Exact-Path-Integral Treatment of the Hydrogen Atom

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The Lagrangian path integral for the hydrogen atom is calculated exactly by rescaling paths and performing the Kustaanheimo-Stiefel transformation in each short-time integral.

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Despite the unquestionable success of Feynman's formulation of quantum mechanics, the path integral for the hydrogen atom has remained to be treated exactly. There are some earlier attempts to obtain the exact results via semiclassical approximations[1,2] or to find a partial result via exact calculations.[3] Recently an important procedure has been proposed by Duru and Kleinert[4] for solving exactly the path integral for the Coulomb problem. The proposed procedure consists of two main steps; the reparametrization of paths in terms of a new "time," and the change of variables by the Kustaanheimo-Stiefel (KS) transformation.[5] The KS transformation is known to reduce the Kepler motion in three dimensions into a four-dimensional harmonic oscillation in both classical and quantum mechanics.[6,7] Following this procedure, Duru and Kleinert have formally converted the Hamiltonian path integral for the hydrogen atom into that for an oscillator which is exactly solvable. However, they have performed no actual path integration to confirm any part of the procedure. Although their calculation is inspiring, its superficial nature has incurred some skepticism.[8]

In fact, there are questions in applying such a nonlinear canonical transformation as the KS transformation to a Hamiltonian path integral in a formal manner. In general, a Hamiltonian path integral is not invariant under a nonlinear canonical transformation.[9,10] Therefore it is important to see if the KS transformation performed in each short-time integral would give rise to the desired global change of variables without bringing up any additional effect. For a short-time integral, on the other hand, there is ambiguity in stipulating the local transformation of the canonical momentum insofar as the Hamiltonian scheme is adopted. However, since the KS transformation is a point transformation, it is not essential to deal with the Hamiltonian path integral. The ambiguity associated with the momentum transformation can simply be avoided by starting with the Lagrangian path integral.

The purpose of this paper is to derive the Green's function of the hydrogen atom via a path integral in a way free from ambiguity. We follow the general recipe proposed by Duru and Kleinert.[4] However, we solve the problem explicitly by (i) using the Lagrangian path integral instead of the Hamiltonian path integral, and (ii) applying the KS transformation in a modified version to Cartesian variables in each short-time integral with the midpoint expansion, rather than performing an ambiguous formal change of path-integral variables.

We start with the propagator expressed by the Lagrangian path integral,

$$K(\vec{x}'',\vec{x}';\tau)=\int \exp\{(i/\hbar)\int_{t'}^{t''} L(\dot{\vec{x}},\vec{x})dt\}\mathfrak{D}^3x(t), \quad (1)$$

with the attractive Coulomb Lagrangian, $L(\dot{\vec{x}},\vec{x})=\frac{1}{2}m\dot{\vec{x}}^2+e^2/r$, where $\tau=t''-t'$ and $r=|\vec{x}|$. The Green's function for the Coulomb problem, $G(\vec{x}'',\vec{x}';E)$, can be obtained as a Fourier transform of (1). Unfortunately, no one knows how to carry out the path integration (1) directly on the O(3) basis. Here, we attempt to calculate it on the O(4) basis.

First, following Duru and Kleinert,[4] we reparametrize paths by means of a new "time," $s(t)=\int^t dt/r(t)$. Namely, we rewrite (1) as

$$K(\vec{x}'',\vec{x}';\tau)=\int_0^\infty \delta(\tau-\int_0^\sigma r(s)ds)K(\vec{x}'',\vec{x}';\sigma)r''\,d\sigma. \quad (2)$$

Correspondingly, the Green's function takes the form

$$G(\vec{x}'',\vec{x}';E)=\int \exp[(iE/\hbar)\int^\sigma r(s)ds]K(\vec{x}'',\vec{x}';\sigma)r''\,d\sigma. \quad (3)$$

