Analytic form for the nonrelativistic Coulomb propagator

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An analytic form for the nonrelativistic Coulomb propagator is derived, thus resolving a long-standing problem in Feynman's path-integral formulation of quantum mechanics. Hostler's formula for the Coulomb Green's function is expanded according to the theorem of Mittag-Leffler, then Fourier transformed term by term to give the Coulomb propagator. The result is a discrete summation over the principal quantum number n, involving Whittaker, Laguerre, Hermite, and error functions. As is the case for other nonquadratic potentials, the Coulomb propagator does not have the canonical structure $K=F\exp(iS/\hbar)$. Part of the expansion resembles a form derived by Crandall [J. Phys. A **16**, 3005 (1983)] for the case of reflectionless potentials.

Feynman's path-integral approach[1] is now one of the standard formulations of quantum mechanics, with a remarkable record of success in such applications as quantum electrodynamics, statistical mechanics, and molecular reaction dynamics. Lacking for over 40 years, however, has been a solution within Feynman's formalism of the hydrogen atom or Coulomb problem. In this paper we derive the first known analytic form for the nonrelativistic Coulomb propagator. This result promises to stimulate new applications of propagator techniques to atomic and molecular problems.[2] Earlier work had produced asymptotic[3] and semiclassical[4] approximations to the Coulomb propagator as well as numerical computations of the related density matrix.[5] Several workers, notably Duru and Kleinert,[6] have carried out path integrations for the hydrogen atom, but no explicit forms for the propagator have resulted thereby.

The nonrelativistic Coulomb Green's function, first derived in closed form by Hostler,[7] can be expressed as follows:[8]

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

where

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

the latter function representing a pseudo-one-dimensional Coulomb system. The coordinate variables x and y are defined by

$$x\equiv r_1+r_2+r_{12},\quad y\equiv r_1+r_2-r_{12}\ . \tag{3}$$

The energy is related to the wave number k by

$$E=\hbar^2k^2/2\mu=k^2/2\ ; \tag{4}$$

in a.u., $\hbar=\mu=e=1$. Also,

$$\nu\equiv Z/k\ . \tag{5}$$

M and W are Whittaker functions as defined by Buchholz.[9] We will only need those functions with $\mu/2=1/2$, which we write for brevity as $M_{i\nu}$ and $W_{i\nu}$.

The known Green's function and the sought after propagator have the following spectral representations in terms of the complete set of eigenstates:

$$G^+(\mathbf{r}_1,\mathbf{r}_2,E)=\sum_n\frac{\psi_n(\mathbf{r}_1)\psi_n^*(\mathbf{r}_2)}{E-E_n+i\varepsilon}\ ,$$
$$K(\mathbf{r}_1,\mathbf{r}_2,E)=\sum_n\psi_n(\mathbf{r}_1)\psi_n^*(\mathbf{r}_2)e^{-iE_nt}\ . \tag{6}$$

Thus the Coulomb propagator is the Fourier transform of the Green's function in the form[10]

$$K=\frac{i}{2\pi}\int_{-\infty}^{\infty}(G^+-G^-)e^{-iEt}dE\ . \tag{7}$$

Assuming a structure for K analogous to Eq. (1),

$$K(x,y,t)=-\frac{1}{\pi(x-y)}\left[\frac{\partial}{\partial x}-\frac{\partial}{\partial y}\right]k(x,y,t)\ , \tag{8}$$

we have

$$k=\frac{i}{2\pi}\int_{-\infty}^{\infty}(g^+-g^-)e^{-iEt}dE$$
$$=-\frac{i}{2\pi}\sum_n\oint_{C_n}(g^+-g^-)e^{-iEt}dE$$
$$+\frac{i}{2\pi}\int_0^{\infty}(g^+-g^-)e^{-iEt}dE\ , \tag{9}$$

where each C_n is a small counterclockwise circle enclosing the pole at $E=E_n=-Z^2/2n^2$. The sum above represents the bound-state contribution to the propagator. Setting $E=k^2/2$ and noting that $g^-(k)=g^+(-k)$, we obtain

$$k(x,y,t)=\sum_{n=1}^{\infty}Z_nM_n(Zx/n)M_n(Zy/n)e^{Z^2\beta/2n^2}$$
$$+\frac{i}{2\pi}\int_{-\infty}^{\infty}g^+(x,y,k)e^{-k^2\beta/2}k\,dk\ . \tag{10}$$

It has been noted that $W_n=(-1)^{n+1}n!M_n$ for integer n. For compactness in subsequent formulas we have introduced $\beta\equiv it$. Fourier transforms will thus appear as Laplace transforms and the propagator will have the form of a density matrix (with β standing for $1/k_BT$).

