Morse-potential Green's function with path integrals

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An integral representation for the Green's function of the one-dimensional Morse potential is obtained by solving path integrals. To test the method employed, the correct bound-state energy spectrum and the wave functions are derived.

I. INTRODUCTION

In spite of conceptual beauty and useful applications in field theories, so far very few quantum-mechanical problems have been treated by Feynman's path integrals. Since only the quadratic potentials can be solved exactly, one has to look for appropriate transformations to express the problem in hand in terms of the oscillator or free-particle Green's functions. For these transformations, although there are complications and lack of rigor,[1] one has to employ canonical transformations. For example, to solve the path integral for the three-dimensional H atom, one transforms to the four-dimensional harmonic-oscillator potential.[2] In this Brief Report we solve the path integral for the one-dimensional Morse-potential Green's function. It is well known that the Morse potential[3] is a very useful approximation for the molecular-vibration problem and its Schrödinger equation is exactly soluble. Thus, to test the validity of our transformations in dealing with path integrals, we can compare our results with the known wave functions and the energy spectrum. On the other hand, since the calculation of the transition amplitudes in molecular physics is very important, although it is one dimensional, the formula derived in this paper for the Morse potential may be useful by itself too.

II. PATH INTEGRAL FOR ONE-DIMENSIONAL MORSE POTENTIAL

The probability amplitude for a particle of mass m traveling from a position x_a at time $t_a \equiv 0$ to x_b at time $t_b \equiv T$, in the Morse potential

$$U(x) = V_0(e^{-2ax} - 2e^{-ax}) \ , \tag{1}$$

can be written as a phase-space path integral in Cartesian coordinates:

$$K(x_b,T;x_a,0) = \int \frac{\mathscr{D}x\,\mathscr{D}p}{2\pi} \exp\left[\frac{i}{\hbar}\int_0^T dt \left(p\dot{x} - \frac{1}{2m}p^2 - V_0(e^{-2ax} - 2e^{-ax})\right)\right] \ . \tag{2}$$

The above kernel is understood as the limit of the usual time-graded form:

$$K(x_b,T;x_a,0) = \lim_{\substack{n\to\infty \\ \epsilon\to 0}} \int \prod_{i=1}^{n} dx_i \prod_{i=1}^{n+1} \frac{dp_i}{2\pi} \exp\left[\frac{i}{\hbar}\sum_{i=1}^{n+1}\left(p_i(x_i - x_{i-1}) - \frac{p_i^2}{2m} - U(x_i)\right)\right] \ , \tag{3}$$

where

$$\epsilon = t_i - t_{i-1}, \quad (n+1)\epsilon = t_b - t_a \equiv T$$

and

$$x_0 = x_a, \quad x_{n+1} = x_b \ .$$

Since the canonical transformations we are going to employ are of the "point" type, we can as well work with the Lagrangian path integral. We prefer to use the phase-space form of Eq. (2) simply for keeping track of the normalization.

Having in mind the variable change used in solving the Schrödinger equation for the Morse potential, we introduce the new coordinate $\xi \in (0,\infty)$ with the point canonical transformation

$$x = -\frac{2}{a}\ln\xi, \quad p = -\frac{a}{2}\xi p_\xi \tag{4}$$

generated by the function

$$F_2(x,p_\xi) = e^{-ax/2}p_\xi \ .$$

Since there is an extra integration over the momentum, compared to the coordinates in integral (3), we get a contribution $(-a\xi_b/2)$ to the Jacobian from $dp_{n+1} \to dp_{\xi n+1}$. Then the path integral (3) becomes

$$K(x_b,T;x_a,0) = -\frac{a}{2}\xi_b \int \frac{\mathscr{D}\xi\,\mathscr{D}p_\xi}{2\pi} \exp\left[\frac{i}{\hbar}\int_0^T dt\left(p_\xi\dot{\xi} - \frac{\xi^2}{2(4m/a^2)}p_\xi^2 - V_0\xi^4 + 2V_0\xi^2\right)\right] \ . \tag{5}$$