Writing (3) in the form,

$$G(\vec{x}'',\vec{x}';E)=\int \exp(ie^2\sigma/\hbar)P_E(\vec{x}'',\vec{x}';\sigma)d\sigma, \tag{4}$$

we express P_E in (4) on the time-division basis,

$$P_E(\vec{x}'',\vec{x}';\sigma)=\lim_{\epsilon\to 0}\left(\frac{m}{2\pi i\hbar\epsilon}\right)^{3N/2} r_N\bar{r}_N^{-3/2}\int \exp\left(\frac{i}{\hbar}\sum_{j=1}^{N} S(\vec{x}_j)\right)\prod_{j=1}^{N-1}(\bar{r}_j^{-3/2}d^3x_j), \tag{5}$$

where $S(\vec{x}_j)=(m/2\epsilon\bar{r}_j)(\Delta\vec{x}_j)^2+\epsilon E\bar{r}_j$ and $\epsilon=(t_j-t_{j-1})/\bar{r}_j$, $\bar{r}_j$ being the midpoint value of r_j to be defined later.

Next, in order to reduce each short-time integral in (5) into the Gaussian form, we consider the change of variables from $x^a=(x,y,z)$ in R^3 to Cartesian variables $u^b=(u^1,u^2,u^3,u^4)$ in R^4 by the KS transformation,[5]

$$x^a=\sum_{b=1}^{4}A^{ab}(u)u^b \quad (a=1,2,3), \tag{6}$$

where

$$A(u)=\begin{bmatrix} u^3 & u^4 & u^1 & u^2 \\ -u^4 & u^3 & u^2 & -u^1 \\ -u^1 & -u^2 & u^3 & u^4 \\ -u^2 & u^1 & -u^4 & u^3 \end{bmatrix} \tag{7}$$

satisfies the condition $\tilde{A}A=rI$ or $\sum_{b=1}^4(u^b)^2=r$. As is obvious, the matrix $A(u)$ of (7) maps only a subspace of $R^4\ni u$ onto $R^3\ni x$. A constraint such as $u^1u^4+u^2u^3=0$ is needed to specify the subspace. Undoubtedly such a constraint will complicate path integration in the new variables. What we are presently concerned with is, however, the change of intervals rather than coordinates themselves. Applying (6) for each j, we obtain the KS transformation for the intervals,

$$\Delta x_j^a=2\sum_{b=1}^{4}A^{ab}(\bar{u}_j)\Delta u_j^b \quad (a=1,2,3), \tag{8}$$

where $\bar{u}_j^b=\frac{1}{2}(u_j^b+u_{j-1}^b)$ and $\Delta u_j^b=u_j^b-u_{j-1}^b$. We also observe that although $\sum_b A^{4b}(u)u^b=0$ the quantity defined by

$$\xi_j=2\sum_{b=1}^{4}A^{4b}(\bar{u}_j)\Delta u_j^b \tag{9}$$

does not vanish in general. When u_j is constrained, ξ_j is a function of Δx_j^a. If no constraint is assumed, it behaves as an independent variable, and the matrix $A(\bar{u})$ in (8) and (9) maps $(\Delta u^1,\Delta u^2,\Delta u^3,\Delta u^4)$ onto $(\Delta x,\Delta y,\Delta z,\xi)$. This is in contrast to the situation that $A(u)$ of (7) maps (u^1,u^2,u^3,u^4) onto $(x,y,z,0)$. Therefore, if the three-dimensional path integral (5) can be converted into an equivalent four-dimensional form, we may lift the constraint and try the set of transformations (8) and (9), which we call the modified KS transformation, in changing variables.

In fact by inserting into (5) the following idem factor,

$$\prod_{j=1}^{N}\left[\left(\frac{m}{2\pi i\hbar\epsilon}\right)^{1/2}\int_{-\infty}^{\infty}\exp\left(\frac{im}{2\hbar\epsilon\bar{r}_j}\xi_j^2\right)\bar{r}_j^{-1/2}d\xi_j\right]=1, \tag{10}$$

we can simply convert (5) without altering its physical contents into the four-dimensional form,

$$P_E(\vec{x}'',\vec{x}';\sigma)=\lim_{\epsilon\to 0}\left(\frac{m}{2\pi i\hbar\epsilon}\right)^{2N} r_N\bar{r}_N^{-2}\int \exp\left(\frac{i}{\hbar}\sum_{j=1}^{N}\hat{S}(\vec{x}_j)\right)\prod_{j=1}^{N-1}(\bar{r}_j^{-2}d^3x_j\,d\xi_j)d\xi_N \tag{11}$$

with

$$\hat{S}(\vec{x}_j)=(m/2\epsilon\bar{r}_j)[(\Delta\vec{x}_j)^2+\xi_j^2]+\epsilon E\bar{r}_j. \tag{12}$$

