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Semiclassical position entropy for hydrogen-like atoms

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Abstract

The classical and semiclassical position entropies for the three-dimensional Coulomb problem are obtained explicitly for all values of angular momentum, without recourse to asymptotic expansions. The analytic results relate the classical period of the motion, total energy, position entropy and dependence upon the principal quantum number n . It is demonstrated that the position entropy varies with energy E as $\ln|E|^{-1}$.

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1. Introduction

Information theoretic concepts are playing more and more a role in quantum mechanics and quantum computing. Information concepts have been employed in both fundamental discussions and in practical applications including synthesis and analysis of electron densities in position and momentum space [1]. Indeed, the sum of quantum position and momentum entropies has been advocated as a measure of wavefunction quality [1].

Quantum entropy provides a quantitative description about the uncertainty or lack of knowledge of an observable. For instance, the entropy is one measure of the delocalization of a wavepacket. The Shannon entropy provides an unambiguous measure which is complementary to the information content of a system. With the recent research into quantum computing [2] there has been added attention on the fundamental physical limits of computation [3, 4] and here also the quantum entropy plays a role.

The entropy S is the information storage capacity of matter. For information I measured in bits, aside from the Boltzmann constant k_B , there is simply a $\ln 2$ conversion factor, $I = S/k_B \ln 2$ [3, 5]. Both Shannon information and Boltzmann entropy are grounded on taking the logarithm of the total number of states accessible to a physical system.

In this paper, we establish the semiclassical position entropy for the Coulomb problem, for all values of the angular momentum ℓ . This is an important instance since it applies to hydrogen-like atoms. The resulting semiclassical entropy relations have high utility. This is because otherwise numerical computation may be required, or when closed form results for quantum systems are available, the multiple sum and product expressions do not readily yield physical information. In the latter case [6], asymptotics for (orthogonal) associated Laguerre

polynomials give partial information. The current investigation carries over to other classes of potentials, giving insight into the effect on information content of other physical interactions. As an example of this, we also describe the position entropy appropriate for the s-states of the Hulthén potential. By using this potential energy function, we can model the effect of charge screening.

The entropic uncertainty relation gives a lower bound to the sum of position $S^{(x)}$ and momentum $S^{(p)}$ entropies [8],

$$S_Q^{(x)} + S_Q^{(p)} \geq D(1 + \ln \pi) \quad (1)$$

for a D -dimensional system. This inequality stresses the reciprocity of position and momentum spaces. For if the wavefunction is concentrated in coordinate space, it will necessarily be more diffuse in momentum space, and vice versa. Not surprisingly, the bound in (1) is attained by Gaussian wavefunctions [8]. Relation (1) extends to other pairs of noncommuting observables A and B , $S^{(A)} + S^{(B)} \geq s_{AB}$, where s_{AB} is a positive constant. From equation (1) follows the Heisenberg uncertainty relation, showing that this inequality is stronger. Recently, we were able to explicitly obtain the entropy sum in equation (1) in the classical limit for systems with power law potentials [7] in one dimension. For potentials with power q , we found that the position entropy varies with energy E as $\ln E^{1/q}$ and the momentum entropy as $\ln E^{1/2}$.

The entropy sum appears in many other lower and upper bounds. Another lower bound including standard deviations Δx of position and Δp_x of momentum is [9]

$$S_Q^{(x)} + S_Q^{(p)} \geq 1 - \ln 2 - \ln \left(\frac{\Delta x \Delta p_x}{h} \right). \quad (2)$$

An upper bound to the entropy sum can be prescribed in terms of the second moments in position and momentum space [1].

In the case of the Coulomb potential we recall that the classical period depends upon total energy E as $T(E) \sim |E|^{-3/2}$. We find that the classical position entropy varies as $S_C^{(x)} \sim \ln E^{-1}$. By invoking an asymptotic relation [10], we then know that the quantum entropy of position behaves as $S_Q^{(x)} \sim \ln E_n^{-1}$ for the n th energy eigenstate. Since we also know the values E_n , we determine explicitly the dependence of the semiclassical position entropy upon principle quantum number n . Below we make all these relations quantitative. We emphasize that we explicitly account for nonzero values of the angular momentum.

2. Classical and semiclassical entropy of position for the Coulomb problem

In this section we assume a potential function $V(r) = -k/r$, where $k = Ze^2$ and Z is the atomic number. For angular momentum quantum number $\ell = 0$, the two classical turning points are at the origin and $r_c = -k/E$, while for $\ell > 0$, we denote the two turning points as r_{\pm} .

