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Classical partition function of a rigid rotator or polyatomic gases

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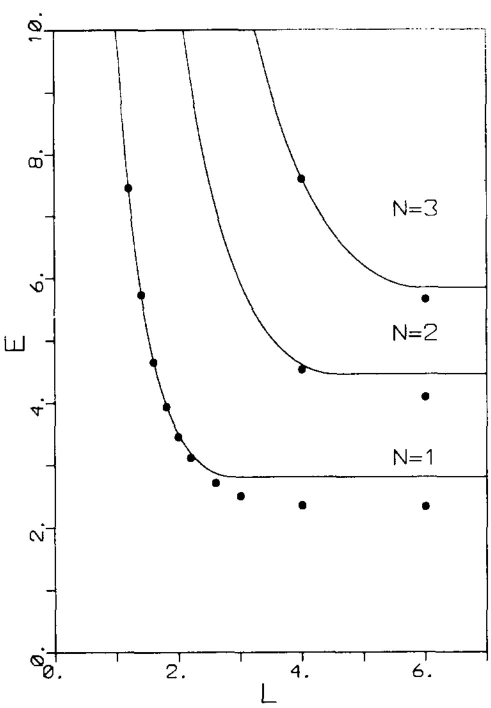

Fig. 1. Plots of the energy of a quantum bouncer as a function of the distance to the upper boundary. The dots indicate the predictions of the Schrödinger equation (taken from Ref. 1). The energy is in units of mgl and the distance is in units of $l = (\hbar^2/2m^2g)^{1/3}$.

those shown in Table I. The largest error, for the transition $n = 2 \rightarrow n = 1$, is less than 6%.

Equation (2) may be rewritten in terms of l to yield a relation between the energy and the height L, i.e.,

$$\epsilon_n^{3/2} - (\epsilon_n - \lambda)^{3/2} = 3\pi n/2, \tag{4}$$

where $\lambda = L/l$.

The energy levels ϵ_n for the first three states as functions of λ are shown in Fig. 1. If $\epsilon < \lambda$ the particle cannot reach the upper boundary and the presence of this boundary is irrelevant. Eigenvalues obtained from the Schrödinger equation[1] are shown as dots in the figure. Again, while the predictions of the Bohr–Sommerfeld–Wilson quantization are too large, the error decreases with increasing quantum number n for all values of L.

As noted by Aguilera-Navarro *et al.*, in the limit that L becomes small, the energy levels are those of a particle in a box. Thus, in the limit $\lambda/\epsilon \ll 1$, Eq. (4) reduces to $\epsilon_n = (n\pi/\lambda)^2$ or the more familiar expression

$$E_n = n^2\pi^2\hbar^2/2mL^2. \tag{5}$$

The two-dimensional motion of a quantum bouncer was also discussed by Gibbs.[2] In this case the boundary at $y = 0$ is rotated to an angle θ with the vertical and another reflecting boundary is placed at an angle θ with the horizontal. (For a charge in a uniform field this corresponds to the motion in an infinite conductor with two perpendicular boundaries and the electric field at an angle θ with one of the boundaries.)

This problem can also be generalized to the enclosed case, but the solutions of the Schrödinger equation for this system were not obtained by Aguilera-Navarro *et al.* The energy levels may also be obtained from the Bohr–Sommerfeld–Wilson quantization as follows.

Introducing a set of coordinates[2] in the rotated system $s = x \sin\theta + y\cos\theta$ and $t = -x\cos\theta + y\sin\theta$, the energy may be written as

$$E = (p_s^2 + p_t^2)/2m + mg(s\cos\theta + t\sin\theta). \tag{6}$$

This equation is separable. For each component of the motion

$$\epsilon_{n_{s(t)}}^{3/2} - (\epsilon_{n_{s(t)}} - \lambda_{s(t)})^{3/2} = 3\pi n_{s(t)}/2, \tag{7}$$

where

$$\epsilon_{n_{s(t)}} = E_{n_{s(t)}}/mgl_{s(t)}, \quad \lambda_{s(t)} = L_{s(t)}/l_{s(t)},$$
$$l_s = (\hbar^2/2m^2g\cos\theta)^{1/3},$$
$$l_t = (\hbar^2/2m^2g\sin\theta)^{1/3} \quad \text{and} \quad L_t/L_s = \tan\theta.$$

The total energy of the system is

$$E_{n_sn_t} = E_{n_s} + E_{n_t}. \tag{8}$$

An energy level diagram as a function of θ for the case $L \rightarrow \infty$ using the eigenvalues obtained from the Schrödinger equation was given by Gibbs.[2] A similar diagram may be constructed using Eqs. (7) and (8).

