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Quantum energy spectrum from the integral Schrödinger equation

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Abstract. The integral form of the Schrödinger equation for bound-state levels, considered by Schwinger, is used for evaluation of the energy spectrum. The method is based upon calculation of the series for powers of eigenvalues of the coupling constant, as given by multiple integrals of products of the potential and free Green functions. Some qualitative properties of the solutions can be easily proved in a general way. The integrals are appropriate, in particular, for calculation by means of the Monte Carlo method. The semiclassical approximation is derived for the one-dimensional case. A number of examples show the effectiveness of the method.

1. Introduction

We shall consider the quantum mechanical bound-state problem for a finite-range potential well. The Hamiltonian is of the form $\hat{H} = \hat{H}_0 - \lambda\hat{V}$, where $\hat{H}_0 = -\Delta$ is the kinetic energy operator, the potential energy operator $\hat{V}$ is given by a (properly normalized) function $V(x)$ describing the well, and λ is a potential strength coefficient (the coupling constant). For a bound-state wavefunction $\Psi_\varepsilon(x)$, square-integrable in the s-dimensional Euclidean space, the Schrödinger equation, $(\hat{H} + \varepsilon)\Psi_\varepsilon = 0$, can be transformed to an integral form, which is a homogeneous second-kind Fredholm equation

$$\lambda^{-1}\Psi_\varepsilon = \hat{G}_\varepsilon\hat{V}\Psi_\varepsilon \tag{1}$$

where $\hat{G}_\varepsilon = (\hat{H}_0 + \varepsilon)^{-1}$ is the free-motion Green function. It is assumed that the potential is localized to a finite region in space, i.e. $\lim V(x) = 0$ as $|x| \to \infty$. For any positive value of ε, the eigenvalues of the integral operator in the RHS of (1) describe a set of self-similar potentials, having a bound state with the energy ε. As is clear from the physical arguments, the spectrum of the coupling constants, for any given binding energy $\varepsilon > 0$, is infinite and bounded from below by the lowest eigenvalue $\lambda_0(\varepsilon)$, corresponding to a minimum coupling constant, at which the potential has its ground state at ε. The spectrum of the coupling constants is discrete, unlike the energy spectrum. (A typical example is shown in figure 1. For any $\lambda > 0$, there is a finite number of bound levels with $\varepsilon \geqslant 0$, and a continuous spectrum at $\varepsilon < 0$. Any fixed $\varepsilon > 0$ corresponds to an infinite number of the eigenvalues $\lambda_n(\varepsilon)$, three of which are presented in the figure.) The value of the ground-state energy ε_0 is one of the most important features of any quantum mechanical problem, and it is the λ-dependence of ε_0 that can be calculated as a function inverse to $\lambda_0(\varepsilon)$.

The integral representation of the Schrödinger equation was used by Schwinger [1] in order to prove a number of general properties of the energy spectrum. The purpose of this work is to show that (1) can be also used for a *numerical* calculation of the lower state energies. It is found that the method is quite practical in some respects, and sometimes has certain advantages as compared with more traditional methods based upon the differential equation.

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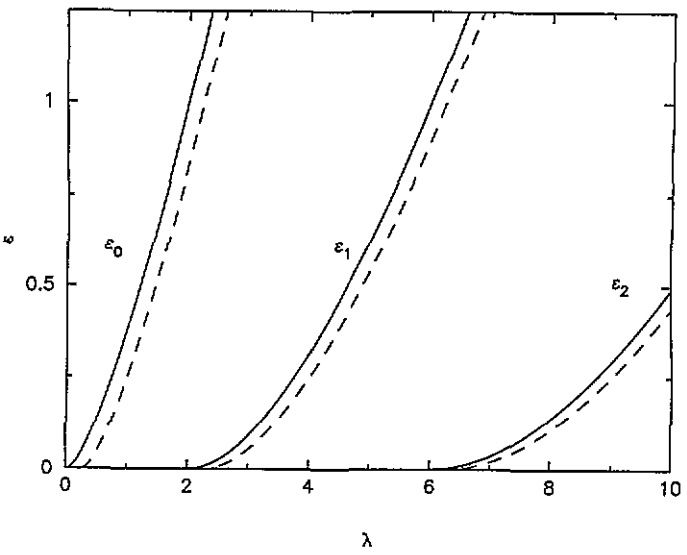

Figure 1. Lower bound levels for potential $\lambda/\cosh^2 x$, equation (41). The broken curves show the semi-classical approximation.

2. Trace invariants

2.1. Definition

Let us consider a sequence of invariants for the integral operator in (1), which are the traces of its powers,

$$S_N(\varepsilon) = \mathrm{Tr}(\hat{G}_\varepsilon \hat{V})^N = \sum_{n=0}^{\infty} \lambda_n^{-N}. \tag{2}$$

If N is high enough, the first terms in the series are dominant, and one can get $\lambda_0, \lambda_1, \ldots$ immediately and with reasonable accuracy, calculating the traces. (A discussion is given in section 6.)

Under proper assumptions on the form of the potential, the traces exist and the series are convergent, at least for sufficiently large N. In order to evaluate each trace, one has to calculate a multiple integral, in coordinate or momentum representation:

$$\begin{aligned} S_N(\varepsilon) &= \int\cdots\int \mathrm{d}^s x_1 \ldots \mathrm{d}^s x_N V(x_1) G_\varepsilon(x_1 - x_2) V(x_2) \ldots V(x_N) G_\varepsilon(x_N - x_1) \\ &= \int\cdots\int \mathrm{d}^s k_1 \ldots \mathrm{d}^s k_N \tilde{G}_\varepsilon(k_1) \tilde{V}(k_1 - k_2) \tilde{G}_\varepsilon(k_2) \ldots \tilde{G}_\varepsilon(k_N) \tilde{V}(k_N - k_1) \end{aligned} \tag{3}$$

where $\mathrm{d}^s x$ and $\mathrm{d}^s k$ are the volume elements in the (s-dimensional) coordinate and momentum spaces; $\tilde{G}_\varepsilon$ and $\tilde{V}$ are the Fourier transforms of G_ε and V, respectively:

$$\tilde{G}_\varepsilon(k) = (k^2 + \varepsilon)^{-1} \qquad G_\varepsilon(x) = (2\pi)^{-s} \int \mathrm{d}^s k \mathrm{e}^{\mathrm{i}kx} \tilde{G}_\varepsilon(k) \tag{4}$$

$$\tilde{V}(k) = (2\pi)^{-s} \int \mathrm{d}^s x \mathrm{e}^{-\mathrm{i}kx} V(x). \tag{5}$$