We first recall the classical period of motion $T(E)$ for this potential, as it is needed in detail for the position density and its derivation is of physical interest. The period is given by

$$T(E) = \sqrt{\frac{2m}{E}} \int_{r_-}^{r_+} \frac{dr}{[1 - V_{\text{eff}}(r)/E]^{1/2}} \quad (3)$$

where m is the reduced mass and the effective potential $V_{\text{eff}}(r) = V(r) + \ell(\ell + 1)\hbar^2/2mr^2$. By introducing $c_{\ell} \equiv \ell(\ell + 1)\hbar^2/2mE$ and

$$r_{\pm} = \frac{1}{2E} (-k \pm \sqrt{k^2 + 4E^2 c_{\ell}}) \quad (4)$$

the period can be written as

$$T(E) = \sqrt{\frac{2m}{E}} \int_{r_-}^{r_+} \frac{r \, dr}{\sqrt{(r-r_-)(r-r_+)}}. \quad (5)$$

It is convenient to scale the integration by way of the geometric mean of the turning points $\sqrt{r_- r_+} = \sqrt{-c_\ell}$, resulting in

$$T(E) = \sqrt{\frac{2m}{E}} \sqrt{r_- r_+} \int_{1/x}^x \frac{r \, dr}{\sqrt{(r-1/x)(r-x)}} \quad (6)$$

where $x \equiv \sqrt{r_+/r_-}$. The integral can be evaluated in several ways, giving

$$T(E) = \sqrt{\frac{m}{2}} \frac{\pi k}{|E|^{3/2}}. \quad (7)$$

In the quantum case, the well-known energy levels are given by $E_n = -mk^2/2\hbar^2 n^2$, $n = 1, 2, \dots$. These relations illustrate the semiclassical connection $T(E) = h\partial n/\partial E$.

Equation (7) for a hydrogen-like system is the analogue of Kepler's law. Indeed, this connection motivates one of the ways of performing the integral in equation (6). If we take a clue from the classical equation of the orbit, we may substitute

$$r(\phi) = c/(1 - \epsilon \cos \phi). \quad (8)$$

Then it turns out that $\epsilon^2 = 1 - c^2$, $1/\epsilon = (1 + x^2)/(1 - x^2)$, and $1/c = k/2|E|\sqrt{-c_\ell}$, showing how ϵ and c are related to the angular momentum and energy. Although contour integration may be used to evaluate equation (6), the trigonometric substitution (8) is a physically transparent method.

The classical probability distribution in space (spatial density) is given by [11]

$$P_C(r) = \frac{1}{T(E)} \frac{\sqrt{2m}}{\sqrt{E - V_{\text{eff}}(r)}} \quad r_- \leq r \leq r_+ \quad (9)$$

so that for the Coulomb problem,

$$P_C(r) = \frac{\sqrt{2m}}{T(E)\sqrt{E}} \frac{r}{\sqrt{(r-r_-)(r-r_+)}} \quad r_- \leq r \leq r_+. \quad (10)$$

The classical position entropy is given by

$$S_C^{(r)} = - \int_{r_-}^{r_+} P_C(r) \ln P_C(r) \, dr. \quad (11)$$

By substituting equation (10) into (11) and noting the normalization of the spatial density, we immediately have

$$S_C^{(r)} = \ln \left[\frac{T(E)\sqrt{E}}{\sqrt{2m}} \right] - \frac{\sqrt{2m}}{T(E)\sqrt{E}} \int_{r_-}^{r_+} \frac{r}{\sqrt{(r-r_-)(r-r_+)}} \times \left\{ \ln r - \frac{1}{2} \ln[(r-r_-)(r-r_+)] \right\} \, dr. \quad (12)$$

It is useful to manipulate the integrals on the right side of equation (12) by using integration by parts, making use of the relation

$$\frac{r}{\sqrt{(r-r_-)(r-r_+)}} = \frac{1}{2} \frac{(r_- + r_+)}{\sqrt{(r-r_-)(r-r_+)}} + \frac{d}{dr} \sqrt{(r-r_-)(r-r_+)}. \quad (13)$$

The sum of two of the resulting integrals is given by

$$\int_{r_-}^{r_+} \frac{[\ln(r - r_-) + \ln(r - r_+)]}{\sqrt{(r - r_-)(r - r_+)}} dr = \pi^2. \quad (14)$$

In finding equation (14), we have used the formula

$$\int_a^b (x - a)^{\mu-1} \ln(x - a)(b - x)^{\nu-1} dx = (b - a)^{\mu+\nu-1} B(\mu, \nu) [\ln(b - a) + \psi(\mu) - \psi(\mu + \nu)] \quad b > a \quad \text{Re } \mu > 0 \quad \text{Re } \nu > 0 \quad (15)$$

which is easily derived from a known result in [12], where $\psi \equiv \Gamma'/\Gamma$ is the digamma function, such that $\psi(1/2) = -\gamma - 2 \ln 2$, $\psi(1) = -\gamma$, $\gamma \simeq 0.577 215$ is the Euler constant, and B is the Beta function.