The problem now is to carry out the integration in (18). This becomes possible after we represent $g^+(x,y,k)$ in a Mittag-Leffler or rational fractional expansion.[11] If a function $f(z)$ is meromorphic, i.e., analytic and bounded everywhere in the complex z plane, except for simple poles at $z=z_1,z_2,\ldots,$ with corresponding residues $r_1,r_2,\ldots,$ then $f(z)$ can be represented as a series of rational fractions, viz.,

$$f(z)=f(0)+\sum_n r_n\left[\frac{1}{z-z_n}+\frac{1}{z_n}\right] . \tag{11}$$

Identifying $f(z)$ with $g^+(x,y,k)$ in Eq. (2), we set $z=i\nu$, $z_n=n$ (at the poles of the gamma function), and

$$r_n=(ik)^{-1}\frac{(-1)^n}{(n-1)!}M_n(-iky)W_n(-ikx)$$
$$=-(ik)^{-1}nM_n(-ikx)M_n(-iky) .$$

Note that the variable k is left intact, notwithstanding its relation to ν. We obtain thereby

$$g^+(x,y,k)=g_0^+(x,y,k)+\frac{\nu}{k}\sum_{n=1}^{\infty}(n-i\nu)^{-1}M_n(-ikx)M_n(-iky) , \tag{12}$$

where g_0^+ is the free-particle Green's function

$$g_0^+(x,y,k)=(ik)^{-1}M_0(-iky)W_0(-ikx)$$
$$=-\frac{2}{k}\sin(ky/2)e^{ikx/2} . \tag{13}$$

An equivalent representation of the Coulomb Green's function as a discrete summation over n had been earlier given by Hostler,[12] viz.,

$$g^+(x,y,k)=ik\sum_{n=1}^{\infty}n^{-1}(n-i\nu)^{-1}xye^{ik(x+y)/2}L_{n-1}^{(1)}(-ikx)L_{n-1}^{(1)}(-iky)$$
$$=g_0^+(x,y,k)-k\nu\sum_{n=1}^{\infty}n^{-2}(n-i\nu)^{-1}xye^{ik(x+y)/2}L_{n-1}^{(1)}(-ikx)L_{n-1}^{(1)}(-iky) . \tag{14}$$

This has become known as the Sturmian expansion of the Green's function[13] since it contains hydrogenic functions with arguments independent of quantum number n, in contrast to Coulomb eigenfunctions, which involve n in both index and argument. The above Laguerre polynomials are related to our Whittaker functions as follows:

$$M_n(-ikx)=-\frac{ikx}{n}e^{ikx/2}L_{n-1}^{(1)}(-ikx) . \tag{15}$$

We will make use of the Rodrigues formula for Laguerre polynomials:

$$L_n^{(m)}(\alpha z)=(n!)^{-1}z^{-m}e^{\alpha z}D_z^n z^{n+m}e^{-\alpha z} . \tag{16}$$

Thus, for the Whittaker functions (15), we may write

$$M_n(-ikx)=-\frac{ik}{n!}(D_{x'}^{n-1}x'^n e^{ik(x'-x/2)})_{x'=x} . \tag{17}$$

With (5) and (17) in (12), the Green's function can be expressed as

$$g^+=g_0^+-k\sum_{n=1}^{\infty}(k-iZ_n)^{-1}Z_n(n!)^{-2}[\partial_{x'}^{n-1}\partial_{y'}^{n-1}(x'y')^n e^{ik\xi}]_{x'=x,y'=y} , \tag{18}$$

having introduced the abbreviations $Z_n\equiv Z/n$ and $\xi\equiv x'+y'-x/2-y/2$.

