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I. Computational method

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Accurate specific molecular state densities by phase space integration. I. Computational method

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The semiclassical determination of the *specific* density of quantum states, $\rho(E;J)$, at energy E with fixed total angular momentum J is discussed for small molecules. Monte Carlo integration allows the accurate numerical determination of the phase space volume of systems with $J > 0$ and arbitrary anharmonicity. The corresponding semiclassical number of states can be corrected for the effects of zero point motion in analogy to the well-known Whitten–Rabinovitch procedure. In this paper, the procedures are tested by comparison with rigid rotor harmonic oscillator models, while a comparison with recent exact quantum calculations on H_3^+ and HD_2^+ is described in the following paper. We conclude that, if the intramolecular potential is known or assumed, this numerical semiclassical procedure is a viable and simple way to get state densities of a much improved accuracy.

I. INTRODUCTION

The specific, average microcanonical number of quantum states, $N(E;J)$, of a molecular system at given energy E and total angular momentum J, and its derivative with respect to energy, the specific density of states $\rho(E;J)$, are important data needed in theories of molecular behavior. This is especially so in the statistical theory of unimolecular decay, so textbooks and review papers on this topic (e.g., Refs. 1–6) discuss how to calculate $N(E)$ and sometimes also $N(E;J)$. In principle, this is easy: one must only compute all quantum states of the molecule for a given J and up to a given E, and fit some smoothing function through the ensuing staircase. In practice, one meets the fact that normal, chemically bound, polyatomic (i.e., more than diatomic) molecules, for which a complete set of quantum energies far from the ground state has been or can today be calculated, is virtually zero. A first exception from this rule was the calculation[7] of *all* bound quantum states for *one* angular momentum of the molecular ion H_3^+, for which a very precise potential energy surface is available.[8]

All practical calculations of $N(E;J)$ are therefore still bound to use one of two approximations. *Either* they use approximate quantum energies, e.g., those of uncoupled, nonrotating multiple harmonic oscillators, supplemented by some approximate treatment of rotation and anharmonicity, *or* they make use of the semiclassical correspondence

$$N(E;J) \simeq \frac{1}{h^s}\,\Gamma(E;J), \tag{1}$$

correlating the number of quantum states with the classical volume of phase space Γ, taken up to energy E at angular momentum J, and measured in units of the size of the quantum cell h^s. Here s is the number of degrees of freedom of the system, while $d = 2s$ is the dimension of phase space. The first of these approximations is most appropriate for large molecules, in which even at energies near and above the first dissociation threshold the average excitation in any single degree of freedom is small, and where one has no choice anyhow. The second is to be preferred if one needs accurate values of $N(E;J)$ near the dissociation level for *small* molecules of, say, three to five atoms, where the errors of the first kind of treatment are large. The cheap availability of computing power makes it nowadays feasible—provided the intramolecular potential is known—to compute $\Gamma(E;J)$ for such molecules by Monte Carlo integration with an accuracy of 1% or better. This method was pioneered 30 years ago by Bunker,[9] but only recently has been more widely used,[10–16] though in most cases for nonrotating molecules. But then the question arises: How exact is formula (1), which we know to *hold asymptotically* for large E, at those energies where we need it? The problem arises from the zero point motion of quantum oscillators. Whereas the phase space volume starts from $E = 0$, the first quantum state is at the zero point energy E_z. So up to an appreciable value of the reduced energy

$$E' = \frac{E - E_z}{E_z}, \tag{2}$$

the true $N(E;J)$ is markedly below its simple semiclassical value. Here, and *in this whole paper*, E is measured from the bottom of the potential well, as is appropriate for a semiclassical procedure. Rotation behaves differently: Since it has no zero point energy the semiclassical expression interpolates the staircase from the beginning, but to get the correct asymptotic number of states the semiclassical substitution $J \to J + \frac{1}{2}$ must generally be used.