We also have the vanishing combination of integrals

$$\int_{r_-}^{r_+} [\ln(r - r_-) + \ln(r - r_+)] \frac{d}{dr} \sqrt{(r - r_-)(r - r_+)} dr = 0 \quad (16)$$

and the integral

$$\int_{r_-}^{r_+} \ln r \frac{d}{dr} \sqrt{(r - r_-)(r - r_+)} dr = i\pi \left[-\frac{1}{2}(r_- + r_+) + \sqrt{r_+ r_-} \right]. \quad (17)$$

The latter integral has been obtained subject to the convention $\ln(-1) = -i\pi$. By using equations (13)–(17), we have thus far found for the integral in equation (12)

$$\begin{aligned} & \int_{r_-}^{r_+} \frac{r}{\sqrt{(r - r_-)(r - r_+)}} \left\{ \ln r - \frac{1}{2} \ln[(r - r_-)(r - r_+)] \right\} dr \\ &= \frac{(r_- + r_+)}{2} \int_{r_-}^{r_+} \frac{\ln r}{\sqrt{(r - r_-)(r - r_+)}} dr \\ &+ \frac{\pi^2}{4} (r_- + r_+) + i\pi \left[-\frac{1}{2}(r_- + r_+) + \sqrt{r_+ r_-} \right]. \end{aligned} \quad (18)$$

The first term on the right of equation (12) indicates the dependence $S_C^{(r)}(E) \sim \ln|E|^{-1}$ + constant. In addition, we note that the ratio $(r_- + r_+)/T(E)\sqrt{E}$ is independent of the energy.

The remaining integral in equation (18) can be evaluated in terms of an infinite series, by the way of binomial expansion:

$$\int_{r_-}^{r_+} \frac{\ln r}{\sqrt{(r - r_-)(r - r_+)}} dr = \frac{1}{\sqrt{-\pi r_+}} \sum_{j=0}^{\infty} \frac{\Gamma(j + 1/2)}{j! r_+^j} \int_{r_-}^{r_+} \frac{r^j \ln r}{\sqrt{r - r_-}} dr \quad (19)$$

and we indicate several means of evaluating the integral on the right side of this equation. This integral may be obtained starting from

$$\int_{r_-}^{r_+} \frac{r^p}{\sqrt{r - r_-}} dr = 2(r_+ - r_-)^{1/2} r_-^p {}_2F_1(1/2, -p; 3/2; 1 - r_+/r_-) \quad (20)$$

which follows simply from the change of variable $y(r) = (r - r_-)/(r_+ - r_-)$ and the use of the integral representation of the hypergeometric function. By operating with $\partial/\partial p$ on both sides of equation (20) we obtain

$$\begin{aligned} & \int_{r_-}^{r_+} \frac{r^p \ln r}{\sqrt{r - r_-}} dr = 2(r_+ - r_-)^{1/2} r_-^p \left[\ln r_- {}_2F_1(1/2, -p; 3/2; 1 - r_+/r_-) \right. \\ & \left. + \frac{\partial}{\partial p} {}_2F_1(1/2, -p; 3/2; 1 - r_+/r_-) \right]. \end{aligned} \quad (21)$$

The partial derivative on the right side of equation (21) can be evaluated by means of a special case of equation (A.4) of the appendix. We note that when p is an integer, the hypergeometric function of equation (20) is terminating, giving a polynomial of degree p . The appendix outlines a different method of evaluating the integral on the right side of equation (18).

By invoking the asymptotic relation $S_Q^{(r)} \sim S_C^{(r)} - 3(1 - \ln 2)$ [10] for the quantum entropy of position, we have also demonstrated the dependence

$$S_Q^{(r)}(E) \sim \ln|E|^{-1} + \text{constant} \quad (22)$$

where the Coulomb energies $E_n \sim -1/n^2$. A great benefit of our approach in obtaining (22) and related results is that we avoid solving for the wavefunction ψ , forming the quantum probability $|\psi|^2$, inserting into the expression for the quantum position entropy

$$S_Q^{(r)} = - \int |\psi(r)|^2 \ln|\psi(r)|^2 d^3r \quad (23)$$

and then performing asymptotic evaluations.