The integrals can be represented by means of the following recursive procedure, which resembles that in constructing the perturbative series for the Green function:

$$S_N(\varepsilon) = \int K_N(k,k;\varepsilon)\frac{\mathrm{d}^s k}{k^2+\varepsilon} \tag{6}$$

$$K_N(k_1,k_2;\varepsilon) = \int K_{N-1}(k_1,k;\varepsilon)\frac{\mathrm{d}^s k}{k^2+\varepsilon}\tilde{V}(k-k_2) \tag{7}$$

$$K_1(k_1,k_2;\varepsilon) \equiv \tilde{V}(k_1-k_2)\,. \tag{8}$$

Here K_N is the kernel for the Hermitean operator $\hat{K}_N = \hat{V}(\hat{G}_\varepsilon\hat{V})^{N-1}$.

Now the problem is to compute the multiple integrals, yet there are some general arguments to be considered before appealing to numerical methods.

2.2. *Symmetries*

If the potential has a symmetry, one can reduce the integration appropriately, separating states having different symmetry properties. Namely, let Γ be a space symmetry group preserving the form of the potential, $G_\varepsilon(\gamma x) \equiv G_\varepsilon(x)$, $V(\gamma x) \equiv V(x)$, where $\gamma \in \Gamma$ is a space transformation. As is well known [2] the eigenstates are distributed in classes corresponding to irreducible unitary representations of Γ. The Green function can be written as a sum over all unitary irreducible group representations,

$$\hat{G}_\varepsilon = \sum_\rho \hat{G}^\rho_\varepsilon \hat{P}_\rho \tag{9}$$

where $\hat{P}_\rho$ is a projection to a given unitary irreducible representation acting in the space of functions on the group orbit in $\mathbf{R}^s$, and the partial Green operator $\hat{G}^\rho_\varepsilon$ acts in the co-set space $\mathbf{M} = \mathbf{R}^s/\Gamma$ and is obtained by means of an appropriate averaging over the group Γ. In the coordinate representation, where $\hat{V}$ is diagonal, the decomposition of (9) is appropriate. A similar decomposition should be applied to the potential operator $\hat{V}$, if one prefers the momentum representation, where $\hat{G}_\varepsilon$ is diagonal.

Setting the decomposition into (2), we get

$$S_N(\varepsilon) = \sum_\rho S^\rho_N(\varepsilon) \tag{10}$$

where only the levels corresponding to a given unitary group representation ρ contribute to the partial trace function S^ρ_N, which is given by a reduced integral,

$$\begin{aligned} S^\rho_N(\varepsilon) &= \int_{\mathbf{M}}\cdots\int_{\mathbf{M}} \mathrm{d}\mu(r_1)\ldots\mathrm{d}\mu(r_N)V(r_1)G^\rho_\varepsilon(r_1,r_2)V(r_2)\ldots V(r_N)G^\rho_\varepsilon(r_N,r_1) \\ &= \int_{\mathbf{M}}\cdots\int_{\mathbf{M}} \mathrm{d}\mu(k_1)\ldots\mathrm{d}\mu(k_N)\tilde{G}_\varepsilon(k_1)\tilde{V}^\rho(k_1,k_2)\tilde{G}_\varepsilon(k_2)\ldots\tilde{G}_\varepsilon(k_N)\tilde{V}^\rho(k_N,k_1) \end{aligned} \tag{11}$$

and the integrals are calculated in the co-set space $\mathbf{M}$ with an appropriate measure $\mathrm{d}\mu$.

Let us consider two simple examples:

(i) *Symmetry under reflection:* $V(x) = V(-x)$, $\Gamma = Z_2$, and $\mathbf{M}$ is a half-space. The group has 2 irreducible representations, $\rho = \pm$,

$$G_\varepsilon(x_1-x_2) = G^+_\varepsilon(x_1,x_2) + G^-_\varepsilon(x_1,x_2) \tag{12}$$

where

$$G_\varepsilon^{\pm}(x_1, x_2) = \tfrac{1}{2}[G_\varepsilon(x_1 - x_2) \pm G_\varepsilon(x_1 + x_2)] = \pm G_\varepsilon^{\pm}(x_1, -x_2)\,. \tag{13}$$

Similarly, one can define $\tilde{V}^{\pm}(k_1, k_2)$ and set it into (11). The levels having even and odd wavefunctions contribute separately to $S_N^+(\varepsilon)$ and $S_N^-(\varepsilon)$.

(ii) *Rotational symmetry in* $\mathbf{R}^3$: $V(x) = V(r)$, $r = |x|$, and $\Gamma = SO(3)$. Each unitary representation is given by an (integer) angular momentum l, and

$$G_\varepsilon^l(r_1, r_2) = \int_{-1}^{+1} G_\varepsilon(x_1 - x_2) P_l(z)\,\mathrm{d}z \tag{14}$$

where $(x_1 \cdot x_2) = r_1 r_2 z$, and $P_l(z)$ is the Legendre polynomial. The result, given in [3], is a product of modified Bessel functions of the argument $\varepsilon^{1/2} r$. Similarly, one can define $\tilde{V}^l(k_1, k_2)$ and set it into (11). Another way of dealing with the problem with spherical symmetry is to consider the Schrödinger equation for the radial wavefunction, with the centrifugal potential $l(l+1)/r^2$ added to λV, where the boundary condition at $r = 0$ is fixed by using G_ε^- instead of G_ε. Of course, the method can be extended easily to $\mathbf{R}^s$ with $\Gamma = SO(s)$.