Now, to get rid of the ξ^2 factor of the kinetic energy term with p_ξ^2, we introduce an auxiliary time variable s by

$$dt = ds/\xi^2 \text{ or } t = \int^s ds'/\xi^2(s') \ . \tag{6}$$

Note that the parameter s is a monotonically increasing function of t. (A similar type of time-variable change has been used previously for solving the H-atom path integral. Recently, Ho and Inomata[4] explicitly worked out the point canonical transformation in each short-time interval using a midpoint expansion.) Together with the constraint

$$T = \int^S ds/\xi^2(s), \quad S = s_b - s_a$$

Eq. (5) takes the form

$$K(x_b,T;x_a,0)=\int\left(\frac{a}{2}\right)\xi_b\left(\frac{1}{\xi_b{}^2}\right)\int_0^\infty dS\,\delta\left(T-\int_0^S\frac{ds}{\xi^2(s)}\right)\frac{\mathscr{D}\xi(s)\mathscr{D}p_\xi(s)}{2\pi}$$
$$\times\exp\left[\frac{i}{\hbar}\int_0^S ds\left(p_\xi\xi'-\frac{1}{2(4m/a^2)}p_\xi{}^2+2V_0-V_0\xi^2\right)\right] .$$

Here the factor $(1/\xi_b{}^2)$ is the normalization of the δ function and a prime denotes the derivative with respect to s. With the introduction of the Fourier representation of the δ function, the Green's function can be written as

$$K(x_b,T;x_a,0)=\left(\frac{a}{2}\right)\int_{-\infty}^{\infty}\frac{dE}{2\pi}e^{iET}\int_0^\infty dS\,e^{2iV_0S/\hbar}\int\left(\frac{1}{\xi_b}\right)\frac{\mathscr{D}\xi\mathscr{D}p_\xi}{2\pi}\exp\left[\frac{i}{\hbar}\int_0^S ds\left(p_\xi\xi'-\frac{1}{2M}p_\xi{}^2-\tfrac{1}{2}M\omega^2\xi^2-\frac{\hbar E}{\xi^2}\right)\right] , \quad (7)$$

where

$$M\equiv 4m/a^2,\quad \omega\equiv\sqrt{2V_0/M}=\tfrac{1}{2}a\sqrt{2V_0/M} . \quad (8)$$

If we integrate over $\mathscr{D}p_\xi(s)$, we obtain

$$K(x_b,T;x_a,0)=\left(\frac{a}{2}\right)\int_{-\infty}^{\infty}\frac{dE}{2\pi}e^{iET}\int_0^\infty dS e^{2iV_0S/\hbar}\int\left(\frac{1}{\xi_b}\right)\mathscr{D}\xi\exp\left[\frac{i}{\hbar}\int_0^S ds\left(\frac{M}{2}\xi'^2-\tfrac{1}{2}M\omega^2\xi^2-\frac{\hbar E}{\xi^2}\right)\right] . \quad (9)$$

In Eqs. (7) and (8) we observe that the Jacobian resulting from the coordinate and the time transformations has the factor ξ_b. Since the Green's function K is expressible in terms of the wave functions $\psi_n(x_a)$ and $\psi_n(x_b)$ as

$$K(x_b,T;x_a,0)=\sum_n e^{-iE_nT}\psi_n(x_b)\psi_n^*(x_a) ,$$

we would like to have equal contributions from ξ_a and ξ_b to the Jacobian. To have a symmetric Jacobian in terms of points a and b, we rewrite the factor $1/\xi_b$ as

$$\frac{1}{\xi_b}=\frac{1}{(\xi_a\xi_b)^{1/2}}\exp\left(-\tfrac{1}{2}\ln\frac{\xi_b}{\xi_a}\right)=\frac{1}{\sqrt{\xi_a\xi_b}}\exp\left(-\frac{1}{2}\int_0^S ds\,\frac{\xi'}{\xi}\right)=\frac{1}{\sqrt{\xi_a\xi_b}}\exp\left(\frac{i}{\hbar}\int_0^S ds\,\frac{i\hbar\xi'}{2\xi}\right) . \quad (10)$$

With the above form of $1/\xi_b$, the Green's function (9) becomes

$$K(x_b,T;x_a,0)=\frac{a}{2}\int_{-\infty}^{\infty}\frac{dE}{2\pi}e^{iET}\int_0^\infty dS\,e^{2iV_0S/\hbar}$$
$$\times\frac{1}{\sqrt{\xi_a\xi_b}}\int\mathscr{D}\xi\exp\left\{\frac{i}{\hbar}\int_0^S ds\left[\frac{M}{2}\left(\xi'+\frac{i\hbar}{2M\xi}\right)^2+\frac{\hbar^2}{8M\xi^2}-\tfrac{1}{2}M\omega^2\xi^2-\frac{\hbar E}{\xi^2}\right]\right\} . \quad (11)$$