The most useful formula to correct Eq. (1) for the existence of zero point motion has been provided by Whitten and Rabinovitch,[17,18] and is also discussed in the textbooks.[1,2] For a nonrotating s-fold harmonic oscillator Eq. (1) leads to

$$N(E) = \frac{E^s}{s!\Pi\hbar\omega_i}. \tag{3}$$

This is corrected to

$$N(E) = \frac{[E - \beta w(E')E_z]^s}{s!\Pi\hbar\omega_i} \tag{4a}$$

with

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$$\beta = (s-1)\frac{\Sigma\omega_i^2}{(\Sigma\omega_i)^2} \tag{4b}$$

and

$$w(E') = \begin{cases} (5.00\cdot E' + 2.73\sqrt{E'} + 3.51)^{-1} & 0.1 < E' < 1 \\ \exp(-2.4191\cdot E'^{0.25}) & 1 < E' < 8. \end{cases} \tag{4c}$$

Here sums and products are over the s oscillators. Equation (4c) is often extended to $E\to\infty$. This formula was derived on a purely empirical basis from model calculations employing sets of independent, *harmonic* oscillators with a wide variety of frequencies, whose distribution was characterized by their dispersion β, Eq. (4b). Its physical content can best be understood by showing its similarity to asymptotic series derived first by Haarhoff[19,20] for the same purpose (see below).

The Whitten–Rabinovitch treatment was later extended to include the average excitation of internal and external rotational degrees of freedom in canonical and microcanonical ensembles.[18,20–24] It was also applied to systems in which rotation with fixed total angular momentum J was specified,[15,24–26] and combined with anharmonic corrections intended to make up for the anharmonicity of real molecular oscillators. However, these extensions of the original Whitten–Rabinovitch scheme have never been tested against true quantum results, since a sufficient number of quantum energies for a comparison were not available for any real molecule.

This situation is improving now, and the purpose of this paper is to show how one can compute accurate, semiclassical, specific numbers of state, and compare them first with RRHO (rigid rotor harmonic oscillation) models. The final comparison, however, must be done with quantum energies of real molecules. This is done in the following paper,[27] in which semiclassical data are compared with several large sets of quantum states computed for H_3^+ (Ref. 7) and HD_2^+ by Tennyson and his collaborators. This comparison supports the statement that it is possible to obtain accurate, semiclassical state counts and state densities, which include all rotational and anharmonic effects, semiclassically from phase space integration.

The plan of the paper is as follows. In Sec. II we discuss the Monte Carlo evaluation of phase space volumes. In Sec. III we discuss J-specific numbers of state, and how to implement the Whitten–Rabinovitch correction for separable and nonseparable models. Section IV presents our results for the rigid rotor harmonic oscillator (RRHO) model, where the exact quantum state count is obtained easily, and first conclusions. The comparison with quantum energies of H_3^+ and HD_2^+ is postponed to the following paper.[27]

II. MONTE CARLO INTEGRATION OF THE PHASE SPACE VOLUME

The use of Monte Carlo methods for multidimensional integration is well documented in textbooks (e.g., Ref. 28). After early attempts[9] it has been applied recently by several authors to integrate molecular phase space volumes.[10–16] Let us state first that, even if one needs only the state density $\rho(E;J)$, it is advisable to obtain it by first calculating $N(E;J)$ for a range of energies, and then differentiating. $N(E;J)$, for a series of values of E, can be obtained in a single Monte Carlo run, in which hit or miss for *several* values of E are collected in each loop. Otherwise, either a δ function must be approximated under the integral, or the energy has to be introduced as one of the coordinates in the Hamiltonian. In practice, it turns out that a local fit to a power law

$$N(E;J) = \text{const}\cdot E^t \tag{5a}$$

is always very good, yielding

$$\rho(E;J) = \text{const}\cdot t\cdot E^{t-1}. \tag{5b}$$

So even if ρ is the physically more appealing quantity, we will restrict our discussion in the following to $N(E;J)$.

Our specific methods to perform phase space integration have been described before.[16,29] In short, we start from the body-fixed Pollak–Wyatt Hamiltonian[30] in the form of Eq. (2) in Ref. 30(b), which uses mass-scaled Jacobi coordinates R, r, γ, and their conjugate momenta P_R, P_r, P_γ. It consists of the terms

$$H = T_{\text{kin}} + T_{\text{rot}} + T_{\text{tum}} + V(r,R,\gamma), \tag{6a}$$

