Classical Number and Density of States

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Expressions for the number and density of states of a classical Hamiltonian are used widely in statistical theories of chemical kinetics (1–3). The number of states, represented by $G(E)$, is a census of the available states in the Hamiltonian from an energy of zero to E. The density of states, $N(E)$, is the derivative of $G(E)$ with respect to energy evaluated at E. The classical expressions for $G(E)$ and $N(E)$ can be derived by treating the quantum numbers for the Hamiltonian as continuous variables. Though this is a straightforward procedure, the physical meaning of the classical number and density of states is obscured and correspondences which exist between classical and quantum mechanics are not readily apparent. In this article, classical expressions are formulated for the number and density of states of harmonic oscillators and rigid rotors by using a semiclassical principle and volumes of n-dimensional hypersurfaces. It is anticipated that this presentation, which is direct and easily understood, will retain some of the analogies between classical and quantum mechanics and provide some physical insight into the significance of the classical number and density of states.

The significance of the number and density of states is readily apparent if one considers the classical parition function Q. Since the number of states in the interval $E \to E + dE$ is $dG(E) = N(E)dE$, the classical partition function is

$$Q = \int_0^\infty N(E) \exp(-E/kT)\, dE \tag{1}$$

From Q and its derivative dQ/dT, all the macroscopic thermodynamic properties such as the Gibbs free energy, entropy, and internal energy can be determined (4). Thus, the density of states is the microscopic element in the macroscopic thermodynamic properties.

A theorem in classical statistical mechanics (5) says that the number of states for one degree of freedom with momenta p and coordinate q is

$$dpdq/h \tag{2}$$

where $dpdq$ is the phase space volume associated with p and q, and h is Planck's constant. Thus, for one degree of freedom the volume of phase space associated with a single state is h. The number of states $G(E)$ is then the total phase space volume V divided by h, i.e.,

$$G(E) = V_1/h \tag{3}$$

where the subscript 1 is attached to V to indicate we are only considering one degree of freedom.

Equation (3) is readily understood by applying it to a harmonic oscillator for which the classical Hamiltonian is

$$H(p,q) = p^2/2m + fq^2/2 = p^2/2m + 2\pi^2 m\nu^2 q^2 \tag{4}$$

where ν is the frequency for the oscillator. The phase space volume is that enclosed by the energy E and is formally given by

$$V_1 = \iint_{H(p,q)=0}^{H(p,q)=E} dpdq \tag{5}$$

Though eqn. (5) looks rather intimidating, the phase space volume is simply the area of an ellipse, since the Hamiltonian for the harmonic oscillator is the equation for an ellipse. The area of an ellipse is πab where a and b are the semiaxes. For
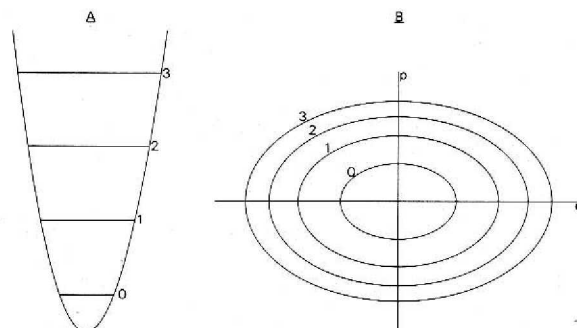

Figure 1. (a) The n = 0, 1, 2, and 3 energy levels for a harmonic oscillator. (b) Phase space volumes for the n = 0, 1, 2, and 3 harmonic oscillator energy levels.

the harmonic oscillator Hamiltonian the semiaxes equal $(2mE)^{1/2}$ and $(E/2\pi^2 m\nu^2)^{1/2}$. Thus, the phase space volume for the harmonic oscillator is

$$V_1 = E/\nu \tag{6}$$

and the classical number of states is then

$$G(E) = E/h\nu \tag{7}$$

It is meaningful to compare the classical expression for the harmonic oscillator number of states with the quantal one. The quantal energy levels are given by $E = (n + 1/2)h\nu$ and are illustrated in Figure 1(a). In Figure 1(b), the phase space volumes for the quantum levels $n = 0, 1, 2,$ and 3 are depicted. The area inside the inner ellipse is $h/2$ and the areas between the remaining ellipses are each h. The reader can verify this relationship between the areas by measuring the length at the semiaxes in Figure 1(b). For a specific quantum level n, the classical number of states from eqn. (7) is $n + 1/2$. The quantal number of states is $n + 1$, and at sufficiently large n the difference between the classical and quantal $G(E)$ is negligible.

The relation between the classical and quantal number of states for a harmonic oscillator can be further understood by considering the Einstein-Brillouin-Keller semiclassical quantization rule (6). This rule states that, for any physical system in which the coordinates are periodic functions of time, there exists for each coordinate the quantum condition

$$\oint p(q)dq = (n + \alpha/4)h \tag{8}$$

where the cyclic integral $\oint$ means the integration is taken over one period of the coordinate q. The integer α is called the Maslov index and is equal to 2 for the harmonic oscillator. In the Sommerfeld-Wilson quantization rule of the "old" quantum theory, α was assumed to equal zero for all systems (7).

