Semiclassical Approximation for the Nonrelativistic Coulomb Propagator

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An approximation to the Coulomb propagator, correct to first order in $\hbar$, is derived. This function has the structure $K=F(\lambda,\mu,\nu)\exp[iS(\lambda,\mu,\nu)]$, in terms of auxiliary variables λ,μ,ν introduced in the solution of the corresponding Hamilton-Jacobi equation.

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A long-missing element in Feynman's path-integral formulation of quantum mechanics[1] has been the propagator for the Coulomb problem, $K(\vec{r}_1,\vec{r}_2,t)$. Duru and Kleinert[2] and other workers[3] have carried out the path integration for the hydrogenic problem but no explicit form for the propagator has thereby resulted. In this note I will derive an approximate form for the Coulomb propagator by working with the time-dependent Schrödinger equation rather than the path integral. I note that a number of integral representations related to K have previously been given,[4] as well as a numerical solution for the corresponding statistical density matrix.[5] In earlier work, I studied the asymptotic behavior of the Coulomb propagator.[6] I have, in addition, recently derived related propagators in the domain of Coulomb Sturmian eigenstates.[7]

Hostler and Pratt[8] first discovered a closed form for the time-independent Coulomb Green's function $G(\vec{r}_1,\vec{r}_2,E)$. The retarded (outgoing-wave) solution can be written[9]

$$G^+(\vec{r}_1,\vec{r}_2,E)=G^+(x,y,k)=-\frac{1}{\pi(x-y)}\left(\frac{\partial}{\partial x}-\frac{\partial}{\partial y}\right)g^+(x,y,k),\quad (1)$$

with

$$g^+(x,y,k)=(ik)^{-1}\Gamma(1-i\nu)\times M_{i\nu}^{1/2}(-iky)\,W_{i\nu}^{1/2}(-ikx),\quad (2)$$

in terms of the following variables and parameters:

$$x\equiv r_1+r_2+r_{12},\quad y\equiv r_1+r_2-r_{12},\quad E=\hbar^2k^2/2m,\quad \nu=z/ka_0,\quad \mathrm{Im}k>0.\quad (3)$$

M and W are Whittaker functions as defined by Buchholz.[10] Remarkably, the Coulomb Green's function depends on just the two combinations of variables, x and y, whereas rotational symmetry alone would imply a function of three variables, say r_1, r_2, and r_{12}. This reduction is a consequence of the SO(4) or SO(3,1) dynamical symmetry of the Coulomb problem, connected as well with an additional constant of the motion—the Runge-Lenz vector.[11]

The Coulomb propagator is the solution of the time-dependent Schrödinger equation

$$\left(i\hbar\frac{\partial}{\partial t}+\frac{\hbar^2}{2}\nabla_1^2+\frac{z}{r_1}\right)K(\vec{r}_1,\vec{r}_2,t)=0\quad (4)$$

subject to the initial condition

$$K(\vec{r}_1,\vec{r}_2,0)=\delta(\vec{r}_1-\vec{r}_2).\quad (5)$$

I employ atomic units, $\hbar=e=m=1$, but temporarily retain $\hbar$ for use as an expansion parameter. Since K and G are related by a Fourier transform,[12]

$$G^+=-i\int_0^\infty Ke^{iEt}dt,\quad (6)$$

we can conclude that the propagator likewise depends on $\vec{r}_1$ and $\vec{r}_2$ only through the combinations x and y. I assume therefore that $K=K(x,y,t)$.