where

$$T_{\text{kin}} = T_R + T_r + T_\gamma, \tag{6b}$$

which in detail can be found in the references. The terms in T_{kin} come from internal vibrations and Coriolis forces, and contain the γ-dependent part of the rotational energy. T_{rot} and T_{tum} are the rotational energies connected with the in-plane rotation and the tumbling motion of the molecular plane, respectively. The external rotation is further described (after Nikitin[4]) by the angular momenta J, $K = J_x$, and $M = J_Z$, and their conjugate angles ξ, ψ, φ. Here J_x is the component of J normal to the molecular plane, J_Z that in the laboratory Z direction. (Note already here, that the M degeneracy is traditionally *not* included in formulas and tables of state numbers and densities.) The integrals over J, M, ξ, and φ can be performed, and after some manipulation and the semiclassical substitution of J by $J+\frac{1}{2}$ (which is necessary in order to obtain the correct total sum of rotational states, and allows also to use all formulas for $J=0$) we arrive at the eight-dimensional integral

$$N(E;J) = \frac{J+(1/2)}{2\pi h^3}\int \Theta(E-H_J)\,dR\,dP_R\,dr\,dP_r\,d\gamma \times dP_\gamma\,d\cos\vartheta\,d\psi. \tag{7}$$

Here $\Theta(\cdot)$ is the unit step function ($=1$ for positive argument, $=0$ elsewhere), and H_J the body-fixed Hamiltonian in which the angular momentum **J** is expressed by its prescribed modulus J (semiclassically replaced by $\sqrt{J(J+1)}$ in the computations), the tumbling angle ϑ between **J** and the normal to the molecular plane, and the azimuthal angle ψ. Since $K = J\cdot\cos\vartheta$ is not conserved (except for a rigid symmetric top), ϑ and ψ cannot be taken out of the integral.

Equation (7) could easily be Monte Carlo integrated, but this is still not the optimal choice, since the efficiency of Monte Carlo integration increases very much if one can lower the dimension of the integral. One way to do this[29] is to compute the density $\tilde{N}(E;J,R)$ on a grid of R values, and to postintegrate this function over R by some multipoint rule (e.g., Simpson's) to get

$$N(E;J) = \int \tilde{N}(E;J,R)\,dR. \tag{8}$$

A second possibility comes from the fact, that one final momentum integration, say that over P_R, can be performed explicitly by using the energy which is available after the Monte Carlo sampling has been done for all other coordinates. That is, we put

$$H_J = E = \frac{1}{2\cdot\mathcal{M}} P_R^2 + \text{other terms}, \tag{9a}$$

which means that the full allowed interval for P_R is

$$\Delta P_R = 2\cdot(2E\cdot\mathcal{M} - \text{other terms})^{1/2}, \tag{9b}$$

if the argument of the root is positive (otherwise the Monte Carlo point is a miss.) Here $\mathcal{M}$ is the three-body reduced mass

$$\mathcal{M} = \left(\frac{m_a m_b m_c}{m_a + m_b + m_c}\right)^{1/2}. \tag{10}$$

A third reduction of the dimension of the integral is possible, and will be of particular interest if one wants to extend the treatment to four- and five-atomic molecules. It has already been observed[12,31] that, if the kinetic energy is a simple sum of squared momenta, the integration over *all* momenta can be done analytically, and the result (the volume of the momentum ellipsoid) convoluted with the residual integral. Unfortunately, with $J > 0$ the kinetic energy is *not* such a simple sum, since Coriolis terms containing products of J_x and the momenta P_R and P_r exist [Eq. (11) in Ref. 30]. However, there is actually no need to integrate in terms of conjugate coordinates and momenta. Any set of coordinates, in which H_J can be expressed, will do. We therefore make the volume preserving substitution

$$\{R,r,\gamma,P_R,P_r,P_\gamma,\cos\vartheta,\psi\} \to \{R,r,\gamma,Y_R,Y_r,P_\gamma,\cos\vartheta,\psi\}, \tag{11}$$

where $Y_R = \mathcal{M}\cdot\dot{R}$ and $Y_r = \mathcal{M}\cdot\dot{r}$, which leads to the nonrotational kinetic energy

$$T_{\text{kin}} = \frac{1}{2\mathcal{M}}\cdot[(\mathcal{M}\cdot\dot{R})^2 + (\mathcal{M}\cdot\dot{r})^2 + (R^{-2} + r^{-2})\cdot P_\gamma^2]. \tag{12}$$