The cyclic integral in eqn. (8) is an equivalent way of finding the phase space volume in eqn. (5), and one can write $V_1 = (n + 1/2)h$. Since $(n + 1/2)h = E/\nu$ for a harmonic oscillator, eqn. (8) is in essence the same as eqn. (6). Therefore, the fundamental basis for eqns. (2) and (8) is the same.

With very little difficulty the above discussion can be extended to Hamiltonians with more than one degree of freedom. We will first consider a collection of harmonic oscillators and then rigid rotors. For s degrees of freedom the classical number of states is an extension of eqn. (2) (5);

$$G(E) = V_s/h^s \tag{9}$$

where V_s takes the form

$$V_s = \iint_{H=0}^{H=E} dp_1 \ldots dp_s dq_1 \ldots dq_s \tag{10}$$

The Hamiltonian for s harmonic oscillators is

$$H(p_1 \ldots p_s q_1 \ldots q_s) = \sum_{i=1}^{s} (p_i^2/2m_i + 2\pi^2 m_i \nu_i^2 q_i^2) \tag{11}$$

Evaluation of the phase space volume for s harmonic oscillators is straightforward if one recognizes that eqn. (11) is the equation for a $2s$-dimensional ellipsoid with semiaxes along p_i and q_i. For a specified energy E eqn. (11) can be written in the more general form

$$E = \sum_{i=1}^{s} (p_i^2/a_i^2 + q_i^2/b_i^2) \tag{12}$$

where $a_i = (2m_i)^{1/2}$ and $b_i = (1/2\pi^2 m_i \nu_i^2)^{1/2}$.
If we define $p_i' = p_i/a_i$ and $q_i' = q_i/b_i$, eqn. (12) is transformed to the equation of a $2s$-dimensional hypersphere (ball)

$$E = \sum_{i=1}^{s} [(p_i')^2 + (q_i')^2] \tag{13}$$

which has a well known volume of (8)

$$V^{\text{hypersphere}} = \pi^s E^s/s! \tag{14}$$

The volume of the ellipsoid is easily found from eqn. (14) by recognizing that the volume elements $dp_1 \ldots dp_s dq_1 \ldots dq_s$ and $dp_1' \ldots dp_s' dq_1' \ldots dq_s'$ are related via

$$dp_1 \ldots dp_s dq_1 \ldots dq_s = \begin{vmatrix} \dfrac{\partial p_1}{\partial p_1'} & \cdots & \dfrac{\partial p_1}{\partial q_s'} \\ \vdots & & \vdots \\ \dfrac{\partial q_s}{\partial p_1'} & \cdots & \dfrac{\partial q_s}{\partial q_s'} \end{vmatrix} dp_1' \ldots dp_s' dq_1' \ldots dq_s' \tag{15}$$

The determinant in eqn. (15) is the Jacobian for the transformation and all of its elements are zero except the diagonal ones. The value of the determinant is the constant term

$$\prod_{i=1}^{s} a_i b_i$$

and the volume element

$$dp_1 \ldots dp_s dq_1 \ldots dq_s = \prod_{i=1}^{s} a_i b_i \, dp_1' \ldots dp_s' dq_1' \ldots dq_s'$$

Thus, the volume of the ellipsoid is equal to the volume of the hypersphere times the multiplicative factor

$$\prod_{i=1}^{s} a_i b_i$$

i.e.,

$$V^{\text{ellipsoid}} = \pi^s E^s \prod_{i=1}^{s} a_i b_i/s! \tag{16}$$

The phase space volume for the s harmonic oscillators is found by inserting the values for a_i and b_i into eqn. (16). The resulting expression for the number of states is

$$G(E) = E^s/s! \prod_{i=1}^{s} h\nu_i \tag{17}$$

and one should note the similarity with eqn. (7). The density of states $\partial G(E)/\partial E$ is

$$N(E) = E^{s-1}/(s-1)! \prod_{i=1}^{s} h\nu_i \tag{18}$$
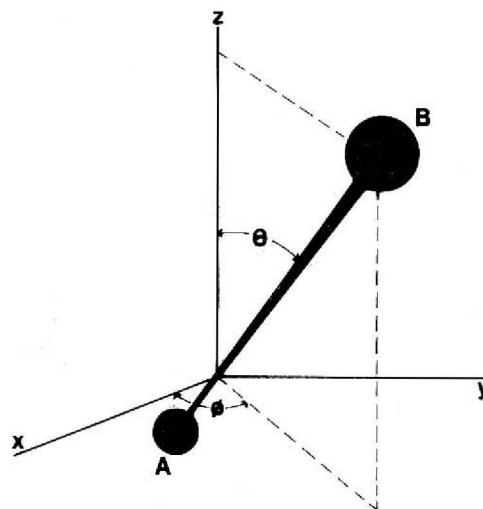

Figure 2. Illustration of a rigid rotor with two degrees of freedom.