Now the modified KS transfromation appears to be given a place to work. At this point, however, it is crucial to define the midpoint value of r_j by $\bar{r}_j=\sum_{b=1}^4(\bar{u}_j^b)^2\equiv\bar{u}_j^2$, so as to assure the property, $\tilde{A}(\bar{u}_j)A(\bar{u}_j)=\bar{r}_jI$. With this, the modified KS transformation yields $(\Delta\vec{x}_j)^2+\xi_j^2=4\bar{r}_j(\Delta u_j)^2$ and $\partial(\vec{x},\xi)/\partial(u)_j=2^4\bar{r}_j^2$. Thus we can write (11) as

$$P_E(\vec{x}'',\vec{x}';\sigma)=2^{-4}\int\hat{K}(u'',u';\sigma)r''^{-1}d\xi'', \tag{13}$$

where

$$\hat{K}(u'',u';\sigma)=\lim_{\epsilon\to 0}\left(\frac{2m}{\pi i\hbar\epsilon}\right)^{2N}\int \exp\left[\frac{i}{\hbar}\sum_{j=1}^{N}\left(\frac{2m}{\epsilon}(\Delta u_j)^2+\epsilon E\bar{u}_j^2\right)\right]\prod_{j=1}^{N-1}(d^4u_j). \tag{14}$$

The last path integral (14) is nothing but the propagator for an isotropic oscillator of mass $M=4m$ and frequency $\omega=(-E/2m)^{1/2}$ in R^4, which can be evaluated exactly in the usual manner,

$$\hat{K}(u'',u';\sigma)=F^4(\sigma)\exp\{-\pi F^2(\sigma)[(u'^2+u''^2)\cos\omega\sigma-2u'\cdot u'']\}, \tag{15}$$

with $F(\sigma)=(M\omega/2\pi i\hbar\sin\omega\sigma)^{1/2}$.

By reducing the Coulomb problem to the oscillator problem with the help of the modified KS transformation, we have completed the path integration. Yet, we have to calculate the remaining ξ integral in (13). As it should be, (11) goes back to (5) if all ξ integrations are carried out. Actually, in obtaining (15), the integrations over all ξ_j but ξ'' must have been done with the u integrations in (14). Therefore, the integration remaining in (13) is the final elimination process of the additional degree of freedom introduced for making use of the modified KS transformation. In other words, the ξ integration in (13) projects the propagator of an oscillator in R^4 into the path integral for the Coulomb problem in R^3. It is important that the Coulomb propagator is by no means equivalent to the propagator of an oscillator. The ξ projection of the oscillator path integral is the Coulomb path integral.

To carry out the ξ integration in (13) explicitly, we employ the polar coordinate representation,[12]

$$u=r^{1/2}\begin{bmatrix}\sin(\theta/2)\cos[(\alpha+\phi)/2]\\ \sin(\theta/2)\sin[(\alpha+\phi)/2]\\ \cos(\theta/2)\cos[(\alpha+\phi)/2]\\ \cos(\theta/2)\sin[(\alpha+\phi)/2]\end{bmatrix}, \tag{16}$$

where α is an additional angular variable ($0\leq\alpha<4\pi$). Certainly, $u^2=u\cdot u=r$, and the constraint, which we have removed, implies $\alpha=0$. It is also straightforward to show that $\partial\xi/\partial\alpha=r$ and

$$u'\cdot u''=(r'r'')^{1/2}[\sin\tfrac{1}{2}\theta'\sin\tfrac{1}{2}\theta''\cos\tfrac{1}{2}(\alpha''-\alpha'+\phi''-\phi')+\cos\tfrac{1}{2}\theta'\cos\tfrac{1}{2}\theta''\cos\tfrac{1}{2}(\alpha'-\alpha''+\phi''-\phi')]. \tag{17}$$