Now T_{kin} *has* the required form, and the integral finds its final form

$$N(E;J) = \frac{2J+1}{3h^3}\cdot(2\mathcal{M})^{3/2}\int\frac{(E - T_{\text{rot}} - T_{\text{tum}} - V)^{3/2}}{(r^{-2} + R^{-2})^{1/2}} \times dR\,dr\,d\gamma\,d\cos\vartheta\,d\psi. \tag{13a}$$

In our most recent calculations we have actually used

$$\tilde{N}(E;J,R) = \frac{2J+1}{3h^3}\cdot(2\mathcal{M})^{3/2} \times \int\frac{(E - T_{\text{rot}} - T_{\text{tum}} - V)^{3/2}}{(r^{-2} + R^{-2})^{1/2}} \times dr\,d\gamma\,d\cos\vartheta\,d\psi, \tag{13b}$$

and postintegrated Eq. (8) with Simpson's rule. The Monte Carlo step has thus been reduced from eight to four dimensions.

A final remark concerns the manner by which we do the Monte Carlo integration itself. Basically, one has to generate sampling vectors in phase space covering it *uniformly*, so that the integral can be approximated by the average of the integrand taken at the sampling points. These vectors are usually constructed from components taken out of a sequence of the common *pseudorandom numbers*, i.e., deterministically computed numbers, which simulate true random numbers with respect to both, equidistribution *and* absence of correlation in the sequence. But the latter property is not really needed; on the contrary, it is *better* if each generated point "knows," where the earlier points are, and is placed in the gaps as well as possible. The only condition is that this occurs in a way, which allows to stop the sequence *at any length* and still preserve equidistribution. Sequences of points with such properties are called *quasirandom point sequences* (e.g., Refs. 32 and 33). For a given number of points they cover the phase space much more uniformly than random points, which means that the Monte Carlo integrals converge faster. While the asymptotic error using pseudorandom point sequences is $\propto N^{-1/2}$, where N is the number of sampling points, it is $\propto (\log N)^s/N$ for quasirandom sequences. (This holds for continuous integrands.) In practice, as we have documented elsewhere,[29] for integrals of the sort discussed here *one can save more than 1 order of magnitude of computer time.* Strangely enough, even the existence of textbooks, in which quasirandom sequences are discussed in the context of multidimensional integration,[28,34] has not made them popular in the physics community.

Of the several types of quasirandom sequences, which have been proposed, we have used Halton sequences.[35] One reason was, that they are easily produced by an algorithm,[29] which is not slower than a good generator of pseudorandom vectors. However, other types of quasirandom numbers exist,[33,36] for which it has been shown theoretically that they should produce even better asymptotic convergence of integrals. For some of them explicit algorithms have still not yet been published. Moreover, it is theoretically not established, *when* the asymptotic regime becomes valid, so the practical usefulness of different types of quasirandom sequences has to be answered empirically, and must still be considered an open question.

All of our Monte Carlo calculations have been done with control of the variance of groups of ten calculations, identical except for the random numbers. The number of samples was then adjusted to a value, which made the rms error of the Monte Carlo step in our calculations less than 1%.

III. STATE NUMBERS IN THE RRHO MODEL

In this section we want to compare semiclassically computed numbers of states of a rotating molecule (whose parameters correspond to those of H_3^+ and HD_2^+, cf. Table I) without and with Whitten–Rabinovitch correction to the exact state counts obtained easily if one makes the rigid rotor harmonic oscillator (RRHO) assumption. Such a model is

TABLE I. Classical vibrational frequencies and rotational constants for rotating H_3^+ and HD_2^+, i.e., at the equilibrium of the molecule under centrifugal distortion. Values are given in cm^{-1}.

	J	ω_1[a]	ω_2[b]	ω_3[c]	A	B[d]
H_3^+	0	3437.8	2776.6		43.8921	43.8921
	10	3372.2	2632.9		42.3716	42.3716
	30	2943.8	1742.3		33.5426	33.5426
HD_2^+	0	2934.2	2100.4	2267.6	36.5803	21.9569
	10	2891.7	2025.6	2213.3	36.0960	21.2880
	30	2630.6	1511.7	1890.0	33.8143	16.8422

[a] Species A_1.

[b] Species E in H_3^+, A_1 in HD_2^+.

[c] Species B_2 in HD_2^+.