The quantal number of states for s harmonic oscillators is found exactly by a direct count of the available energy levels, and important differences are found between the classical and quantal number of states at low energies (1). However, as the total energy is increased, the classical and quantal number of states become the same. This can be seen by considering the semiempirical Whitten-Rabinovitch expression for the quantal $G(E)$

$$G_{\text{wr}}(E) = (E_v + aE_{\text{zp}})^s/s! \prod_{i=1}^{s} h\nu_i \tag{19}$$

which is an excellent approximation (1). The quantal vibrational energy E_v plus the zero-point energy E_{zp} equals the classical energy E; i.e., $E = E_v + E_{\text{zp}}$. The factor a is a function of E_v, ranging from 0 at $E_v = 0$ to 1 at large values of E_v. Thus, at high vibrational energies $a = 1$ and the classical and quantal expressions for $G(E)$ are identical.

The final two illustrations of using volumes in phase space to find the classical expression for the number of states are for rigid rotors with one and two degrees of freedom. A rigid rotor with one degree of freedom is an important model for internal rotations in molecules, while a rigid rotor with two degrees of freedom is used to describe the external rotational motion of diatomic molecules. A depiction of a rigid rotor with two degrees of freedom, ϕ and θ, is given in Figure 2. For a rigid rotor with one degree of freedom there is only motion in the ϕ plane.

The Hamiltonian for a rigid rotor with one degree of freedom is

$$H(p_\phi,\phi) = p_\phi^2/2I \tag{20}$$

where I is the moment of inertia, and in the absence of any symmetry, ϕ varies from 0 to 2π. For a fixed value of ϕ the phase space volume is

$$V_{1r}(\phi) = \int_{-(2IE)^{1/2}}^{(2IE)^{1/2}} dp_\phi = (8IE)^{1/2} \tag{21}$$

To find the total phase space volume integration over all possible values of ϕ is necessary, and assuming no symmetry

$$V_{1r} = \int_{0}^{2\pi} V_{1r}(\phi) d\phi = 2(8\pi^2 EI)^{1/2} \tag{22}$$

From eqn. (7), the number of states for the rigid rotor is

$$G_{1r}(E) = 2(8\pi^2 EI)^{1/2}/h \tag{23}$$

If the rigid rotor has symmetry, $G(E)$ is divided by the symmetry number σ, since integrating over 2π yields equivalent structures.

The quantal expression for the number of states of a rigid rotor with one degree of freedom is nearly identical to the classical one. The quantal energy levels are given by $E_{1r} = m^2 h^2 / 8\pi^2 I$, $m = 0, 1, 2 \ldots$, where m is the rotational quantum number [9]. All levels except $m = 0$ are doubly degenerate. Therefore, the quantal number of states is $2m^* + 1$, where m^* is the quantum number corresponding to the energy E at which $G(E)$ is calculated. Thus, $m^* = (8\pi^2 E I)^{1/2}/h$ and the quantal and classical number of states only differ by the number 1, which is not a significant difference for large m^*.

The last example is a rigid rotor with two degrees of freedom for which the Hamiltonian is

$$H(p_\theta, p_\phi, \theta, \phi) = p_\theta^2/2I + p_\phi^2/2I\sin^2\theta \qquad (24)$$

where θ varies from 0 to π and ϕ from 0 to 2π as above. This Hamiltonian is also the equation for an ellipse with semiaxes of $a = (2IE)^{1/2}$ and $b = (2IE\sin^2\theta)^{1/2}$. Therefore, for fixed values of θ and ϕ the phase space volume is $V_{2r}(\theta, \phi) = 2IE\sin\theta$. Integration over θ and ϕ is necessary to find the total phase space volume to give

$$V_{2r} = \int_0^{2\pi} \int_0^\pi V(\theta, \phi) d\theta d\phi = 8\pi^2 EI \qquad (25)$$

Thus, the expression for the classical number of states for a rigid rotor with two degrees of freedom is

$$G_{2r}(E) = 8\pi^2 EI/h^2 \qquad (26)$$

As above, if there is symmetry $G_{2r}(E)$ is divided by the symmetry number. For a rigid rotor with two degrees of freedom the quantal energy levels are $E_{2r} = J(J + 1)h^2/8\pi^2 I$, $J = 0, 1, 2 \ldots$. It is easily shown if $J^2 \gg J$ the quantal and classical expressions for the number of states are identical [9].

Conclusion

Following the above discussion, expressions can be easily derived for the classical number and density of states of Hamiltonians which consist of harmonic oscillators and rigid rotors with one and two degrees of freedom. What is required is finding the volume of the $2s$-dimensional ellipsoid, eqn. (16), defined by the classical Hamiltonian. In many situations oscillators must be treated as anharmonic and there is also coupling between vibrational and rotational degrees of freedom. To date, general expressions have not been derived for the number and density of states for such situations. If equations can be found for the phase space volumes of these Hamiltonians, the number and density of states can be found as described above. Though difficult, the derivation of equations for such volumes seems to be a particularly worthwhile research project.

Literature Cited

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