3. Classical and semiclassical entropy of position for s-states of the Hulthén potential

In this section we summarize results corresponding to s-states of the two-parameter Hulthén potential [13, 14]

$$V(r) = -V_0 \frac{e^{-r/a}}{1 - e^{-r/a}} \quad (24)$$

where $V_0 > 0$ and $a > 0$ is a screening length. This interaction provides an example of the modification of the entropy due to the presence of screening for these spherically symmetric states. Physically we expect a more spatially diffuse wavefunction for the Hulthén potential than for the Coulomb potential, leading to a higher corresponding position entropy. We note that the Coulomb limit obtains from equation (24) when $a \rightarrow \infty$ such that $V_0 a = k$.

For the potential given by equation (24), the period of motion, equation (3), can be evaluated after a change of variable, resulting in, for $\ell = 0$,

$$T(E) = \pi \sqrt{\frac{2m}{|E|}} a (1 - \sqrt{x_+}) \quad (25)$$

where $x_+(E) \equiv 1/(1 - V_0/E)$. It can be seen that the $V_0 \rightarrow 0$ limit properly gives the Coulomb result (7). One method of finding the period is to write it in terms of the hypergeometric function ${}_2F_1(1, 1/2; 2; z) = 2(1 - \sqrt{1-z})/z$.

The position entropy (11) can be calculated by using techniques typified in the appendix. The result may be written as

$$S_C^{(r)} = \ln \left[\frac{T(E)\sqrt{|E|}}{\sqrt{2m}} \right] + \frac{a\pi\sqrt{m}}{T(E)\sqrt{2|E|}} \left\{ 2(1 - \sqrt{x_+}) \left[-1 + \frac{1}{2}(i\pi - \ln x_+) \right] \right. \\ \left. \times \frac{(1 - x_+)}{2\sqrt{x_+}} \frac{\partial}{\partial \beta} {}_2F_1(1, \beta; 2; 1 - 1/x_+) \Big|_{\beta=1/2} \right\}. \quad (26)$$

The last term in this equation may be written explicitly by the way of equation (A.4). Once again the asymptotic relation $S_Q^{(r)} \sim S_C^{(r)} - 3(1 - \ln 2)$ connects the classical to the semiclassical position entropy. For small V_0 , the energy dependences of various factors in equation (26) are $T(E)\sqrt{|E|} \sim 1/|E|$, $1 - \sqrt{x_+} \sim 1/|E|$ and $\ln x_+(E) \sim V_0/E$. Furthermore, the derivative term in braces in equation (26) is easily shown to vary as V_0^2/E^2 to lowest order, so that when divided by $T(E)\sqrt{|E|}$ this term contributes according to $1/E$. Therefore, in the Coulomb limit, the relation (22) is recovered for s-states.

4. Summary

Information theoretic concepts are becoming of increasing interest in quantum mechanics and quantum computing. In this paper, we have presented general expressions for the classical and semiclassical entropies of position for the three-dimensional Coulomb problem, for all values of the angular momentum quantum number ℓ . This is an important example in that it describes the simplest bound atomic or ionic system. The results for $\ell > 0$ include the effect of the centrifugal barrier in the potential energy. In the process, we may have obtained new algebraic and logarithmic integrals, including those presented in the appendix. By making use of an asymptotic relation between the classical and quantum position entropies [10] we obtained the quantum entropy of position for energy eigenstates in the semiclassical approximation.

The resulting semiclassical entropy relations have high utility. This is because otherwise numerical computation may be required, or when closed form results for quantum systems are available, the multiple sum and product expressions [6] do not readily yield physical information. The current investigation carries over to other classes of potentials, giving insight into the effect on information content of other physical interactions. We presented an example of this aspect by calculating the position entropy for s-states of the Hulthén potential. This potential contains a screening length a , wherein a certain $a \rightarrow \infty$ limit corresponds to the Coulomb problem. Since a screened system is generally less tightly bound than its unscreened counterpart, quantum mechanically we expect a more spatially spread wavefunction and consequently a higher position entropy than for a pure Coulombic system. Additionally, both the position and momentum entropies corresponding to power-law potentials have recently been examined elsewhere [7].

For the Coulomb potential, we have been able to explicitly relate the corresponding system period, energy and entropy. We found that the classical position entropy varies as $S_C^{(r)} \sim \ln|E|^{-1}$, so that the quantum entropy of position behaves as $S_O^{(r)} \sim \ln|E_n|^{-1}$ for the n th energy eigenstate. Knowing the values E_n , we have determined explicitly the dependence of the semiclassical position entropy upon the principle quantum number n . Obviously the position entropy increases with n .