If we look at the path integral in this last equation,

$$\mathsf{K}(\xi_b,S;\xi_a,0)\equiv\frac{1}{\sqrt{\xi_a\xi_b}}\int\mathscr{D}\xi\exp\left\{\frac{i}{\hbar}\int_0^S ds\left[\frac{M}{2}\left(\xi'+\frac{i\hbar}{2M\xi}\right)^2-\tfrac{1}{2}M\omega^2\xi^2-\frac{2M\hbar E-\hbar^2/4}{2M\xi^2}\right]\right\} ,$$

or its phase-space form

$$\mathsf{K}(\xi_b,S;\xi_a,0)=\frac{1}{\sqrt{\xi_a\xi_b}}\int\frac{\mathscr{D}\xi\mathscr{D}p_\xi}{2\pi}\exp\left[\frac{i}{\hbar}\int_0^S ds\left(p_\xi\xi'-\frac{p_\xi{}^2}{2M}-\tfrac{1}{2}M\omega^2\xi^2-\frac{2M\hbar E-\hbar^2/4}{2M\xi^2}+\frac{i\hbar p_\xi}{2M\xi}\right)\right] , \quad (12)$$

we see that the symmetrization of the Jacobian (from $1/\xi_b$ to $1/\sqrt{\xi_a\xi_b}$) introduces purely quantum-mechanical contributions to the action:

$$\hbar^2/8M\xi^2+i\hbar p_\xi/2M\xi . \quad (13)$$

Note that the Jacobian $1/\xi_b$ was the result of $dp_{n+1}\rightarrow dp_{\xi n+1}$ transformation and of the normalization of $\delta(T-\int_{s_a}^{s_b}ds/\xi^2)$ at point b. However, we could write the path integral (3) as well, by starting the time division of the momentum variables at $i=0$ and ending at $i=n$, as

$$K(x_b,T;x_a,0)=\lim_{\substack{n\to\infty\\ \epsilon\to 0}}\int\prod_{i=1}^n dx_i\prod_{i=0}^n\frac{dp_i}{2\pi}\exp\left[\frac{i}{\hbar}\sum_{i=0}^n\left(p_i(x_i-x_{i+1})-\frac{p_i{}^2}{2M}-U(x_{i+1})\right)\right] . \quad (14)$$

Thus if we would start with the above path integral, instead of (3) we would get a contribution $-a\xi_a/2$ to the Jacobian from $dp_0\rightarrow dp_{\xi 0}$ transformation. Then after normalizing the δ function $\delta(T-\int_{s_a}^{s_b}ds/\xi^2)$ at point a, the resulting Jacobian would be $-(a/2)\xi_a\xi_a{}^{-2}=-(a/2)/\xi_a$. When we symmetrize this factor, we obtain

$$\frac{1}{\xi_a}=\frac{1}{\sqrt{\xi_a\xi_b}}\exp\left(-\frac{i}{\hbar}\int_0^S ds\,\frac{i\hbar\xi'}{2\xi}\right) \quad (15)$$

instead of (10), which gives for $\mathsf{K}(\xi_b,S;\xi_a,0)$

$$\mathsf{K}(\xi_b,S;\xi_a,0)=\frac{1}{\sqrt{\xi_a\xi_b}}\int\frac{\mathscr{D}\xi\mathscr{D}p_\xi}{2\pi}\exp\left[\frac{i}{\hbar}\int_0^S ds\left(p_\xi\xi'-\frac{p_\xi^2}{2M}-\tfrac{1}{2}M\omega^2\xi^2-\frac{2M\hbar E-\hbar^2/4}{2M\xi^2}-\frac{i\hbar p_\xi}{2M\xi}\right)\right] . \tag{16}$$