The "quantum bouncer" or charge in a uniform electric field is an interesting example for discussion in a quantum mechanics course. The Bohr–Sommerfeld–Wilson quantization predictions of the energy levels can provide a useful introduction to the quantum-mechanical calculation and also an opportunity to illustrate the limitations of the "old" quantum theory.

[1]V. C. Aguilera-Navarro, H. Iwamoto, E. Ley-koo, and A. H. Zimerman, Am. J. Phys. **49**, 648 (1981).
[2]R. L. Gibbs, Am. J. Phys. **43**, 25 (1975).

Classical partition function of a rigid rotator or polyatomic gases

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It is a very important example or problem in textbooks on statistical mechanics to calculate the partition function, and therefore the free energy, of a rigid rotator or polyatomic gases. There are two standard approaches to obtain the partition function in classical statistical mechanics. The first one is to use the Eulerian angles θ, φ, ψ as the generalized coordinates and express the Hamiltonian of the rigid rotator in three dimensions as[1]

$$H_1 = \frac{1}{2I_1\sin^2\theta}[(p_\varphi - p_\psi\cos\theta)\cos\psi - p_\theta\sin\theta\sin\psi]^2 + \frac{1}{2I_2\sin^2\theta}[(p_\varphi - p_\psi\cos\theta)\sin\psi - p_\theta\sin\theta\cos\psi]^2 + \frac{1}{2I_3}p_\psi^2, \tag{1}$$

where p_θ, p_φ, and p_ψ are the conjugate generalized momenta of the generalized coordinates θ, φ, ψ, respectively. The rotational partition function can be written as[2-6]

$$Q = \frac{1}{h^3}\int_0^\pi d\theta \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_{-\infty}^{+\infty} dp_\theta \times \int_{-\infty}^{+\infty} dp_\varphi \int_{-\infty}^{+\infty} dp_\psi \exp\frac{-H_1}{kT} \quad (2)$$

and by using Eq. (1) we obtain

$$Q = 8\pi^2(8\pi^3 I_1 I_2 I_3)^{1/2}(kT)^{3/2}/h^3. \quad (3)$$

The second approach[7-9] expresses the energy of a rigid rotator with three degrees of freedom as[10]

$$H_2 = \frac{M_\xi^2}{2I_1} + \frac{M_\eta^2}{2I_2} + \frac{M_\zeta^2}{2I_3}, \quad (4)$$

where ξ, η, ζ are the coordinates in a rotating frame of reference whose axes coincide with the principal axes of the rotator, while M_ξ, M_η, M_ζ are the corresponding angular momenta. The partition function can be written as

$$Q = \frac{1}{h^3}\int d\phi_\xi \, d\phi_\eta \, d\phi_\zeta \, dM_\xi \, dM_\eta \, dM_\zeta \exp\frac{-H_2}{kT}. \quad (5)$$

In the product $d\phi_\xi \, d\phi_\eta \, d\phi_\zeta$ of three infinitesimal angles of rotation, $d\phi_\xi \, d\phi_\eta$ may be regarded as an element of $d\Omega$ of solid angle for directions of the ζ axis. The integration over Ω is independent of that over rotation $d\phi_\zeta$ about the ζ axis and gives 4π. The integration over ϕ_ζ gives a further 2π. Integrating also over M_ξ, M_η, M_ζ from $-\infty$ to $+\infty$, we will have the same result as Eq. (3).

Both of the above approaches give the correct answer, but to some serious readers it is very confusing when they ponder over the differences of these two approaches. According to the general principle of classical statistical mechanics, the "volume element" in the phase space is defined as

$$d\tau = \prod_i dp_i \, dq_i,$$

where q_i and p_i must be the independent generalized coordinate and the corresponding generalized momentum, respectively. Eulerian angles and their conjugate momenta are indeed "true" generalized coordinates and momenta, therefore the first approach is legitimate. In contrast to Eq. (1), the angular momenta in Eq. (4) are not independent generalized momenta. It is well known that the Poisson bracket or commutator of any two angular momenta is given by[1]

$$[M_\xi, M_\eta] = -iM_\zeta. \quad (6)$$

To the author's knowledge, although all the textbooks stress the point of the "generalized" coordinates, "generalized" momenta, and their independency in defining the phase space volume element, there exists no textbook on statistical physics making the above confusion explicit for the readers' attention, not even in a footnote nor an appendix. The answer only implicitly exists in a classic monograph by Whittaker.[11,12] In his book it is pointed out that although Eq. (4) is not expressed in terms of the true generalized coordinates, it can be proven that we can formulate the problem by the so-called quasicoordinates. The $d\phi_r$, which are linear combinations of the differentials dq_i's, will not necessarily be the differential of the quasicoordinates ϕ_r and are called the differentials of the quasicoordinates.[11,12] It is very convenient to use quasicoordinates and the quasimomenta in the equation of motion and the phase space volume element to calculate the partition function for the rigid body system. The feasibility and justification for this are rigorously proven by Whittaker.

