Canonical partition function for the hydrogen atom in curved space

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The electronic partition function for the hydrogen atom was recently derived by integration over the Coulomb propagator. A much simpler derivation is given here, based on Schrödinger's exact solution for a hydrogenic atom in a Riemannian space of positive curvature. The energy spectrum is entirely discrete, including states which correspond to the ionized atom. The curvature in Riemannian space is shown to be equivalent to a finite volume in Euclidean space.

In a recent publication we evaluated the electronic partition function for the hydrogen atom by integration over the Coulomb propagator [1]. This is a conceptually straightforward way of avoiding the apparent divergence of the partition function which a naive sum over states might imply. In this paper, we present a much simpler derivation of essentially the same result.

Schrödinger in 1940 obtained an exact solution of the wave equation for a hydrogen atom in a Riemannian space of constant positive Gaussian curvature [2]. We must emphasize from the outset that the actual curvature of space-time in our corner of the Universe is far too feeble to have any perceptible effects on atomic structure. We will show that Riemannian curvature can be regarded as a metaphor for representing a finite volume in 3-dimensional Euclidean space.

For a hydrogenlike atom in a space of positive curvature $1/R$, Schrödinger showed that the energy eigenvalues are given by a remarkably simple formula:

$$E_n = -\frac{Z^2}{2n^2} + \frac{(n^2 - 1)}{2R^2} , \quad n = 1, 2, 3 \cdots , \tag{1}$$

with the familiar Coulomb degeneracies

$$g_n = n^2 . \tag{2}$$

We are using atomic units $\hbar = m = |e| = 1$ and assuming infinite nuclear mass. Distances are accordingly expressed in bohrs $(a_0 = \hbar^2/me^2)$ and energies in hartrees $(E_H = e^2/a_0)$. We also define the dimensionless temperature parameter

$$\beta \equiv E_{\mathrm{H}}/kT = 315774/T \tag{3}$$

with T in kelvins. The two terms of eq. (1) have the forms, respectively, of a Coulombic energy plus a free-particle energy. It would be difficult to imagine a formula with any simpler structure.

The hydrogen atom in positively-curved space has a purely discrete energy spectrum, in contrast to Euclidean hydrogen, which also possesses a continuum. The ground state energy is $E_1 = -Z^2/2$, same as for the Euclidean 1s state. For the following value of the principal quantum number:

$$n_0 \approx \sqrt{ZR}, \tag{4}$$

the energy is approximately equal to zero. We will find $n_0 \sim 10^5$. This can be considered the dividing line between negative-energy bound and positive-energy ionized or "free" hydrogenic states. Note that, in contrast to the Euclidean case, the positive-energy states have a *discrete*, albeit extremely dense, eigenvalue spectrum.

We can now write down the electronic partition function, based on E_1 as the energy origin:

$$
\begin{aligned}
q_{\mathrm{elec}} &= \sum_{n=1}^{\infty} n^2\, e^{-\beta(E_n - E_1)} \\
&= 1 + e^{-\beta Z^2/2} \sum_{n=2}^{\infty} n^2\, e^{\beta Z^2/2n^2}\, e^{-\beta(n^2-1)/2R^2} .
\end{aligned}
\tag{5}
$$

Setting $Z = 0$ reduces eq. (5) to a free-electron partition function:

$$q_0 = \sum_{n=1}^{\infty} n^2\, e^{-\beta(n^2-1)/2R^2} \approx \int_0^{\infty} n^2\, e^{-\beta n^2/2R^2}\, dn = \frac{\sqrt{\pi}R^3}{2\beta^{3/2}} . \tag{6}$$

Identifying this with the free-particle partition function

$$q_0 = (2\pi mkT)^{3/2} V/h^3 = (2\pi\beta)^{-3/2} V , \tag{7}$$

we can associate the volume V in Euclidean space with the radius of curvature R in Riemannian space as follows:

$$V = 2\pi^2 R^3 . \tag{8}$$

(The same formula also relates the hypersurface area of a 4-dimensional hypersphere to the radius R). The above correspondence leads us to interpret the curvature as a metaphor for a finite volume in Euclidean space, whereby

$$R = (V/2\pi^2)^{1/3} . \tag{9}$$

Laboratory-size volumes correspond to radii R of the order of 10^{10} bohrs.