This form of K, which has the quantum-mechanical contribution

$$\hbar^2/8M\xi^2-i\hbar p_\xi/2M\xi \tag{17}$$

in its action, must be equal to the one given by (12). If we write for K the geometrical average of the two integrands of (12) and (16), we obtain the expression

$$\overline{\mathsf{K}}(\xi_b,S;\xi_a,0)=\frac{1}{\sqrt{\xi_a\xi_b}}\int\frac{\mathscr{D}\xi\mathscr{D}p_\xi}{2\pi}\exp\left[\frac{i}{\hbar}\int_0^S ds\left(p_\xi\xi'-\frac{p_\xi^2}{2M}-\tfrac{1}{2}M\omega^2\xi^2-\frac{2M\hbar E-\hbar^2/4}{2M\xi^2}\right)\right] , \tag{18}$$

whose effective Hamiltonian is Hermitian:

$$H_{\rm eff}=\frac{p_\xi^2}{2M}+\tfrac{1}{2}M\omega^2\xi^2+\frac{2M\hbar E-\hbar^2/4}{2M\xi^2} . \tag{19}$$

This effective Hamiltonian is the same as the "ordered" Hamiltonians written in two-dimensional polar coordinates.[5,6] Note that if we do not get a contribution to the Jacobian from point a (or b), we do not have a symmetrization problem. Thus, we do not get an ordering contribution to the Hamiltonian. For example, when we transform the three-dimensional H-atom path integral to the four-dimensional harmonic-oscillator Green's function, the Jacobian is free of end-point coordinates, and we are not faced with an ordering contribution.[2]

After having the form given by Eq. (18) for $\overline{\mathsf{K}}$, the Morse-potential Green's function of (7) becomes (from now on we put $\hbar=1$)

$$K(x_b,T;x_a,0)=-\left(\frac{a}{2}\right)\frac{1}{\sqrt{\xi_a\xi_b}}\int_{-\infty}^{\infty}\frac{dE}{2\pi}e^{iET}\int_0^\infty dS\,e^{2iV_0S}\,\overline{\mathsf{K}}(\xi_b,S;\xi_a,0) . \tag{20}$$

Here, $\overline{\mathsf{K}}(\xi_b,S;\xi_a,0)$ is the kernel for the particle of mass M, moving in (s,ξ) space with $\xi>0$, under the potential

$$U(\xi(s))=\tfrac{1}{2}M\omega^2\xi^2+\frac{2ME-\frac{1}{4}}{2M\xi^2} . \tag{21}$$

To demonstrate that the expression (20) is correct, we write $\overline{\mathsf{K}}$ as

$$\overline{\mathsf{K}}(\xi_b,S;\xi_a,0)=\sum_{n=0}^{\infty}e^{i\mathscr{E}_nS}\psi_n(\xi_b)\psi_n^*(\xi_a) , \tag{22}$$

where the "energy" $\mathscr{E}_n$ is given by

$$\mathscr{E}_n=\omega(2n+1+\sqrt{2ME}) \tag{23}$$

and the "wave function" ψ_n is

$$\psi_n(\xi)=\mathscr{N}e^{-M\omega^2\xi^2/2}(M\omega\xi^2)^sF(-n,2s+\tfrac{1}{2},M\omega\xi^2) \tag{24}$$

with

$$\mathscr{N}=\frac{1}{\Gamma(2s+\frac{1}{2})}[2(M\omega)^{1/2}\Gamma(n+2s+\tfrac{1}{2})/n!]^{1/2} , \tag{25}$$

$$s\equiv\tfrac{1}{4}+\tfrac{1}{2}\sqrt{2ME}>0,\quad n=0,1,2,\ldots ,$$

and F is the confluent hypergeometric function.[7] If we insert (22) into (20), the Morse-potential Green's function becomes

$$K(x_b,T;x_a,0)=-\frac{a}{2\sqrt{\xi_a\xi_b}}\int_{-\infty}^{\infty}\frac{dE}{2\pi}e^{iET}\sum_{n=0}^{\infty}\int_0^\infty dS\,e^{(2iV_0-\mathscr{E}_n)S}\psi_n(\xi_b)\psi_n^*(\xi_a) \tag{26}$$

or, after integrating over dS and dE, we obtain

$$K(x_b,T;x_a,0)=\sum_{\substack{n=0\\ n<V_0/\omega-1/2}}\int_{-\infty}^{\infty}\frac{dE}{2\pi}\frac{-ie^{iET}}{\mathscr{E}_n-2V_0}\left[\left(\frac{a}{2\xi_b}\right)^{1/2}\psi_n(\xi_b)\right]\left[\left(\frac{a}{2\xi_a}\right)^{1/2}\psi_n(\xi_a)\right]^* \tag{27}$$