Using the above arguments to separate levels having different symmetry properties, one gets series and integrals having a better convergence.

3. Small binding energies

The limit of $\varepsilon \to 0$ is of particular interest, since it enables one to get the threshold values of the coupling constant at which binding takes place. The one- and two-dimensional problems are special, because they have bound states for any attracting potential, even for a vanishing coupling [4]. This is evident from (3), since the integral is divergent for $\varepsilon = 0$.

(i) *One-dimensional problem.* At small ε the domain of small k is the reason of the divergence in the integral, which can be evaluated approximately:

$$S_N(\varepsilon) = [\tilde{V}(0) \int \tilde{G}_\varepsilon(k)\,\mathrm{d}k + \mathrm{O}(1)]^N\,. \tag{15}$$

The first term in the series (2) is dominant, as it goes to infinity, and one gets the well known result

$$\sqrt{\varepsilon_0} = \frac{\lambda}{2} \int_{-\infty}^{+\infty} V(x)\,\mathrm{d}x\,. \tag{16}$$

(ii) *Two-dimensional problem.* The traces have a logarithmic divergence at small k, but an argument like that given above cannot be applied immediately, since the integral of $\tilde{G}_\varepsilon$ would also be diverging at large k. Actually, the integral exists because of a decrease in $\tilde{V}$ at some values of k^2, large as compared with ε, owing to a finite potential range. Introducing the cut-off phenomenologically, one gets

$$\varepsilon_0 = \frac{C}{a(\mathbf{D})} \exp\left\{-\left[\frac{\lambda}{\pi} \int_{\mathbf{D}} V(x)\,\mathrm{d}^2 x\right]^{-1}\right\} \tag{17}$$

where $\mathbf{D}$ is a compact domain where the potential is essentially non-zero, $a(\mathbf{D})$ is its area, and C is a λ-independent dimensionless constant, which depends on the shape of $\mathbf{D}$. For

two-dimensional potentials having the central symmetry, this result was given by Landau and Lifshitz [4], with $C = 2\pi$.

(iii) *Three-dimensional problem.* The integral is converging now, and the first bound state appears at a finite value of the coupling constant λ_0. Calculating $S_N(0)$ one can evaluate λ_0 and derive some bounds on the spectrum [1, 5]. It is noteworthy that λ_0 is not analytical near $\epsilon = 0$, as one can see from the integrals. Applying the operator $\sqrt{\varepsilon}\mathrm{d}/\mathrm{d}\varepsilon$ to S_N and setting $\varepsilon = 0$, one has

$$\sum_{n=0}^{\infty} d_n/\lambda_n(0)^{N+1} = \frac{\pi}{2} K_N(0, 0; 0) \tag{18}$$

and the constants d_n determine the behaviour of the coupling constants near $\varepsilon = 0$, namely $\lambda(\varepsilon) = \lambda_n(0)(1 + d_n\sqrt{\varepsilon})$.

4. Higher-excited levels

The semi-classical quantization rule enables one to improve the effectiveness of the method based upon calculation of the traces. Actually, evaluating a few lower eigenvalues λ_n from a number of S_N, one has to neglect the remainder of the infinite series in (2). On the other hand, the semi-classical approach is adequate just for higher eigenvalues, i.e. for excited energy levels, so the remainders can be evaluated properly. Setting the semi-classical approximation for $n \gg 1$, one can sum up the infinite series for $S_N(\varepsilon)$, except for a finite number of the first terms, where the approximation is not accurate enough.

Let us consider a generating function for the trace invariants,

$$g(\varepsilon, \lambda) \equiv \sum_{N=1}^{\infty} \lambda^N S_N(\varepsilon) = \sum_{n=0}^{\infty} \frac{\lambda}{\lambda_n(\varepsilon) - \lambda}. \tag{19}$$

This function can be expressed in terms of the Green function for the total Hamiltonian,

$$g(\varepsilon, \lambda) = \lambda \mathrm{Tr}[\hat{V}(\hat{H} + \varepsilon)^{-1}]. \tag{20}$$

As shown in appendix A1, the semi-classical approximation in the one-dimensional case enables one to get a closed expression for this function (A11) summing up the contributions to the Green function from the classical trajectories

$$g^{\mathrm{cl}}(\lambda, \varepsilon) = \lambda \frac{\partial w}{\partial \lambda} \tan w \tag{21}$$

where $w(\lambda, \varepsilon)$ is given in terms of the action integral (A8).

We shall introduce *truncated* trace invariants and represent them in terms of contour integrals of the generating function,

$$S_N^{(\nu)}(\varepsilon) \equiv \sum_{n=\nu}^{\infty} \lambda_n^{-N} = (2\pi \mathrm{i})^{-1} \int_{C_\nu} \mathrm{d}\lambda \frac{g(\lambda, \varepsilon)}{\lambda^{N+1}}. \tag{22}$$