In the limit as $z\to 0$, K reduces to the free-particle propagator

$$K^0(x,y,t)=(2\pi it)^{-3/2}e^{i(x-y)^2/8t}=(2\pi it)^{-3/2}e^{ir_{12}^2/2t}.\quad (7)$$

As shown by Feynman[1] and others,[13] for Hamiltonians expressible as quadratic forms in generalized coordinates and momenta, the propagator has the structure

$$K(\vec{r}_1,\vec{r}_2,t)=F(t)\exp[iS(\vec{r}_1,\vec{r}_2,t)/\hbar]\quad (8)$$

in which S is the classical action, the solution of the Hamilton-Jacobi equation. For a single particle,

$$S(\vec{r}_1,\vec{r}_2,t)\equiv\int_{\vec{r}_1,0}^{\vec{r}_2,t}L(\vec{r},\dot{\vec{r}})dt\quad (9)$$

along a classically allowed trajectory. The modulating function F depends on t alone, determined such that K satisfies the appropriate time-dependent Schrödinger equation with the initial condition (5).

For nonharmonic potentials, including the Coulomb problem, the simple structure (8) is no longer exact. I propose to represent the Coulomb propagator in the slightly more general form

$$K(\vec{r}_1, \vec{r}_2, t) = F(\vec{r}_1, \vec{r}_2, t)\exp[iS(\vec{r}_1, \vec{r}_2, t)/\hbar] \quad (10)$$

with the preexponential factor now free to contain dependence on $\vec{r}_1$ and $\vec{r}_2$ as well as t. Substituting (10) into (4) we obtain

$$-[S_t + \tfrac{1}{2}(\nabla_1 S)^2 - z/r_1]F + i\hbar[F_t + \nabla_1 F\cdot\nabla_1 S + \tfrac{1}{2}F\nabla_1^2 S] + \tfrac{1}{2}\hbar^2\nabla_1^2 F = 0. \quad (11)$$

Within the semiclassical approximation,[14] the term in $\hbar^2$ is neglected while S and F are determined from the segments of Eq. (11) to zeroth and first order in $\hbar$, viz.

$$S_t + \tfrac{1}{2}(\nabla_1 S)^2 - z/r_1 = 0, \quad (12)$$

and

$$F_t + \nabla_1 F\cdot\nabla_1 S + \tfrac{1}{2}F\nabla_1^2 S = 0. \quad (13)$$

I solved Eq. (12), the Hamilton-Jacobi equation for the Coulomb problem, some time ago.[15] The result can be expressed as

$$S = \nu[\sinh(\lambda-\mu)\cosh(\lambda+\mu) + 3(\lambda-\mu)] \quad (14)$$

in terms of the auxilliary variables λ, μ, and ν defined such that

$$zx = 4\nu^2\sinh^2\lambda,$$
$$zy = 4\nu^2\sinh^2\mu, \quad (15)$$
$$z^2 t = 2\nu^3[\sinh(\lambda-\mu)\cosh(\lambda+\mu) - (\lambda-\mu)].$$

Consistent with $x \geqslant y \geqslant 0$, we have $\lambda \geqslant \mu \geqslant 0$. As defined λ, μ, and ν are real for positive-energy Coulomb states and pure imaginary for bound states.

The first-order equation (13), expressed in terms of the variables x, y, and t, works out to be

$$\tfrac{1}{2}F_t + 2S_x F_x + S_{xx}F + \frac{1}{x}(S_x+S_y)F + \frac{1}{x-y}(S_x-S_y)F = 0 \quad (16)$$

plus the analog with x and y interchanged. For further progress, we must reexpress Eq. (16) in terms of the variables λ, μ, ν. The requisite elements of the Jacobian matrix are enumerated in Table I. The derivatives of S thus work out to be

$$S_x = (2\nu)^{-1}\coth\lambda, \quad S_y = -(2\nu)^{-1}\coth\mu, \quad (17)$$

$$S_{xx} = \frac{1}{16\nu^3\sinh^3\lambda\cosh\lambda}\times\left[\frac{2\sinh^5\lambda\cosh\mu}{J(\lambda,\mu)} - 1\right], \quad (18)$$

where

$$J(\lambda,\mu) \equiv \cosh\mu\, j(\lambda) - \cosh\lambda\, j(\mu),$$
$$j(\lambda) \equiv \sinh^3\lambda + 3\sinh\lambda - 3\lambda\cosh\lambda. \quad (19)$$