[d] The third rotational constant follows from $C = A \cdot B/(A + B)$.

still a gross approximation to a real molecule: The instantaneous moments of inertia are taken to be constant, and Coriolis forces are neglected. For the symmetric top, in addition, the so-called K rotor, i.e., the component of J perpendicular to the molecular plane, is conserved in contrast to a real, nonrigid molecule. For the asymmetric top the quantum count contains additional approximations, but our treatment yields an obvious average over the nonconserved values of K. Formulas for the number of states summed over all J can be found in the literature.[1,2] Similar calculations as those to follow have been published in Refs. 24 and 25.

Our starting point is the well-known fact, that for separable degrees of freedom one gets $N(E;J)$ by convolution

$$N(E;J) = \int_0^E N_{\text{vib}}(E_1;J) \cdot \rho_{\text{rot}}(E - E_1;J) dE_1, \quad (14a)$$

$$= \int_0^E N_{\text{rot}}(E_1;J) \cdot \rho_{\text{vib}}(E - E_1;J) dE_1. \quad (14b)$$

In what follows we restrict ourselves to values of J, where the triatomic molecule is nonlinear. For H_3^+ this means $J < 48$, for HD_2^+ $J < 60$. There are two different rotational constants for equilateral H_3^+,

$$C = \frac{\hbar^2}{2 \cdot \mathscr{M} \cdot (r_0^2 + R_0^2)} \quad (15a)$$

and $B = 2C$, whereas for HD_2^+ we have C as above, but differently,

$$B = \frac{\hbar^2}{2 \cdot \mathscr{M} \cdot r_0^2} \quad (15b)$$

and

$$A = \frac{\hbar^2}{2 \cdot \mathscr{M} \cdot R_0^2}. \quad (15c)$$

Here mass-weighted Jacobi coordinates $r_0 = r_{0\text{true}}(J) \cdot c$ and $R_0 = R_{0\text{true}}(J)/c$ with $c^4 = (m_A + m_B + m_C) m_B m_C / m_A (m_B + m_C)^2$ (Ref. 30) have been used. Values for A, B, C, and the ω_i are shown in Table I.

We treat first the (oblate) symmetric top H_3^+. The harmonic vibrational state count is [Eq. (3)]

$$N_{\text{vib}}(E) = \frac{E^3}{3! \Pi \hbar \omega_i}.$$

The *classical* rotational energy is

$$E_{\text{rot}} = B \cdot J^2 - (B - C) \cdot K^2, \quad (16)$$

and obeys the inequality $E_{\min} = CJ^2 \leqslant E_{\text{rot}} \leqslant E_{\max} = BJ^2$. The number of rotational states (as usual *not* including the spatial degeneracy corresponding to the M degeneracy) is in the given interval

$$N_{\text{rot}}(E;J) = 2J \cdot \left(1 - \sqrt{\frac{E_{\max} - E}{E_{\max} - E_{\min}}}\right), \quad (17)$$

where we must replace $2J$ by its semiclassical value $2J + 1$ as discussed above. So in what follows we work with

$$N_{\text{rot}}(E;J) = \begin{cases} 0, & \text{if } E \leqslant E_{\min} \\ (2J+1) \cdot \left(1 - \sqrt{\dfrac{E_{\max} - E}{E_{\max} - E_{\min}}}\right), & \text{if } E_{\min} \leqslant E \leqslant E_{\max}. \\ 2J + 1, & \text{if } E \geqslant E_{\max} \end{cases} \quad (18)$$

The corresponding density is

$$\rho_{\text{rot}}(E;J) = \frac{J + (1/2)}{\sqrt{E_{\max} - E_{\min}}} \cdot \frac{1}{\sqrt{E_{\max} - E}} \quad \text{if } E_{\min} \leqslant E < E_{\max}$$

$$\rho_{\text{rot}}(E;J) = \infty \quad \text{for } E = E_{\max}$$

$$\rho_{\text{rot}}(E;J) = 0 \quad \text{elsewhere.} \quad (19)$$

This leads finally to

$$N_{\text{vibrot}}(E;J) = \int dE_1 \frac{(E - E_1)^3}{3! \Pi \hbar \omega_i} \cdot \frac{J + (1/2)}{\sqrt{E_{\max} - E_{\min}}} \cdot \frac{1}{\sqrt{E_{\max} - E_1}}, \quad (20)$$

where proper integration limits have to be inserted. The integral is analytical, but we will not display it here.