The contour C_ν in the complex λ plane comes from $+\infty$ above the real axis, crosses the axis between $\lambda_{\nu-1}$ and λ_ν, and leaves for $+\infty$ below the axis. If ν is large enough, one can use the semi-classical approximation in the integral. Changing the variable, $\lambda \to w$, we get

$$S_N^{(\nu)}(\varepsilon) = \frac{1}{2\pi \mathrm{i} \varepsilon^N} \int_{C_\nu} \mathrm{d}w [f(2w/\pi\sqrt{\varepsilon})]^{2N} \tan w \tag{23}$$

where f is defined after (A12) as a function inverse to $v(\xi)$, and the contour crosses the axis between $\pi(\nu-\frac{1}{2})$ and $\pi(\nu+\frac{1}{2})$. Let us deform the contour and make it parallel to the imaginary axis and cross the axis at $w=\pi\nu$, so that in the complex plane $w=\pi\nu+\mathrm{i}y$ and $\tan w=\mathrm{i}\tanh y$. Performing the analytical continuation in w and setting

$$f\left(\frac{2\pi\nu+2\mathrm{i}y}{\pi\sqrt{\varepsilon}}\right)=\rho_\nu(y)\,\mathrm{e}^{-\mathrm{i}\varphi_\nu(y)} \tag{24}$$

we introduce two real functions, $\rho_\nu(y)\equiv\rho_\nu(-y)$ and $\varphi_\nu(y)\equiv-\varphi_\nu(-y)$, which also depend on ε. The result is a rapidly converging real integral,

$$S_N^{(\nu)}(\varepsilon)=\frac{1}{\pi\varepsilon^N}\int_0^\infty \mathrm{d}y[\rho_\nu(y)]^{2N}\sin[2N\varphi_\nu(y)]\tanh y\,. \tag{25}$$

As soon as S_N and $S_N^{(\nu)}$ are calculated to a reasonable accuracy, we get a finite set of equations for lower λ_n,

$$\sum_{n=0}^{\nu-1}\lambda_n^{-N}=S_N-S_N^{(\nu)}\qquad N=N_1,\ldots,N_1+\nu\,. \tag{26}$$

If we start from $N_1=1$, the problem is to solve an order-ν algebraic equation with coefficients obtained from (26). Its roots are $\lambda_0^{-1},\ldots,\lambda_{\nu-1}^{-1}$.

5. Yukawa-type potential

The trace invariants can be calculated explicitly for the Yukawa-type potential, i.e.

$$\tilde V(k)=\frac{\mu}{\pi(k^2+\mu^2)} \tag{27}$$

where μ is a parameter, the inverse potential range. The corresponding potentials in the x-representations are

$$V(x)=\mathrm{e}^{-\mu|x|}\qquad \text{for } s=1 \tag{28}$$

$$V(x)=4\pi\mu\frac{\mathrm{e}^{-\mu|x|}}{|x|}\qquad \text{for } s=3\,. \tag{29}$$

Now the integrals of (3) are like the integrals given by the Feynman diagrams (in the s-dimensional Euclidean field theory), which are regular polygons with all vertices connected to the centre:

$$S_N(\varepsilon)=\left(\frac{\mu}{\pi}\right)^N\int\cdots\int\prod_{n=1}^N\frac{\mathrm{d}^sk_n}{(k_n^2+\varepsilon)[(k_{n+1}-k_n)^2+\mu^2]} \tag{30}$$

(we set $k_{N+1}\equiv k_1$). Using the standard method of field theory, and introducing auxiliary parameters, we can represent the integral in the exponential form:

$$S_N(\varepsilon)=(\mu/\pi)^N\int\cdots\int\prod_{n=1}^N\mathrm{d}\alpha_n\,\mathrm{d}\beta_n\,\mathrm{d}^sk_n\exp\left[-\left(\sum_{n=1}^N[\alpha_nk_n^2+\beta_n(k_{n+1}-k_n)^2]+\alpha\varepsilon+\beta\mu^2\right)\right] \tag{31}$$

where $\alpha = \sum_{n=1}^{N} \alpha_n$, $\beta = \sum_{n=1}^{N} \beta_n$, and the integration domain is $\{\alpha_n > 0, \beta_n > 0\}$. Evaluating the Gaussian integrals in k_n, one gets the determinant of the Jacobi tridiagonal matrix depending on the positive parameters α_n and β_n.

Let us concentrate upon the *one-dimensional* case. The Schrödinger equation has an explicit solution in terms of the Bessel functions (see e.g. [6])

$$\Psi_\varepsilon(x) = C J_\nu(\zeta \, \mathrm{e}^{-\mu|x|/2}) \tag{32}$$

where C is a normalization constant, $\nu = 2\sqrt{\varepsilon}/\mu$, and $\zeta = 2\sqrt{\lambda}/\mu$. The spectrum is given by the boundary condition at $x = 0$:

$$\text{for even levels:} \qquad \Psi'(0) = 0 \qquad \lambda_{2m-2}(\varepsilon) = \frac{\mu^2}{4}(j'_{\nu,m})^2 \tag{33}$$

$$\text{for odd levels:} \qquad \Psi(0) = 0 \qquad \lambda_{2m-1}(\varepsilon) = \frac{\mu^2}{4}(j_{\nu,m})^2 . \tag{34}$$

Here $j_{\nu,m}$ and $j'_{\nu,m}$ ($m = 1, 2, \ldots$) are roots of the Bessel function and its derivative, respectively (we use Watson's notation [7]).

Separating the even and odd levels in the trace invariants $S_N^{\pm}(\varepsilon)$, one has to set

$$\tilde{V}^{\pm}(k_1, k_2) = \frac{\mu}{\pi}\left([(k_1 - k_2)^2 + \mu^2]^{-1} \pm [(k_1 + k_2)^2 + \mu^2]^{-1}\right) \tag{35}$$

instead of the second factor in integrals (30), restricting the integration region to positive k_n. All the integrations can be performed analytically. The lowest trace invariants are given in appendix A2. The result is in agreement with the known summation formulae for series of roots of the Bessel functions (cf e.g. [8]).

It is noteworthy that the calculation of $S_N^-(0)$ was performed in 1781 by Euler (as explained by Watson [7]), and the result was used for evaluation of the smallest zeros of $J_0(\zeta)$.

Concluding this section, we note that any finite-range potential $V(x)$ can be approximated reasonably with a finite superposition of the Yukawa-type potentials of different ranges μ, if the Padé approximation is used for $\tilde{V}(k)$. In principle, the corresponding trace invariants can be calculated analytically.

