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NONRELATIVISTIC PERTURBATION THEORY FOR A DISCRETE SPECTRUM

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We construct a perturbation theory for the radial Schrödinger equation in which all corrections to the eigenfunctions and eigenvalues are expressed solely in terms of that function, the correction to which is looked for (and not in terms of the whole spectrum of eigenfunctions and eigenvalues of the problem). In the k-th approximation, the wave function is evaluated up to terms of order ϵ^{2k}, where ϵ is the perturbation parameter. Knowing the k-th approximation wave function we can obtain the energy up to terms of order ϵ^{2k+1}.

1. It is well known that the Schrödinger equation for the radial wave function $R(r)$ of a particle moving in a spherically symmetric field, can, by means of the substitution

$$\chi = rR = \exp\left[\int_0^r f(r')\,dr' + C\right], \quad f = \chi'/\chi \quad (1)$$

be reduced to the Riccati equation

$$df/dr + f^2 + 2(E - V) - l(l+1)/r^2 = 0 \quad (2)$$

(we use units such that $m = \hbar = 1$).

As the boundary conditions for χ are of the form

$$\chi(r\to 0) \sim r^{l+1}, \quad \chi(r\to\infty) \sim e^{-\varkappa r}, \quad \varkappa = \sqrt{-2E},$$

those for f are

$$f(r\to 0) \sim 1/r, \quad f(r\to\infty) \sim -\varkappa. \quad (3)$$

Let

$$V = V_0 + \varepsilon V_1, \quad (4)$$

where ϵ is a small parameter, and put

$$f = f_0 + \varepsilon F_1(\varepsilon),\ E = E_0 + \varepsilon\mathscr{E}_1(\varepsilon),\ C = C_0 + \varepsilon S_1(\varepsilon), \quad (5)$$

where f_0 is a function satisfying the equation

$$f_0' + f_0^2 + 2(E_0 - V_0) - l(l+1)/r^2 = 0$$

and which is connected with the unperturbed wave function through the relation

$$\chi_0 = \exp\left[\int_0^r f_0\,dr' + C_0\right], \quad (6)$$

which is assumed to be known.

2. Substituting (4) and (5) into (2), we get for F_1 the equation

$$dF_1/dr + 2f_0F_1 + 2(\mathscr{E}_1 - V_1) + \varepsilon F_1^2 = 0. \quad (7)$$

we put

$$F_1(\varepsilon) = f_1 + \varepsilon F_2(\varepsilon), \quad \mathscr{E}_1(\varepsilon) = E_1 + \varepsilon\mathscr{E}_2(\varepsilon), \quad (8)$$

where f_1 satisfies Eq. (7) without the last term, the general integral of which, if we use (6), is of the form

$$f_1(r) = -2\chi_0^{-2}(r)\int_a^r \chi_0^2(r')[E_1 - V_1(r')]\,dr'. \quad (9)$$

It follows from the first condition of (3) that we must put the lower limit equal to zero (otherwise $f_1(r\to 0) \sim r^{-2(l+1)}$); it then follows from the second condition of (3) that as $R\to\infty$

$$\int_0^R \chi_0^2(r)[E_1 - V_1(r)]\,dr \sim e^{-2\varkappa R},$$

i.e., we find the well-known relation

$$E_1 = \int_0^\infty \chi_0^2(r)V_1(r)\,dr. \quad (10)$$

Substituting (9) into (1) and expanding the exponential function up to first order in ϵ, we get the wave function in first approximation

$$\chi_1(r) = \chi_0(r)\left[1 + \varepsilon\int_0^r f_1(r')\,dr' + \varepsilon C_1\right]. \quad (11)$$

From the normalization condition,

$$\int_0^\infty \chi_0^2(r)\,dr = 1 + O(\varepsilon^2)$$

we find

$$C_1 = -\int_0^\infty \chi_0^2(r)\,dr\int_0^r f_1(r')\,dr'. \quad (12)$$

3. Substituting (8) into (7) we get an equation for F_2:

$$dF_2/dr + 2(f_0 + \varepsilon f_1)F_2 + 2\mathscr{E}_2 + f_1^2 + \varepsilon^2F_2^2 = 0. \quad (13)$$

Integration of (13) is hindered by the term of order ϵ^2; neglecting it we can obtain F_2 up to terms of first order in ϵ, inclusive. In line with this we put

$$F_2(\varepsilon) = f_2(\varepsilon) + \varepsilon^2 F_3(\varepsilon), \quad \mathscr{E}_2(\varepsilon) = E_2(\varepsilon) + \varepsilon^2 \mathscr{E}_3(\varepsilon), \tag{14}$$

where

$$f_2(\varepsilon) = f_{20} + \varepsilon f_{21}, \quad E_2(\varepsilon) = E_{20} + \varepsilon E_{21}. \tag{15}$$