If a rigid body is free to rotate about one of its points 0, which is fixed, so that the coordinates of the body can be taken to be the three Eulerian angles (generalized coordinates) θ, φ, ψ, which specify the position of axes $0\xi\eta\zeta$, fixed in the body and moving with it, with reference to axes $0XYZ$ fixed in space. Let an arbitrary displacement ($\delta\theta, \delta\varphi, \delta\psi$) of the body be equivalent to the resultant of small rotation ($\delta\phi_\xi$, $\delta\phi_\eta$, $\delta\phi_\zeta$) around the 0ξ, 0η, 0ζ, respectively, so that $d\phi_\xi$, $d\phi_\eta$, $d\phi_\zeta$ can be taken as the differentials of quasicoordinates, although they are not necessarily the differentials of quasicoordinates ϕ_ξ, ϕ_η, and ϕ_ζ. Let M_ξ, M_η, M_ζ, which are equal to $I_\xi\omega_\xi$, I_η,ω_η, and $I_\zeta\omega_\zeta$, respectively, be the components about the axes $0\xi\eta\zeta$ of the angular momenta of the body at any instant, so that $d\phi_\xi$, $d\phi_\eta$, $d\phi_\zeta$ are the differentials of quasicoordinates corresponding, respectively, to the angular momenta. It was proven rigorously in Ref. 11 that there exist three Euler equations of motion of rigid body expressed in terms of the quasicoordinates.[13] These Euler equations of motion can be derived from the generalized Lagrangian equations of quasicoordinates.[14] From the Euler equations of motion, which are usually expressed in terms of quasicoordinates, the state of the rigid rotator can be specified uniquely by the quasicoordinates and their corresponding angular momenta. The definition of partition function is the sum of state (*Zustandssumme*) and is given by

$$Q = \sum_i e^{-\beta\epsilon i}.$$

According to the above arguments the sum over states can be replaced by an integral over the quasicoordinates and their corresponding angular momenta, which can specify the classical state of this rigid rotator uniquely; therefore using Eq. (5) it is very convenient to obtain the correct answer. But strickly speaking, we can only view Eq. (5) as a convenient form to evaluate the integral because of its simplicity and symmetry form of the H_2. The phase space volume element $d\tau$ should be expressed as Eq. (2) by true generalized coordinates and momenta, but under coordinates transformation from the generalized coordinates to those of quasicoordinates, the transformation Jacobian is just equal to one. The expression in Eq. (2) is more fundamental than that of Eq. (5).

I suggest that textbooks on statistical physics should note this point at least in a footnote or give references for further readings.

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[10] L. D. Landau and E. M. Lifshitz, *Mechanics* (Addison-Wesley, Reading, MA, 1967).
[11] E. T. Whittaker, *A Treatise on the Analytical Dynamics of Particles and Rigid Bodies*, 4th ed. (Cambridge University, Cambridge, 1937), pp. 41–44.
[12] Ta-You Wu, *Classical Dynamics* (Lien-Ching, Taipei, 1977), pp. 149–152.
[13] Almost all textbooks on classical mechanics expressed the Euler equations of motion of rigid body in terms of quasicoordinates instead of true coordinates (Euler angles), but no textbook has pointed this out explicitly.
[14] Reference 11, p. 43.