Appendix

Here we indicate an alternative route for evaluating the integral of equation (18),

$$\int_{1/x}^x \frac{\ln r}{\sqrt{(r-1/x)(r-x)}} dr \quad (\text{A.1})$$

where we have used $x = \sqrt{r_+/r_-}$. We have the closed form result

$$\int_{1/x}^x \frac{r^a}{\sqrt{(r-1/x)(r-x)}} dr = \frac{\sqrt{\pi}\Gamma(a+1)}{\Gamma(a+3/2)} [x^{a+1} {}_2F_1(1/2, 1+a; a+3/2; x^2) - x^{-a-1} {}_2F_1(1/2, 1+a; a+3/2; x^{-2})] \quad (\text{A.2})$$

which easily follows from the integral representation of the Gauss hypergeometric function ${}_2F_1$. The integral (A.1) follows if we differentiate this equation with respect to a and then put a to zero. In addition, a logarithmic integral of original interest in the classical position entropy equation (12) follows by putting $a = 1$ at the end of calculation. In differentiating equation (A.2) with respect to a , there are no difficulties in dealing with factors such as $(d/da)\Gamma(a+w) = \Gamma(a+w)\psi(a+w)$ and $(d/da)x^a = x^a \ln x$, where $\psi = \Gamma'/\Gamma$ is the digamma function [12]. Therefore, we concentrate on how to deal with the ${}_2F_1$ functions.

In developing these results, we may first note the derivative of the Pochhammer symbol $(a)_j = \Gamma(a+j)/\Gamma(a)$,

$$\frac{d}{da}(a)_j = (a)_j[\psi(a+j) - \psi(a)] = (a)_j \sum_{\ell=0}^{j-1} \frac{1}{(a+\ell)} \quad (\text{A.3})$$

where j is an integer. The first term of unity of any hypergeometric function is independent of either the numerator or denominator parameters. Then the derivative of the generalized hypergeometric function with respect to a numerator parameter is given by

$$\frac{\partial}{\partial \alpha_i} {}_pF_q(\alpha_1, \dots, \alpha_p; \beta_1, \dots, \beta_q; z) = \sum_{k=1}^{\infty} \frac{(\alpha_1)_k \cdots (\alpha_p)_k}{(\beta_1)_k \cdots (\beta_q)_k} \frac{z^k}{k!} \sum_{j=0}^{k-1} \frac{1}{(\alpha_i + j)} \quad (\text{A.4})$$

and with respect to a denominator parameter by

$$\frac{\partial}{\partial \beta_i} {}_pF_q(\alpha_1, \dots, \alpha_p; \beta_1, \dots, \beta_q; z) = - \sum_{k=1}^{\infty} \frac{(\alpha_1)_k \cdots (\alpha_p)_k}{(\beta_1)_k \cdots (\beta_q)_k} \frac{z^k}{k!} \sum_{j=0}^{k-1} \frac{1}{(\beta_i + j)}. \quad (\text{A.5})$$

Similarly higher and mixed derivatives may be taken.

As applied to a ${}_2F_1$ function with two arguments linearly depending upon a parameter, we have

$$\frac{\partial}{\partial a} {}_2F_1(a + \gamma_1, b; a + \gamma_2; y) = \sum_{k=1}^{\infty} \frac{(a + \gamma_1)_k (b)_k}{(a + \gamma_2)_k} \frac{y^k}{k!} \sum_{j=0}^{k-1} \left[\frac{1}{(a + \gamma_1 + j)} - \frac{1}{(a + \gamma_2 + j)} \right]. \quad (\text{A.6})$$

This formula completes the analytic specification of the result

$$\begin{aligned} \int_{1/x}^x \frac{r^a \ln r}{\sqrt{(r-1/x)(r-x)}} dr &= \frac{\sqrt{\pi} \Gamma(a+1)}{\Gamma(a+3/2)} \left\{ [\ln x + \psi(a+1) - \psi(a+3/2)] \right. \\ &\quad \times x^{a+1} {}_2F_1(1/2, 1+a; a+3/2; x^2) \\ &\quad + [\ln x - \psi(a+1) + \psi(a+3/2)] x^{-a-1} {}_2F_1(1/2, 1+a; a+3/2; x^{-2}) \\ &\quad + x^{a+1} \frac{\partial}{\partial a} {}_2F_1(1/2, 1+a; a+3/2; x^2) \\ &\quad \left. - x^{-a-1} \frac{\partial}{\partial a} {}_2F_1(1/2, 1+a; a+3/2; x^{-2}) \right\}. \quad (\text{A.7}) \end{aligned}$$

For the $a = 1$ case, we have the difference $\psi(2) - \psi(5/2) = 2 \ln 2 - 5/3$.

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