Noticing that $-2\pi<\Delta\alpha<2\pi$ while $-\infty<\xi<\infty$, and utilizing the above results together with the formulas[13]

$$\exp(z\cos\varphi)=\sum_{m=-\infty}^{\infty}e^{im\varphi}I_m(z), \tag{18}$$

$$I_0((z^2+z'^2+2zz'\cos\varphi)^{1/2})=\sum_{m=-\infty}^{\infty}e^{im\varphi}I_m(z)I_m(z'), \tag{19}$$

we integrate (13) to obtain

$$P_E(\vec{x}'',\vec{x}';\sigma)=2^{-3}(2\pi)F^4(\sigma)\exp[-\pi F^2(\sigma)(r'+r'')\cos\omega\sigma]I_0(2\pi F^2(r'r'')^{1/2}\cos(\tfrac{1}{2}\gamma)), \tag{20}$$

where $\cos\gamma=\cos\theta'\cos\theta''+\sin\theta'\sin\theta''\cos(\phi''-\phi')$. Finally, substituting (20) into (4) and setting $\omega=i\hbar k/2m=i(E/2m)^{1/2}$ yields the Green's function for the Coulomb problem,

$$G(r'',\theta'',\phi'',r',\theta',\phi';E)=(4\pi)^{-1}k^2\int_0^\infty\exp(ie^2\sigma/\hbar)\,\mathrm{csch}^2(\hbar k\sigma/2m)\exp[ik(r'+r'')\coth(\hbar k\sigma/2m)]$$
$$\times I_0(-2ik(r'r'')^{1/2}\cos(\tfrac{1}{2}\gamma)\,\mathrm{csch}(\hbar k\sigma/2m))\,d\sigma \tag{21}$$

which is equivalent to various known integral forms.[13,14]

In an earlier paper,[15] it has been shown that the partial-wave expansion of the propagator is often advantageous. Here we find the partial-wave decomposition of the Green's function particularly useful. Writing (21) as

$$G(r''\theta''\phi'',r'\theta'\phi';E)=\sum_{l=0}^{\infty}(2l+1)G_l(r'',r';E)P_l(\cos\gamma), \tag{22}$$

and using the beautiful formula[16]

$$\sum_{l=0}^{\infty}(2l+1)J_{2l+1}(z)P_l(\cos\gamma)=zJ_0(z\cos\tfrac{1}{2}\gamma), \tag{23}$$

we obtain

$$G_l(r'',r';E)=(8\pi)^{-1}(r'r'')^{-1/2}k\int_0^\infty \exp\left(\frac{ie^2\sigma}{\hbar}\right)\operatorname{csch}\left(\frac{\hbar k\sigma}{2m}\right)\times\exp\left[ik(r'+r'')\coth\left(\frac{\hbar k\sigma}{2m}\right)\right]J_{2l+1}\left(2k(r'r'')^{1/2}\operatorname{csch}\left[\frac{\hbar k\sigma}{2m}\right]\right)d\sigma. \tag{24}$$

Fortunately, the formula

$$\int_0^\infty e^{-2pq}\operatorname{csch}q\exp[\tfrac{1}{2}(x-y)\coth q]J_{2\nu}((xy)^{1/2}\operatorname{csch}q)\,dq=\left(\frac{\Gamma(p+\nu+\frac{1}{2})}{(xy)^{1/2}\Gamma(2\nu+1)}\right)M_{p,\nu}(x)W_{-p,\nu}(y) \tag{25}$$

reduces the radial Green's function (24) into a closed form,[16]

$$G_l(r'',r';E)=\Gamma(p+l+1)[8\pi\hbar kr'r''(2l+1)!]^{-1}M_{p,l+1/2}(2ikr')W_{-p,l+1/2}(-2ikr''), \tag{26}$$

where $p=ime^2\hbar^2k=i(me^4/2\hbar^2E)^{1/2}$. It is a simple matter to symmetrize (26). By making an analytical continuation in E space, we can find both the discrete and continuous eigenfunctions. The discrete energy spectrum arises from the poles of the Γ function in (26); that is, $p+l+1=-n_r$ ($n_r=0,1,2,\ldots$) results in $E_n=-me^4/2\hbar^2n^2$ where $n=n_r+l+1$. A more detailed discussion will be given elsewhere.

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$$\exp(iz'\cos\varphi)=\sum\exp(im\varphi)i^mJ_m(z'),$$

yields (18) if $z'=-iz$, whereas replacing z by iz and z' by iz' reduces (19) to Neumann's addition formula for the ordinary Bessel functions.

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