The following identities are readily verified:

$$\cosh\lambda\, j'(\lambda) = \sinh\lambda\, j(\lambda) + 2\sinh^4\lambda \quad (20)$$

and

$$\cosh\lambda\frac{\partial J}{\partial\lambda} = \sinh\lambda\, J(\lambda,\mu) + 2\sinh^4\lambda\cosh\mu. \quad (21)$$

With use of (21), the second derivative (18) simplifies to

$$S_{xx} = \frac{1}{16\nu^3\sinh^2\lambda}\left(\frac{J_\lambda}{J} - \coth\lambda\right). \quad (22)$$

Reduction of Eq. (16) to an ordinary differential

TABLE I. Elements of the Jacobian matrix $\partial(\lambda,\mu,\nu)/\partial(x,y,t)$. Abbreviations are as follows: $S_\lambda = \sinh\lambda$, $C_\lambda = \cosh\lambda$, $S_\mu = \sinh\mu$, $C_\mu = \cosh\mu$; $j(\lambda) = S_\lambda^3 + 3S_\lambda - 3\lambda C_\lambda$; $J(\lambda,\mu) = C_\mu j(\lambda) - C_\lambda j(\mu)$; $T(\lambda,\mu) = (S_\lambda C_\lambda - \lambda) - (S_\mu C_\mu - \mu)$.

	x	y	t
λ	$(3C_\mu T + 2S_\mu^3)/8\nu^2 S_\lambda J$	$-S_\lambda S_\mu/4\nu^2 J$	$-S_\lambda C_\mu/2\nu^3 J$
μ	$S_\lambda S_\mu/4\nu^2 J$	$(3C_\lambda T - 2S_\lambda^3)/8\nu^2 S_\mu J$	$-C_\lambda S_\mu/2\nu^3 J$
ν	$-S_\lambda C_\mu/4\nu J$	$C_\lambda S_\mu/4\nu J$	$C_\lambda C_\mu/2\nu^2 J$

equation follows from a remarkable operator relation:

$$\frac{1}{2}\frac{\partial}{\partial t}+2S_x\frac{\partial}{\partial x}=\frac{1}{8\nu^3\sinh^2\lambda}\frac{\partial}{\partial\lambda}. \qquad (23)$$

With use of (22) and (23), Eq. (16) simplifies to

$$F_\lambda+\left[\frac{1}{2}\frac{J_\lambda}{J}+\frac{1}{2}\frac{\cosh\lambda}{\sinh\lambda}+\frac{\cosh(\lambda-\mu)}{\sinh(\lambda-\mu)}\right]F=0. \qquad (24)$$

The solution is

$$F(\lambda,\mu,\nu)=[\sinh(\lambda-\mu)]^{-1}\times[\sinh\lambda\, J(\lambda,\mu)]^{-1/2}\times(\text{function of }\mu,\nu). \qquad (25)$$

The symmetry between λ and μ, together with the condition that F approach its free-particle analog as $z\to 0$ [cf. Eq. (7)], implies further that

$$F(\lambda,\mu,\nu)=\tfrac{1}{2}(z^2/4\pi i)^{3/2}\nu^{-9/2}\times[\sinh(\lambda-\mu)]^{-1}\times[\sinh\lambda\sinh\mu\, J(\lambda,\mu)]^{-1/2}. \qquad (26)$$

We arrive thereby at the semiclassical approximation to the Coulomb propagator:

$$K(\vec r_1,\vec r_2,t)\approx F(\lambda,\mu,\nu)e^{iS(\lambda,\mu,\nu)} \qquad (27)$$

with $S(\lambda,\mu,\nu)$ given by (14). This approaches the free-particle propagator as $\lambda,\mu\to\infty$, corresponding to any of the limits $z\to 0$, $x,y\to\infty$, or $t\to 0$. The semiclassical propagator correctly reduces to a delta function in accordance with (5).

In applications to be discussed elsewhere, Coulomb propagators can be used to construct many-electron Green's functions for computation of atomic and molecular eigenvalue spectra.[12]

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