In case of the asymmetric rotor HD_2^+ Eq. (3) is still correct, but an explicit formula replacing Eq. (16) will contain the angle ψ. Since the equivalents of Eqs. (18)–(20) contain the *reciprocals* of the rotational constants B and C, we must perform the average over ψ on the reciprocal of $B(\psi) - C$, and approximate the asymmetric top having rotational constants A and B by a symmetric top whose rotational constant $B_{\rm eff}$ is the *harmonic mean* of A and B

$$\frac{1}{B_{\rm eff}} = \frac{1}{2}\cdot\left(\frac{1}{A} + \frac{1}{B}\right). \tag{21}$$

This means the *moments of inertia are averaged*. This choice of $B_{\rm eff}$ is somewhat better than the arithmetic mean $B_{\rm eff} = \frac{1}{2}(A + B)$ used by others,[24,37] as can be seen by graphing formula (12) with both choices of $B_{\rm eff}$, and comparing this to the results from Monte Carlo integration. We show this in Fig. 1 by plotting

$$F(E;J) = N_{\rm 3D}(E;J)/N_{\rm 2D}(E;J)$$

for $J = 10$, i.e., the ratio of the full phase space volume to that from a planar calculation, in which the molecule is not allowed to tumble. The RRHO parameters are those of H_3^+ *at the equilibrium geometry* for $J = 10$, while the Monte Carlo result is for the real molecule. Only if we take the harmonic mean for $B_{\rm eff}$, we get the expected result that the *low* energy behavior of the molecule is well approximated. Differences at high E come from the breakdown of the RRHO approximation.

Up to now we have compared two semiclassical state counts with each other in order to verify our treatment of the rotors. The next step is to compare *quantum* results from the RRHO model with the semiclassical computation. In this case, if we want a good fit at all but the highest energies, the semiclassical result must be corrected for the effects of zero-point vibration.

We propose here to use the Whitten–Rabinovitch correction, Eq. (4), which consists of an energy dependent shift of the energy scale. Let us first comment on it. Its obvious advantage is that it seems to work very well, its disadvantage that it is purely empirical and not intuitive. In trying to understand what happens, if only formally, we arrived at Fig. 2, which shows in two dimensions the essential difference between the quantum count N of points on a grid, and the semiclassical measure Γ of a phase space volume (an area in this example): If we move the oblique line corresponding to a given E, the number N of points included by this line jumps, while Γ increases continuously. The difference $\Delta = \Gamma/\omega_1\omega_2 - N$ oscillates, and one can verify from the figure that the average Δ *vanishes only to first order*, which is $\propto E^{s-1}$ ($\propto E$ in the example), but not completely, since a term $\propto E^{s-2}$ and smaller terms remain. That this is so also for $s > 2$ and for more arbitrary values of ω_i can be seen from Haarhoff's analytical treatment,[19,20] which, however, yields a nonconvergent series. It has been shown, however,[38] that Haarhoff's first correction (the only finite one for $s = 2$ and 3) can be expressed (for $s \gg 2$) as

$$\Delta_H = N_{\rm scl} - N_{\rm qm} = N_{\rm scl}(E' + 1)^{-2}\cdot\frac{s}{6}\cdot\beta_{\rm WR} \tag{22}$$

with E' and $\beta_{\rm WR}$ given by Eqs. (2) and (4b). In contrast, a linear expansion of Eq. (4a) together with a linear fit of $1/w(E')$ [defined in Eq. (4c)—this fit is very good between $E' = 0.2$ and 10] gives