6. Computational results and examples

6.1. General arguments

The problem is to evaluate the trace invariants which are given by multiple integrals in (3). The quantities, which can be obtained analytically for the Yukawa-type potentials in section 5, must be calculated numerically in general, for instance, by means of the Monte Carlo method. A suitable form of the integral in the one-dimensional case is obtained by means of the substitution $k = \sqrt{\varepsilon}\tan\theta$, so that

$$S_N(\varepsilon) = \varepsilon^{-N/2} \int \prod_{n=1}^{N} \mathrm{d}\theta_n \, \tilde{V}\left(\frac{\varepsilon^{1/2}\sin(\theta_n - \theta_{n+1})}{\cos\theta_n \cos\theta_{n+1}}\right). \tag{36}$$

The integration volume is the cube $-\pi/2 < \theta_n < \pi/2$, and $\theta_{N+1} \equiv \theta_1$. The same change of variables can also be used if the even and odd levels are separated, so that even and odd

potentials, as in (35), must be set into the integral, and the integration domain would be $0 < \theta_n < \pi/2$.

In order to extract the spectrum of λ_n from the sequence of S_N, let us first determine two auxiliary sequences

$$\Lambda'_N \equiv S_N^{-1/N} \qquad \Lambda''_N \equiv S_{N-1}/S_N \,. \tag{37}$$

Following Euler's arguments [7], one has

$$\Lambda'_N < \lambda_0 < \Lambda''_N \,. \tag{38}$$

Correspondingly, the value of λ_0 is given by the intercept of the lower and the higher sequences. The simplest way is to set, in the Nth approximation,

$$\lambda_0 = \frac{\Lambda'_N(\Lambda''_{N-1} - \Lambda''_N) + \Lambda''_N(\Lambda'_N - \Lambda'_{N-1})}{(\Lambda''_{N-1} - \Lambda''_N) + (\Lambda'_N - \Lambda'_{N-1})} \,. \tag{39}$$

Convergence of the method may be improved by subtracting the sum of higher-excited levels from S_N, as proposed in Section 4. As soon as λ_0 is evaluated, the next eigenvalue λ_1 may be treated in the same way, provided that the accuracy in the calculated S_N is sufficient.

6.2. *Modified Pöschl–Teller potential*

The potential function and its Fourier transformation are

$$V(x) = \cosh^{-2} x \qquad \tilde{V}(k) = \frac{\pi k}{2\sinh\left(\frac{1}{2}\pi k\right)} \,. \tag{40}$$

The Schrödinger equation has an analytical solution [9], and the semi-classical spectrum has also a simple form (see (A14)),

$$\lambda_n = (\sqrt{\varepsilon} + n)(\sqrt{\varepsilon} + n + 1) \qquad \lambda_n^{\mathrm{cl}} = \left(\sqrt{\varepsilon} + n + \tfrac{1}{2}\right)^2 . \tag{41}$$

By means of the decomposition in partial fractions of

$$S_N(\varepsilon) = \sum_{n=0}^{\infty} [(\sqrt{\varepsilon} + n)(\sqrt{\varepsilon} + n + 1)]^{-N} \tag{42}$$

one can express the trace invariants in terms of Riemann's zeta functions, e.g.

$$S_1 = 1/\sqrt{\varepsilon} \qquad S_2 = \zeta(2, \sqrt{\varepsilon}) - 2S_1 + \zeta(2, \sqrt{\varepsilon} + 1)$$
$$S_3 = \zeta(3, \sqrt{\varepsilon}) - 3S_2 - \zeta(3, \sqrt{\varepsilon} + 1) \qquad \text{etc} \,. \tag{43}$$

The trace invariants for the even and odd energy levels can be also expressed in terms of the zeta-functions, which are reduced to the Bernoulli numbers for $\sqrt{\varepsilon} = 0, 1, 2, \ldots$. In the semi-classical approximation one has

$$S_N^{\mathrm{cl}} = \zeta\left(2N, \sqrt{\varepsilon} + \tfrac{1}{2}\right) .$$

The appearance of the zeta-function is typical for the semi-classical approximation in general, because of the quantization rule (A13).

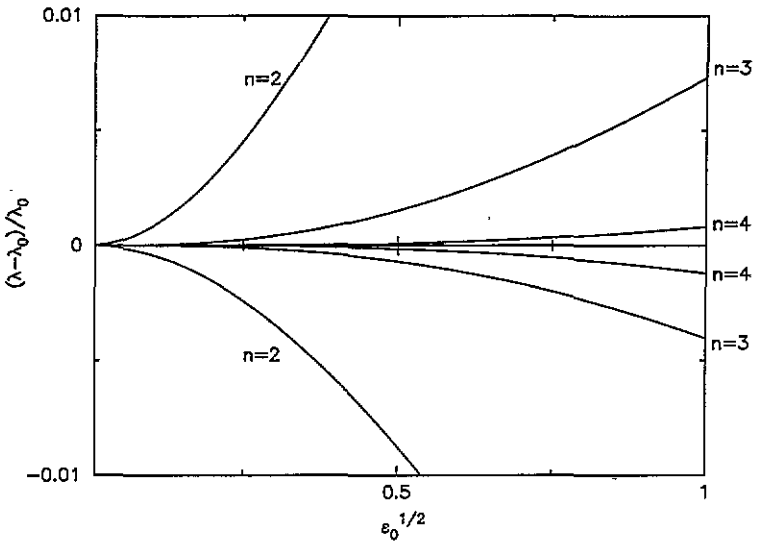

Figure 2. Relative errors in coupling constants as functions of the ground state energy (even state) for various orders of approximation, equation (37). Example of the Yukawa potential (28).

6.3. Square-well potential

The potential function is $V(x) = 1$ for $|x| < 1$ and 0 for $|x| > 1$. The momentum representation is given by

$$\tilde{V}(k) = \frac{\sin k}{\pi k}. \tag{44}$$

The integrals for the trace invariants can be calculated analytically; for example,

$$S_1 = 1/\sqrt{\varepsilon} \qquad S_2 = (e^{-4\sqrt{\varepsilon}} - 1 + 4\sqrt{\varepsilon})/8\varepsilon^2. \tag{45}$$

The exact spectrum is given by solution of two transcedental equations (for even levels and odd levels, respectively), while the semi-classical result (cf (A16)) is

$$\lambda_n^{cl} = \varepsilon + (2n+1)^2\pi^2/16. \tag{46}$$

In the semi-classical approximation, the trace invariants can be expressed in terms of the zeta-functions.