$$=\sum_{\substack{n=0,\\ n<V_0/\omega-1/2}}\exp\left\{-i\left[-V_0\left(1-\frac{\omega}{V_0}(n+\tfrac{1}{2})\right)^2\right]T\right\}\phi_n(\xi_b)\phi_n^*(\xi_a) \tag{28}$$

which displays the correct bound-state energy spectrum,

$$E_n=-V_0\left(1-\frac{\omega}{V_0}(n+\tfrac{1}{2})\right)^2,\quad n=0,1,\ldots<\frac{V_0}{\omega}-\frac{1}{2} , \tag{29}$$

and the correctly normalized wave functions of the Morse potential,

$$\phi_n(\xi)=[2a(s-\tfrac{1}{4})\Gamma(n+2s+\tfrac{1}{2})/n!]^{1/2}\frac{1}{\Gamma(2s+\frac{1}{2})}e^{-M\omega\xi^2/2}(M\omega\xi^2)^{s-1/4}F(-n,2s+\tfrac{1}{2},M\omega\xi^2)$$

which, with definitions $(M\omega)\xi^2 \equiv \eta$ and $s - \frac{1}{4} \equiv l$, takes the usual form[7]:

$$\chi_n(\eta) = [2al\Gamma(n+2l+1)/n!]^{1/2} \frac{1}{\Gamma(2l+1)} e^{-\eta/2}\eta^l F(-n, 2l+1, \eta) \quad . \tag{30}$$

To obtain the scattering states one performs a Sommerfeld-Watson transformation on (27).[2] Since the term $1/\xi^2$ already appears as the centrifugal contribution in polar coordinates in the two-dimensional harmonic-oscillator Hamiltonian, the kernel $\overline{K}(\xi_b,S;\xi_a,0)$ can be calculated explicitly[6]:

$$\overline{K}(\xi_b,S;\xi_a,0) = \{[M\omega(\xi_a\xi_b)^{1/2}]/(i\sin\omega S)\} I_{\sqrt{2ME}}\left[\frac{M\omega\xi_a\xi_b}{i\sin\omega S}\right] \exp\left[\frac{iM\omega}{2}(\xi_a{}^2+\xi_b{}^2)\cot\omega S\right] , \tag{31}$$

where

$$I_{\sqrt{2ME}}(M\omega\xi_a\xi_b/i\sin\omega S)$$

is the modified Bessel function. Introducing (31) into (20), we have an integral formula for the Morse-potential Green's function:

$$K(x_b,T;x_a,0) = \frac{a}{2}\int_{-\infty}^{\infty}\frac{dE}{2\pi}e^{iET}\int_0^{\infty} dS\, e^{2iV_0S}\left[\frac{M\omega}{i\sin\omega S}\right] I_{\sqrt{2ME}}\left[\frac{M\omega\xi_a\xi_b}{i\sin\omega S}\right]\exp\left[\frac{iM\omega}{2}(\xi_a{}^2+\xi_b{}^2)\cot\omega S\right] . \tag{32}$$

III. DISCUSSIONS

Making use of canonical transformations, we have converted the path integral for a Morse potential into the path integral for a harmonic-oscillator potential with an additional centrifugal potential $1/\xi^2$. The type of canonical transformation employed in this example is

$$Q = f(q), \quad P = \left[\frac{df}{dq}\right]^{-1} p \quad ,$$

i.e., it is a point transformation. Thus, the Jacobian resulting from this transformation does not have a momentum dependence. By symmetrizing the Jacobian in a rather heuristic fashion, and taking only the Hermitian part of the Hamiltonian, we obtain a quantum-mechanical contribution to the action which is of the $\hbar^2$ order. The resulting path integral, with the effective Hamiltonian, has exactly the same corrections as the path integrals written in terms of the ordered Hamiltonians. In fact, with our procedure, we can get the ordered formulas for the path integrals written in polar coordinates.[8] On the other hand, if the end-point Jacobian is constant, we conclude that the effective Hamiltonian coincides with the classical one.

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[1]See, for example, L. S. Schulman, *Techniques and Applications of Path Integration* (Wiley, New York, 1981), and references therein.

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