Substituting (18) into the propagator expression (10) and interchanging the order of $\sum_n$ and $\int dk$, we obtain

$$k(x,y,\beta)=\sum_{n=1}^{\infty}Z_nM_n(Z_nx)M_n(Z_ny)e^{\beta Z_n^2/2}+\frac{i}{2\pi}\int_{-\infty}^{\infty}g_0^+(x,y,k)e^{-\beta k^2/2}k\,dk$$
$$-\frac{i}{2\pi}\sum_{n=1}^{\infty}Z_n(n!)^{-2}\left[\partial_{x'}^{n-1}\partial_{y'}^{n-1}(x'y')^n\int_{-\infty}^{\infty}\frac{e^{ik\xi}e^{-\beta k^2/2}}{k-iZ_n}k^2dk\right]_{x'=x,y'=y} . \tag{19}$$

The second part of (19) gives the free-particle propagator

$$k_0(x,y,\beta)=(2\pi\beta)^{-1/2}(e^{-(x-y)^2/8\beta}-e^{-(x+y)^2/8\beta}) . \tag{20}$$

The operation of Eq. (8) on the second term in (20) gives zero, so that only the first term contributes to the three-dimensional propagator K. In fact,

$$K_0(x,y,\beta)=(2\pi\beta)^{-3/2}e^{-(x-y)^2/8\beta} . \tag{21}$$

The following integral can be evaluated:[14]

$$\int_{-\infty}^{\infty}\frac{e^{ik\xi}e^{-\beta k^2/2}}{k-iZ_n}dk=i\pi e^{\beta Z_n^2/2}e^{-Z_n\xi}\text{erfc}\left[\frac{Z_n\beta-\xi}{\sqrt{2\beta}}\right] . \tag{22}$$

To get the extra factor k^2 in Eq. (19), we take $-2\,\partial/\partial\beta$. Thereby

$$k(x,y,\beta)=k_0(x,y,\beta)+\sum_{n=1}^{\infty}Z_nM_n(Z_nx)M_n(Z_ny)e^{\beta Z_n^2/2} -\frac{\partial}{\partial\beta}\sum_{n=1}^{\infty}Z_ne^{\beta Z_n^2/2}(n!)^{-2}\left[\partial_{x'}^{n-1}\partial_{y'}^{n-1}(x'y')^ne^{-Z_n\xi}\text{erfc}\left[\frac{Z_n\beta-\xi}{\sqrt{2\beta}}\right]\right]_{x'=x,y'=y} . \tag{23}$$

The discrete spectrum in (23) can be subsumed into the larger summation after using (17) for the Whittaker functions and the error-function reflection formula: $\text{erfc}(-z)=2-\text{erfc}(z)$. We have now

$$k(x,y,\beta)=k_0(x,y,\beta)+\frac{\partial}{\partial\beta}\sum_{n=1}^{\infty}Z_ne^{\beta Z_n^2/2}(n!)^{-2}\left[\partial_{x'}^{n-1}\partial_{y'}^{n-1}(x'y')^ne^{-Z_n\xi}\text{erfc}\left[\frac{\xi-Z_n\beta}{\sqrt{2\beta}}\right]\right]_{x'=x,y'=y} . \tag{24}$$

Leibniz's rule for differentiation of a product is applied in the form

$$[\partial_{x'}^{n-1}\partial_{y'}^{n-1}x'^ne^{-Z_nx'}y'^ne^{-Z_ny'}f(\xi)]_{x'=x,y'=y}=\sum_{p=0}^{n-1}\sum_{q=0}^{n-1}\binom{n-1}{p}\binom{n-1}{q}(D_x^{n-1-p}x^ne^{-Z_nx})(D_y^{n-1-q}y^ne^{-Z_ny})\partial_\xi^{p+q}f(\xi) . \tag{25}$$

Laguerre functions are introduced via (16). Also

$$\partial_\xi\text{erfc}\left[\frac{\xi-Z_n\beta}{\sqrt{2\beta}}\right]=-\left[\frac{2}{\pi\beta}\right]^{1/2}e^{-(\xi-Z_n\beta)^2/2\beta} \tag{26}$$

and

$$e^{\beta Z_n^2/2}e^{-Z_n\xi}e^{-(\xi-Z_n\beta)^2/2\beta}=e^{-\xi^2/2\beta} . \tag{27}$$

Higher derivatives generate Hermite polynomials:

$$\partial_\xi^me^{-(\xi-Z_n\beta)^2/2\beta}=(-1)^m(\sqrt{2\beta})^{-m}e^{-(\xi-Z_n\beta)^2/2\beta}H_m\left[\frac{\xi-Z_n\beta}{\sqrt{2\beta}}\right] . \tag{28}$$