6.4. Accuracy of the approach

The accuracy of the method has been analysed by comparison with the analytical results for a number of potentials: the exponential well (section 5), the square well, and the potential of (40). The case of the Gaussian well, $V(x) = \exp(-x^2)$, has been also considered and compared with the numerical calculation using the differential form of the Schrödinger equation.

If no analytical calculation of the integral is possible, the Monte Carlo method can be applied. Typically, 10^5 interations are sufficient to achieve an error of less than 0.1% for $N \leqslant 5$, so that a 286 AT computer may be employed. The integrand for S_N^+ is smoother than that for S_N^-, and one needs less iterations for even levels. The computation may be improved for odd levels, if one makes use of the weighted Monte Carlo method [10] with the relation function $\prod((4/\pi)\sin^2\theta_n)$. It is suitable owing to a factor $\prod k_n^2$, which appears in the integrals at small k_n, since $\tilde{V}^-(k_1, k_2)$ is vanishing as $k_1 k_2$ at $k_{1,2} \to 0$.

The typical results and convergence of the method are illustrated in figures 2 and 3.

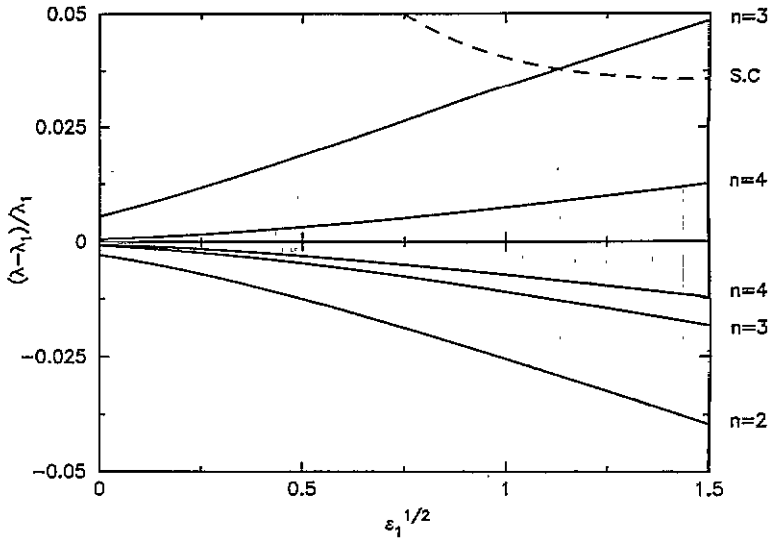

Figure 3. The same as in Figure 2, but for the first excited level (odd state). The broken curve shows the error of the semi-classical approximation.

7. Conclusion

Starting from the integral form of the Schrödinger equation and calculating the trace invariants, one can evaluate the lower part of the energy spectrum with a reasonable accuracy. As shown in several examples of one-dimensional potentials, this method can compete with other numerical methods employed in solving the Schrödinger equation. The approach would acquire an additional significance if it can be applied to essentially multi-dimensional problems, where one has to work with partial differential eqations, which makes the task much more difficult. Future investigations will show whether the method presented here will be helpful for that purpose.

Acknowledgments

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Appendix

A1. Semi-classical approximation

A1.1. Semi-classical generating function. We shall get a semi-classical approximation for the generating function defined in (19),

$$g(\varepsilon,\lambda)=\lambda\mathrm{Tr}[\hat{V}(\hat{H}+\varepsilon)^{-1}]\equiv\lambda\int \mathrm{d}^s x\,V(x)F_\varepsilon(x,x) \tag{A1}$$

where $F_\varepsilon(x,x')$ is the coordinate kernel of the resolvent operator $\hat{G}_\varepsilon^{\mathrm{tot}}=(\hat{H}+\varepsilon)^{-1}$. The latter function is the Laplace transform of the evolution kernel, which is given by the Feynman path

integral. In the present approach, the path integral is evaluated on solutions of the classical equations of motion, and the resolvent is given as a sum of contributions from the classical phase-space trajectories on the energy shell, $p^2 = \lambda V(q) + \varepsilon$, connecting the points with coordinates x and x' (discussion and references may be found in reviews [11, 12]). The sum over the classical trajectories is

$$F_\varepsilon^{\mathrm{cl}}(x,x') = -\frac{2\pi}{(2\pi i\hbar)^{(s+1)/2}} \sum_m B_\varepsilon^{(m)}(x,x') \exp \frac{i}{\hbar}\left[W_\varepsilon^{(m)}(x,x') - \frac{1}{2}\gamma_m \hbar \pi \right]. \tag{A2}$$

(In this section, $\hbar$ is written down explicitly.) The result is expressed in terms of the truncated action integral along the classical trajectories $C_m = \{q(t), p(t)\}$, with a fixed energy ε and the boundary conditions $q(0) = x$, $q(t) = x'$,

$$W_\varepsilon^{(m)}(x,x') = \int_{C_m} \sum_{j=1}^{s} p_j(t)\, \mathrm{d}q_j(t) \tag{A3}$$

which is a solution of two reciprocal Jacobi equations,

$$(\partial W/\partial x_j)^2 - \lambda V(x) = -\varepsilon = (\partial W/\partial x_j')^2 - \lambda V(x')\,. \tag{A4}$$

The pre-exponential factor is given in terms of the second derivatives of W_ε, namely,

$$B_\varepsilon(x,x') = \left(-\frac{\partial^2 W_\varepsilon}{\partial \varepsilon^2} \det M \right)^{1/2} \tag{A5}$$

where M is a matrix with the following elements, and

$$M_{jj'} = \frac{\partial^2 W_\varepsilon}{\partial x_j \partial \varepsilon} \left(\frac{\partial^2 W_\varepsilon}{\partial \varepsilon^2} \right)^{-1} \frac{\partial^2 W_\varepsilon}{\partial x_{j'}' \partial \varepsilon} - \frac{\partial^2 W_\varepsilon}{\partial x_j \partial x_{j'}'}\,. \tag{A6}$$

Finally, γ_m are integers which are given by the behaviour of the trajectory near its turning points in the coordinate space. The integral in (A1) is determined by closed classical trajectories having a given energy $-\varepsilon$, with $x = x'$.