It then follows from (13) that

$$f_2(r) = -\chi_1^{-2}(r) \int_a^r \chi_1^2(r')[f_1^2(r') + 2\mathscr{E}_2]\,dr'. \tag{16}$$

Repeating the argument which led to (10), we see that we must put a = 0 in (16) and that

$$E_2(\varepsilon) = -{}^1/_2 \int_0^\infty \chi_1^2(r) f_1^2(r)\,dr, \tag{17}$$

or

$$E_{20} = -{}^1/_2 \int_0^\infty \chi_0^2(r) f_1^2(r)\,dr,$$

$$E_{21} = -\int_0^\infty \chi_0^2(r) f_1^2(r)\,dr \left[\int_0^r f_1(r')\,dr' + C_1\right], \tag{18}$$

where f_1 and C_1 are given by (9) and (12).

Substituting (14) into (13) we find that

$$dF_3/dr + 2[f_0 + \varepsilon f_1 + \varepsilon^2 f_2(\varepsilon)]F_3 + f_2^2(\varepsilon) + 2\mathscr{E}_3(\varepsilon) + \varepsilon^4 F_3^2 = 0. \tag{19}$$

Putting

$$F_3(\varepsilon) = f_3(\varepsilon) + \varepsilon^4 F_4(\varepsilon), \quad \mathscr{E}_3(\varepsilon) = E_3(\varepsilon) + \varepsilon^4 \mathscr{E}_4(\varepsilon), \tag{20}$$

where $f_3(\epsilon)$ and $E_3(\epsilon)$ are cubic polynomials in ϵ, for instance,

$$f_3(\varepsilon) = f_{30} + \varepsilon f_{31} + \varepsilon^2 f_{32} + \varepsilon^3 f_{33}, \tag{21}$$

we get by analogy with the preceding

$$f_3(r) = \chi_2^{-2}(r) \int_0^r \chi_2^2(r')[f_2^2(r') + 2E_3]\,dr', \tag{22}$$

$$E_3 = -{}^1/_2 \int_0^\infty \chi_2^2(r) f_2^2(r)\,dr, \tag{23}$$

where

$$\chi_2 = C \exp_4 \int_0^r [f_0 + \varepsilon f_1 + \varepsilon^2 f_2(\varepsilon)]\,dr \tag{24}$$

is the wave function in second approximation (the index 4 at the exp-symbol indicates that after evaluating it as a power expansion it is necessary to drop terms of order ϵ^4 and higher; C is a normalization constant which is determined from the condition $\int_0^\infty \chi_2^2(r)\,dr = 1 + O(\epsilon^4)$, taking the normalization of χ_1 into account).

It is now clear that f and E are expanded in power series

$$f = f_0 + \varepsilon[f_1 + \varepsilon[f_2 + \varepsilon^2[f_3 + \varepsilon^4[f_4 \ldots]]\ldots]$$

$$= f_0 + \sum_{k=1}^\infty \varepsilon^{2^{k-1}} f_k(\varepsilon), \tag{25}$$

where f_k is a polynomial in ϵ:

$$f_k(\varepsilon) = \sum_{n=0}^{2^{k-1}-1} \varepsilon^n f_{kn}, \tag{26}$$

with

$$f_k(r) = -\chi_{k-1}^{-2}(r) \int_0^r \chi_{k-1}^2(r')[f_{k-1}^2(r') + 2E_k] \tag{27}$$

and

$$E_k = -{}^1/_2 \int_0^\infty \chi_{k-1}^2(r) f_{k-1}^2(r)\,dr, \tag{28}$$

where

$$\chi_n = C \exp_{2^n} \int_0^r [f_0 + \varepsilon f_1 + \ldots + \varepsilon^{2^{n-1}} f_n(\varepsilon)]\,dr' \tag{29}$$

is the wave function in n-th approximation (the index 2^n at the exp-symbol indicates that terms of order ϵ^{2n} must be dropped in its expansion; C is a normalization constant determined from the condition $\int_0^\infty \chi_n^2\,dr = 1 + O(\epsilon^{2n})$ with account taken of the normalization in previous orders; in (27) one can use unnormalized functions χ_{k-1}). We note that if the wave function has nodes, one must in the complex plane go around the corresponding singularities in the integrals (either from above or from below - it does not matter which, since they do not contribute).

It follows from the obtained formulae that all corrections of order ϵ^2 to the energy are always negative. We note also that by comparing, for instance, (18) with the expressions of the usual perturbation theory we can evaluate a number of complicated sums.