We express the hydrogenic partition function in the form

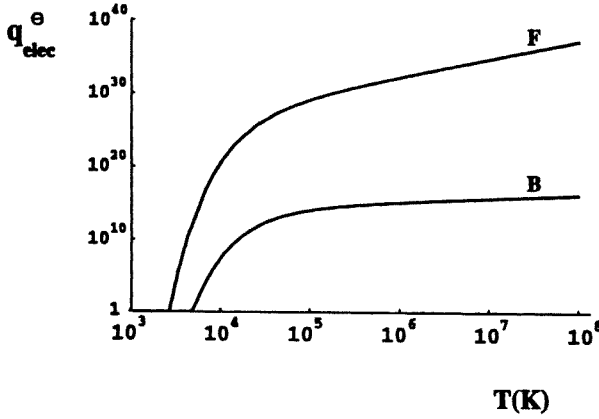$$q_{\mathrm{elec}} = q_{\mathrm{bound}} + q_{\mathrm{free}}\, e^{-\beta Z^2/2} . \tag{10}$$

Fig. 1. Bound (B) and free (F) contributions to the standard-state hydrogen atom partition function.

Thus defined, the bound part is based on the ground state as energy origin, $E_1 \equiv 0$, while the free part uses $E(n_0) \equiv 0$.

We evaluate the indefinite integral

$$f(x) \equiv \int x^2 \exp\left[\frac{\beta Z^2}{2x^2} - \frac{\beta x^2}{2R^2}\right] dx = -\frac{R^2 x}{\beta} \exp\left[\frac{\beta Z^2}{2x^2} - \frac{\beta x^2}{2R^2}\right]$$
$$+ \left\{\frac{\sqrt{\pi}}{2\sqrt{2}\beta^{3/2}} (R^3 - i\beta Z R^2)e^{i\beta Z/R}\mathrm{erf}\left[\sqrt{\frac{\beta}{2}}\left(\frac{x}{R} + i\frac{Z}{x}\right)\right] + \mathrm{C.C.}\right\}. \quad (11)$$

For some special values of x:

$$f(\infty) = \frac{\sqrt{\pi} R^3}{2\beta^{3/2}} = (2\pi\beta)^{-3/2} V = q_0, \tag{12}$$

$$f(n_0) = f(\sqrt{ZR}) \approx \tfrac{1}{3}(ZR)^{3/2}. \tag{13}$$

We note in addition that $f(n_0) \gg f(n^*)$ for $n_0 \gg n^* \gg 1$.

By approximating summations over slowly-varying terms by integrals we obtain

$$q_{\mathrm{bound}} \approx 1 + e^{-\beta Z^2/2}\left[\sum_{n=2}^{n^*} n^2\, e^{\beta Z^2/2n^2}\, e^{\beta n^2/2R^2} + f(n_0) - f(n^*)\right]$$
$$\approx 1 + \tfrac{1}{3}(ZR)^{3/2}\, e^{-\beta Z^2/2} \tag{14}$$

since the parts involving n^* are negligible compared to either 1 or $f(n_0)$ at all temperatures. Also

$$q_{\mathrm{free}} \approx f(\infty) - f(n_0) \approx q_0 \tag{15}$$

since $f(n_0)$ is negligible compared to q_0.

The two contributions to the electronic partition function for hydrogen are plotted in fig. 1. These are referred to the thermodynamic standard state, with volume given by

$$V^\theta = N_A kT/p^\theta = 5.5375 \times 10^{26} T \text{ bohr}^3 \tag{16}$$

with $p^\theta = 1$ bar. The curves labelled B and F represent, respectively, q^θ_{bound} and $q^\theta_{free} e^{-\beta/2}$. Visually, these curves are indistinguishable from their analogs obtained via the Coulomb propagator in ref. [1].

References

[1] S.M. Blinder, J. Math. Phys. 36 (1995) 1208. This paper contains references to earlier work on the hydrogen partition function.
[2] E. Schrödinger, Proc. Irish Acad. A46 (1940) 9;
    see also: N. Bessis and G. Bessis, J. Phys. A. Math. Gen. 12 (1979) 1991.