In the *one-dimensional* case, one can get an explicit result for the generating function. All finite trajectories are closed, and each of them is specified by the energy and the number of revolutions m. The momentum in (A3) depends on the energy and the running coordinate q, $p(q) = \sqrt{\lambda V(q) - \varepsilon}$, but not on x and x'. Respectively,

$$W_\varepsilon^{(m)}(x,x') = \int_x^{x'} p(q)\, \mathrm{d}q + 2mw \qquad B_\varepsilon^{(m)}(x,x') = [4p(x)p(x')]^{-1/2} \tag{A7}$$

so that for $x = x'$ the Jacobi action is independent of x and proportional to the number of revolutions, as well as γ_m, which equals the number of turns on the paths. The result is

$$W_\varepsilon^{(m)} = 2mw \qquad \gamma_m = 2m \qquad w(\lambda,\varepsilon) = \int_{x_1}^{x_2} \mathrm{d}q \sqrt{\lambda V(q) - \varepsilon} \tag{A8}$$

where x_1 and x_2 are the classical turning points, $V(x_{1,2}) = \varepsilon/\lambda$. The integral in (A1) is calculated with $B_\varepsilon(x,x)$, given in (A7), producing a factor independent of m,

$$\int_{x_1}^{x_2} \mathrm{d}q \frac{V(q)}{\sqrt{\lambda V(q) - \varepsilon}} = 2\frac{\partial w}{\partial \lambda}\,. \tag{A9}$$

Now the series in m can be summed up using

$$1+2\sum_{m=1}^{\infty} e^{2imz} = i\cot z \qquad z = \frac{w}{\hbar} - \frac{\pi}{2} \tag{A10}$$

where the series is made convergent by appending a vanishing positive imaginary part to z, which stems from the analytical continuation in ε, inherent to the resolvent operator. The factor of 2 is due to the fact that for $m \neq 0$ each trajectory appears twice, corresponding to the left and right revolutions in the potential well.

We have ultimately

$$g^{cl}(\lambda, \varepsilon) = \frac{\lambda}{\hbar}\frac{\partial w}{\partial \lambda}\tan\frac{w}{\hbar}. \tag{A11}$$

The spectrum is given by poles of this function, $w_n = (n+\frac{1}{2})\hbar\pi$, in agreement with the Bohr–Sommerfeld quantization rule.

A1.2. Quantization rule. Practically, one has to evaluate a function of one variable, $\xi = \sqrt{\varepsilon/\lambda}$,

$$v(\xi) = \frac{2}{\pi}\int_{x_1}^{x_2} dq\sqrt{V(q)/\xi^2 - 1} \equiv \frac{2w}{\pi\sqrt{\varepsilon}} \tag{A12}$$

and to evaluate the inverse function, $v = v(\xi) \rightsquigarrow \xi = f(v)$. The semi-classical spectrum is obtained if we set

$$\lambda_n^{cl}(\varepsilon) = \frac{\varepsilon}{\xi_n^2} \qquad \xi_n = f\left((2n+1)\hbar/\sqrt{\varepsilon}\right). \tag{A13}$$

(The accuracy of this method can be improved [13] for singular potentials and small ε if we replace $(2n+1)$ by $(2n+\gamma)$, with an appropriate constant γ, which is determined by the potential behaviour near its singularity and at large x. We shall not get into the details now.)

We shall assume, for simplicity, that $V(x) = V(-x) \geqslant 0$, and $V(0) = \max V(x) = 1$, so $v(\xi)$ is defined for $0 < \xi \leqslant 1$, and $v(1) = 0$. One has, for instance,

$$V(x) = \cosh^{-2} x \qquad \Rightarrow \qquad \xi v(\xi) = 2(1-\xi) \tag{A14}$$

$$V(x) = \exp(-|x|) \qquad \Rightarrow \qquad \xi v(\xi) = \frac{8}{\pi}(\sqrt{1-\xi^2} + \xi\arcsin\xi) - 4\xi \tag{A15}$$

$$V(x) = 1 \quad \text{for } |x| < 1 \qquad V(x) = 0 \quad \text{for } |x| > 1 \qquad \Rightarrow \qquad \xi v(\xi) = \frac{4}{\pi}\sqrt{1-\xi^2} \tag{A16}$$

$$V(x) = 1 - x^2 \quad \text{for } |x| < 1 \qquad V(x) = 0 \quad \text{for } |x| > 1 \qquad \Rightarrow \qquad \xi v(\xi) = 1 - \xi^2 \tag{A17}$$

$$V(x) = 1 - x^{\alpha} \quad \text{for } |x| < 1 \qquad V(x) = 0 \quad \text{for } |x| > 1$$
$$\Rightarrow \qquad \xi v(\xi) = c(1-\xi^2)^{1/2+1/\alpha} \tag{A18}$$

where $\alpha > 0$ and

$$c = \frac{4\Gamma(\alpha^{-1})}{(\alpha+2)\sqrt{\pi}\,\Gamma(\alpha^{-1}+\frac{1}{2})}.$$