After substituting $x'=x$ and $y'=y$, the variable ξ can be redefined to

$$\xi\equiv(x-y)/2 . \tag{29}$$

After some lengthy algebra, we arrive at our principal result:

$$k(x,y,\beta)=k_0(x,y,\beta)+\frac{\partial}{\partial\beta}\sum_{n=1}^{\infty}Z_n^{-1}M_n(Z_nx)M_n(Z_ny)e^{\beta Z_n^2/2}\text{erfc}\left[\frac{\xi-Z_n\beta}{\sqrt{2\beta}}\right] +\frac{2Z}{\sqrt{\pi}}\frac{\partial}{\partial\beta}e^{-\xi^2/2\beta}\sum_{n=2}^{\infty}n^{-3}\sum_{\substack{p,q=0\\(p,q\neq0,0)}}^{n-1}(-\sqrt{2\beta})^{-p-q}\frac{x^{p+1}}{p!}\frac{y^{q+1}}{q!} \times L_{n-p-1}^{(p+1)}(Z_nx)L_{n-q-1}^{(q+1)}(Z_ny)H_{p+q-1}\left[\frac{\xi-Z_n\beta}{\sqrt{2\beta}}\right] . \tag{30}$$

The first sum in (30) contains those contributions from the Leibniz sums in which erfc is not differentiated and the Whittaker functions reassemble by virtue of (17). The second sum, which excludes $p=q=0$, is simpler left in terms of Laguerre polynomials.

The three-dimensional Coulomb propagator is obtained by the operation of (8) on (30). We display here just the diagonal element, with $\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}$, or $x=y=2r$:

$$K(\mathbf{r},\mathbf{r},\beta)=(2\pi\beta)^{-3/2}+\frac{1}{\pi}\frac{\partial}{\partial\beta}\sum_{n=1}^{\infty}Z_n(M_n'M_n'-M_nM_n'')e^{\beta Z_n^2/2}\operatorname{erfc}\left[\frac{2r-Z_n\beta}{\sqrt{2\beta}}\right]$$
$$+2Z\pi^{-3/2}\frac{\partial}{\partial\beta}e^{-2r^2/\beta}\sum_{n=2}^{\infty}n^{-3}\sum_{\substack{p,q=0\\(p,q\neq 0,0)}}^{n-1}(-\sqrt{2\beta})^{-p-q}\frac{(2r)^{p+q+2}}{p!q!}$$
$$\times\left[\frac{(p+1)(p-q+1)}{4r^2}L_{n-p-1}^{(p+1)}L_{n-q-1}^{(q+1)}+Z_n^2L_{n-p-2}^{(p+2)}L_{n-q-2}^{(q+2)}-Z_n^2L_{n-p-3}^{(p+3)}L_{n-q-1}^{(q+1)}\right]$$
$$\times H_{p+q-1}\left[\frac{2r-Z_n\beta}{\sqrt{2\beta}}\right]. \quad (31)$$

The omitted arguments of the M and L functions above are all equal to $2Z_nr$. A notion of the convergence of the above series can be obtained from the limit $r\rightarrow 0$, which reduces (31) to

$$K(0,0,\beta)=(2\pi\beta)^{-3/2}+\frac{Z}{2\pi\beta}+(2\beta)^{-1/2}\pi^{-3/2}\sum_{n=1}^{\infty}Z_n^2+\frac{1}{2\pi}\sum_{n=1}^{\infty}Z_n^3e^{\beta Z_n^2/2}\operatorname{erfc}(-Z_n\sqrt{\beta/2}). \quad (32)$$

This can be rearranged to a rather intriguing series involving the Riemann ζ function:

$$\frac{K(0,0,\beta)}{K_0(0,0,\beta)}=4\sqrt{\pi}\sum_{n=0}^{\infty}\frac{\zeta(n)}{\Gamma\left[\frac{n-1}{2}\right]}(\beta Z^2/2)^{n/2}. \quad (33)$$

A combination of bound eigenfunctions and error functions as in Eq. (30) also occurs in the propagators for the delta-function potential[15] and for reflectionless potentials.[16] The latter result, derived by Crandall, shows a remarkable resemblance to the first line of Eq. (30). The analog of the second summation in (30) evidently cancels out for reflectionless potentials.

The representation of the Coulomb propagator derived above does not have the canonical structure in Feynman's path-integral formalism for quadratic forms:[1]

$$K=F\exp(iS/\hbar). \quad (34)$$

This accounts for the failure of earlier attempts to derive the Coulomb propagator from the classical action function.[17] In common with Crandall's result, however, the short-time approximation to the above propagator does indeed connect with a path integral.

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