Exact and inexact solutions to a difference–differential equation

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Dynamical systems with retarded and advanced interactions can have surprising behavior and in dealing, say, with action at a distance theories of electromagnetic forces, one must exercise appropriate caution. In a recent issue of this Journal,[1] standard expansion techniques were applied to the equation

$$M\ddot{x}(t) = -\tfrac{1}{2}k\,\{x[t-|x(t)|/s] + x[t+|x(t)|/s]\}. \quad (1)$$

Before reviewing that expansion we rescale both space and time units and allow the dependent variable to be a vector. The equation becomes

$$\mathbf{y}''(\tau) = -\tfrac{1}{2}[\mathbf{y}(\tau+|\mathbf{y}(\tau)|) + \mathbf{y}(\tau-|\mathbf{y}(\tau)|)], \quad (2)$$

where y (or $\mathbf{y}$) is the new dependent variable, $\tau = t(k/M)^{1/2}$, $y(\tau) = s^{-1}(k/M)^{1/2}x(t)$, prime $= d/d\tau$, and $|\mathbf{y}| = (\mathbf{y}\cdot\mathbf{y})^{1/2}$. We can also take $\mathbf{y}$ to be a scalar, like x. Note that in the scalar case the absolute value symbol is unnecessary since the two terms interchange when x changes sign.

The large s expansion of Ref. 1 becomes a small $|y|$ expansion and we have

$$\mathbf{y}'' = -[\mathbf{y} + (1/2)|\mathbf{y}|^2\mathbf{y}'' + (1/4!)|\mathbf{y}|^4\mathbf{y}^{(4)} + \cdots] \quad (3)$$

(when $\mathbf{y}$ has no argument it is evaluated at τ). Now assume that fourth- and higher-order terms can be dropped. Then it is easy to see that the truncated Eq. (3) can be written

$$\mathbf{y}'' = -\mathbf{y}/(1+\tfrac{1}{2}|\mathbf{y}|^2) = -\nabla V_{\text{eff}}, \quad (4)$$

with

$$V_{\text{eff}}(\mathbf{y}) = \log(1+\tfrac{1}{2}|\mathbf{y}|^2), \quad (5)$$

and the gradient is with respect to $\mathbf{y}$. The following is a solution to Eq. (4):

$$\mathbf{y}(\tau) = R\,(\hat{e}_1\cos\Omega\tau + \hat{e}_2\sin\Omega\tau), \quad (6)$$

provided R and Ω are appropriately related ($\hat{e}_1$ and $\hat{e}_2$ are orthogonal unit vectors and we are now restricted to two or more dimensions). From Eq. (6),

$$\mathbf{y}''(\tau) = -\Omega^2\mathbf{y}(\tau). \quad (7)$$

Therefore comparing Eqs. (4) and (7) we require

$$\Omega^2 = 1/(1+\tfrac{1}{2}R^2), \quad (8)$$

which fixes Ω as a decreasing function of R.

But there is an explicit solution of the exact equation which shows Eq. (2) to be far richer than is suggested by Eq. (4). To see this, substitute Eq. (6) into the *original* equation, Eq. (2). This yields

$$-\Omega^2\mathbf{y} = -\tfrac{1}{2}[\mathbf{y}(\tau-R) + \mathbf{y}(\tau+R)]. \quad (9)$$

Now $\mathbf{y}(\tau\pm R)$ involves $\cos[\Omega(\tau\pm R)]$ and $\sin[\Omega(\tau\pm R)]$. If it should happen that $\Omega R = 2\pi n$, $n = 1,2,\ldots$ then Eq. (9) will be identically satisfied provided $\Omega = 1$. Therefore we have found the following exact solutions to Eq. (2):

$$y_n(t) = 2n\pi(\hat{e}_1\cos\tau + \hat{e}_2\sin\tau). \quad (10)$$

But this is just the tip of the iceberg, for the sines and cosines in Eq. (9) can be expanded and it is seen that several terms cancel. The result (regathering into vectors) is

$$-\Omega^2\mathbf{y} = -\cos\Omega R\,\mathbf{y}. \quad (11)$$

Therefore, whenever

$$\Omega^2 = \cos\Omega R, \quad (12)$$

we have an *exact* solution. Expansion of the cosine in Eq. (12) shows that there is an exact solution with Ω given approximately by Eq. (8), but study of Eq. (12) (e.g., by graphing its left and right sides) shows that for large enough R there can be many frequencies Ω and for any $\Omega \leqslant 1$ there is an infinity of R's that solve Eq. (12) and hence Eq. (2).

The solution given here was suggested by a well-known solution of Schild[2] to the more complicated equations of time symmetric electrodynamics. His idea was that for circular motion the retardation and advance are constant and we have used that trick.

At this point in our discussion the danger of truncation seems to be confined to the possibility of overlooking solutions. However, the truncated solution will show behavior different from that shown by the solution to Eq. (4); in particular it will be highly unstable. To see this we study a somewhat simpler case. Consider the differential–difference equation[3]

$$\frac{d^2f(t)}{dt^2} = -\tfrac{1}{2}[f(t+a) + f(t-a)], \quad (13)$$