For higher excited levels, large v and, respectively, small ξ are essential, which simplifies evaluation of the integral and getting the spectrum. In order to investigate the behaviour of $v(\xi)$ at $\xi \ll 1$, it is suitable to use the following representation, obtained by differentiation and a change of variables:

$$-[v(\xi)+\xi v'(\xi)] = \frac{4}{\pi}\int_0^{x_2} \frac{\xi}{\sqrt{V(q)-\xi^2}}\,\mathrm{d}q = \frac{8}{\pi}\int_{\theta_0}^{\pi/2} \varphi_\xi(\theta)\,\mathrm{d}\theta \qquad \text{(A19)}$$

where $\sin\theta_0 = \xi$, and q is substituted for θ by

$$V(q) = \frac{\xi^2}{\sin^2\theta} \qquad \varphi_\xi(\theta) = -\frac{V(q)}{V'(q)} \qquad \text{(A20)}$$

One can see, in particular, that $\xi v(\xi)$ is regular at $\xi = 0$, and $\lim_{\xi\to 0}\varphi_\xi(\theta) \equiv \varphi_0(\theta)$ exists, if $V(q)$ has an exponential asymptotics. Thus we have the expansion

$$\xi v(\xi) = \frac{4}{\pi}(v_0 - v_1\xi) + \mathrm{O}(\xi^2) \qquad \text{(A21)}$$

where

$$v_0 = \int_0^{+\infty} \mathrm{d}q\sqrt{V(q)} \qquad v_1 = 2\int_0^{\pi/2} \varphi_0(\theta)\,\mathrm{d}\theta\,. \qquad \text{(A22)}$$

If $V(q) \equiv 0$ for $q > q_0$, then $v_1 = 0$ and the expansion goes in powers of ξ^2, cf (A16)–(A18).

A2. Trace invariants for the Yukawa-type potential

For the one-dimensional Yukawa-type potential (28), the trace invariants are expressed by series of powers of zeros of the Bessel functions and their derivatives, namely

$$S_N^+(\varepsilon) = (2/\mu)^{2N}\sum_{m=1}^{\infty}(j'_{\nu,m})^{-2N} \qquad S_N^-(\varepsilon) = (2/\mu)^{2N}\sum_{m=1}^{\infty}(j_{\nu,m})^{-2N}$$
$$S_N(\varepsilon) = S_N^+(\varepsilon) + S_N^-(\varepsilon) \qquad \text{(A23)}$$

where $\varepsilon = (\nu\mu/2)^2$. The integrals in (30) can be calculated analytically, and the results are given below:

$$\mu^2 S_1^+ = \frac{1+\kappa}{\kappa(1+2\kappa)} \qquad \mu^2 S_1^- = \frac{1}{1+2\kappa} \qquad \mu^2 S_1 = \frac{1}{\kappa} \qquad \text{(A24)}$$

$$\mu^4 S_2^+ = \frac{2+4\kappa+\kappa^2}{2\kappa^2(1+2\kappa)^2(1+\kappa)} \qquad \mu^4 S_2^- = \frac{1}{2(1+2\kappa)^2(1+\kappa)} \qquad \mu^4 S_2 = \frac{1+\kappa}{\kappa^2(1+2\kappa)^2} \qquad \text{(A25)}$$

$$\mu^6 S_3^+ = \frac{6+19\kappa+16\kappa^2+2\kappa^3}{2\kappa^3(1+2\kappa)^3(1+\kappa)(3+2\kappa)}$$
$$\mu^6 S_3^- = \frac{1}{(1+2\kappa)^3(1+\kappa)(3+2\kappa)} \qquad \mu^6 S_3 = \frac{2+\kappa}{2\kappa^3(1+2\kappa)^2(1+\kappa)} \qquad \text{(A26)}$$

$$\mu^8 S_4^+ = \frac{48 + 248\kappa + 472\kappa^2 + 400\kappa^3 + 139\kappa^4 + 10\kappa^5}{8\kappa^4(1+2\kappa)^4(1+\kappa)^2(3+2\kappa)(2+\kappa)}$$

$$\mu^8 S_4^- = \frac{11 + 10\kappa}{8(1+2\kappa)^4(1+\kappa)^2(3+2\kappa)(2+\kappa)} \tag{A27}$$

$$\mu^8 S_4 = \frac{12 + 56\kappa + 90\kappa^2 + 55\kappa^3 + 10\kappa^4}{4\kappa^4(1+2\kappa)^4(1+\kappa)^2(3+2\kappa)}$$

$$\mu^{10} S_5^+ = \frac{240 + 1456\kappa + 3414\kappa^2 + 3903\kappa^3 + 2222\kappa^4 + 550\kappa^5 + 28\kappa^6}{8\kappa^5(1+2\kappa)^5(1+\kappa)^2(3+2\kappa)(2+\kappa)(5+2\kappa)}$$

$$\mu^{10} S_5^- = \frac{19 + 14\kappa}{8(1+2\kappa)^5(1+\kappa)^2(3+2\kappa)(2+\kappa)(5+2\kappa)} \tag{A28}$$

$$\mu^{10} S_5 = \frac{48 + 272\kappa + 574\kappa^2 + 551\kappa^3 + 224\kappa^4 + 28\kappa^5}{8\kappa^5(1+2\kappa)^5(1+\kappa)^2(3+2\kappa)(2+\kappa)}$$

where $\kappa \equiv \sqrt{\varepsilon}/\mu = \nu/2$. For $\kappa = \frac{1}{4}$, one has $J_{1/2}(\zeta) = \sqrt{2/\pi\zeta}\sin\zeta$, and the S_N^- are proportional to the Bernoulli numbers,

$$\mu^{2N} S_N^-(\mu^2/16) = \frac{2^{4N-1}}{(2N)!}(-1)^{N+1} B_{2N}\,. \tag{A29}$$

It is notable that the form of the denominators can be obtained directly from a Landau-type analysis of singularities of the integrals in (30), which are like the Feynman integrals for a one-dimensional field theory. The analytical calculation of the integrals can be performed recursively by means of one of the existing computer systems. The series of inverse powers of roots of the Bessel functions, S_N^-, are known for any ν also from the infinite product representation [14].

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