and for $Im(k_0 z) > 0$ i.e. $|\arg(z)| > |\arg(k_0)|$, the regular solution is square integrable, which is essential for calculating k_n^1.

If the parameters of (4.6) are $V_0 = 1 : r_0 = 2$, there is only one imaginary root of (4.10)

$$k_0 = 0.319023$$

and after introducing perturbation (4.13) with $\varepsilon = 0.1$, the bound state wave number is

$$k_{ex} = 0.293993.$$

Let us now compare the exact solution with the perturbation series. The coefficient k_0^1 is

$$k_0^1 = -\ 0.245923$$

which gives the approximate k

$$k = 0.294431.$$

The second order contribution is given by k_0^2, which is

$$k_0^2 = -\ 0.083643$$

and gives for k

$$k = 0.294012.$$

One complex zero of (4.10) is

$$k_0 = 3.666495 - i\,1.05808$$

and the coefficient k_0^1 is

$$k_0^1 = 0.056189 + i\,0.010513$$

giving the approximate value for the resonance

$$k = 3.672114 - i\,1.057029.$$

The approximate result is in a good agreement with exact k

$$k_{ex} = 3.672111 - i\,1.05703.$$

5. *Conclusion*

We have shown how to develope a perturbation method for the eigenvalues of Schrödinger equation, without defining a complete set of eigenstates. The resulting expansion coefficients are only given in terms of the wave function and its derivatives of that particular eigenstate. It was also shown that the resonances can be treated on an equal basis with the bound states.

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TEORIJA SMETNJE BEZ POTPUNOG SKUPA

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Pokazat ćemo kako razviti teoriju perturbacije za vlastite vrijednosti Schrödingerove jednadžbe bez upotrebe potpunog skupa vlastitih funkcija. Koeficijenti razvoja ovise jedino o stanju na kojem se vrši perturbacija. To se postiže na taj način da se problem vlastitih vrijednosti zamijeni algebarskom jednadžbom.