4. The fact that all corrections to the wave function and to the eigenvalue can in the one-dimensional case be expressed solely in terms of the function for the corrections of which we are looking (and not in terms of the whole spectrum of eigenfunctions and eigenvalues of the problem as in the usual perturbation theory) is a consequence of the fact that the Green function G(r, r′) of the second order equation can be expressed merely in terms of one solution of this equation; in the present case:

$$G(r,r')=\begin{cases}\chi(r)\chi(r')\int\limits_a^{r'}\frac{dr_1}{\chi^2(r_1)}, & r'<r\\ \chi(r)\chi(r')\int\limits_a^{r}\frac{dr_1}{\chi^2(r_1)}, & r'>r\end{cases}\qquad(30)$$

Knowing the Green function, the perturbation theory for the discrete spectrum can be formulated as follows (all relations to be given in the following remain valid when there is no spherical symmetry).

The Schrödinger equation $[H_0 - E + \epsilon V]|\psi\rangle = 0$ can in the case of a discrete spectrum be written down in terms of the Green function of the unperturbed equation as follows

$$|\psi\rangle = \varepsilon GV|\psi\rangle, \qquad(31)$$

where

$$G=\frac{1}{E-H_0}=\sum_n{}'\frac{|\varphi_n\rangle\langle\varphi_n|}{E-E_n},\quad (H_0-E_n)|\varphi_n\rangle=0. \qquad(32)$$

It is necessary to write Eq. (31) in such a form that it can be iterated. We write it in the form

$$|\psi\rangle = \varepsilon E^1G|\psi\rangle + \varepsilon G(V-E^1)|\psi\rangle, \qquad(33)$$

where

$$E^1=E-E_0=\frac{\langle\varphi|V|\psi\rangle}{\langle\varphi|\psi\rangle}. \qquad(34)$$

Let us study the first term in (33). Putting

$$|\psi\rangle=|\varphi\rangle+\varepsilon|\psi^1\rangle,\quad |\psi^1\rangle=|\psi_1\rangle+\varepsilon|\psi_2\rangle+\dots \qquad(35)$$

we get instead of (33)

$$|\psi\rangle=|\varphi\rangle+\varepsilon G(V_1-E^1)|\psi\rangle+\varepsilon^2E^1G|\psi^1\rangle. \qquad(36)$$

This equation can already be iterated; for instance, in first order perturbation theory we get, taking (34) into account,

$$|\psi_1\rangle=G(V-E_1)|\varphi\rangle,\quad E_1=\langle\varphi_0|V|\psi\rangle,$$
$$E_2=\langle\varphi|VG(V-E_1)|\varphi\rangle. \qquad(37)$$

If we use Eq. (30) for the Green function we get, as we should have expected, Eqs. (11) and (17), but in the next approximations we get very complicated formulae, and it is difficult to reduce them to the compact Eqs. (25)–(29).

5. As an example of an application of the obtained relations we find the ground state energy of a particle moving in a Yukawa potential

$$V=-\frac{\alpha}{r}\exp(-\lambda r) \qquad(38)$$

up to terms of order $(\lambda a)^{[7]}$, where a is the Bohr radius. Introducing Coulomb units we can write (2) in the form

$$\frac{df}{dr}+f^2+2\left[E-\lambda+\frac{1}{r}+\left(\frac{e^{-\lambda r}-1}{r}+\lambda\right)\right]=0 \qquad(39)$$

and we shall consider the quantity

$$\frac{e^{-\lambda r}-1}{r}+\lambda=\lambda^2r\sum_{n=0}^{\infty}\frac{(-\lambda r)^n}{(n+2)!}$$

as the perturbation potential (λ^2 plays the role of ϵ). In zeroth approximation we have

$$\chi_0=2re^{-r},\quad E_0=-1/2+\lambda. \qquad(40)$$

Using (9), (10), and (12) we get in first approximation

$$f_1=\frac{2}{(2+\lambda)^2}\left[\frac{\lambda(4+\lambda)}{2}+e^{-\lambda r}\frac{[1+(2+\lambda)r]-2r-1}{r^2}\right]$$
$$E_1=-\lambda^2\frac{3+\lambda}{(2+\lambda)^2},$$
$$C_1=-\frac{\lambda^2}{(2+\lambda)^2}\left[3-\frac{\lambda}{2}\sum_{n=0}\left(-\frac{\lambda}{2}\right)^n\frac{n+4}{n+3}\right]. \qquad(41)$$

Substituting (41) into (11) and (17) and using the fact that it follows from (25) that the third approximation starts with terms of order λ^8 we get after elementary calculations

$$E=-\frac{1}{2}+\lambda-\frac{3}{4}\lambda^2+\frac{1}{2}\lambda^3-\frac{11}{16}\lambda^4+\frac{21}{16}\lambda^5-\frac{559}{192}\lambda^6+\frac{613}{96}\lambda^7\dots \qquad(42)$$

In conclusion we note that these results can easily be generalized to a wider set of Sturm-Liouville type problems than the Schrödinger equation.

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164