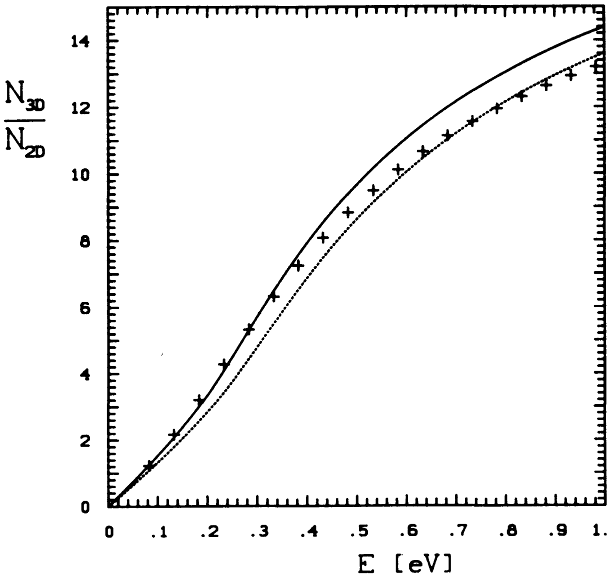

FIG. 1. Ratio of semiclassical numbers of state for H_3^+ in $J = 10$ with (3D), and without (2D) allowing the tumbling of the molecular plane. Crosses: Monte Carlo results for the real molecule (exact within the limits of the semiclassical treatment). Full line: RRHO model, [Eq. (20)], with $B_{\rm eff}$ equal to the harmonic mean of A and B [Eq. (21)]. Dotted line: RRHO model with $B_{\rm eff}$ equal to the arithmetic mean of A and B. The dotted curve disagrees with the crosses for *low* energies, where the RRHO model is good; at high energy the RRHO model itself is in error.

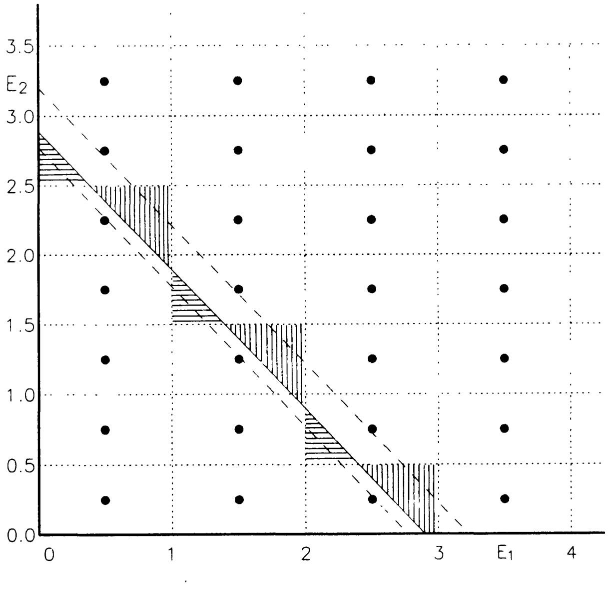

FIG. 2. Scheme to illustrate the difference between quantal state count and semiclassical volume integration exemplified for a pair of harmonic oscillators. For fixed total energy (slant lines) quantum mechanics counts the dots, or, equivalently, the volume of the corresponding rectangular boxes, while the semiclassical phase space volume is the triangle below the energy line. Their difference is the difference of the two hatched areas, which oscillates when E is monotonously increased, but does *not* completely average to zero. See the text before Eq. (22).

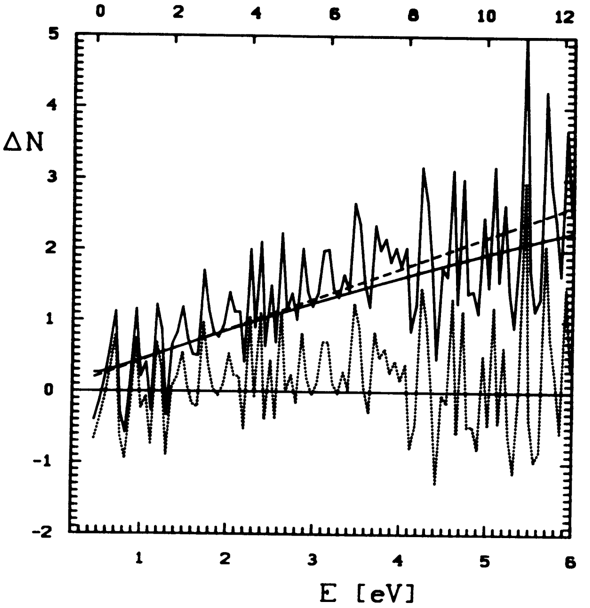

FIG. 3. Differences of various approximations to the number of states for a RRHO model of HD_2^+ in $J = 10$. Full jagged line: uncorrected semiclassical minus quantal calculation. Dotted: corrected semiclassical minus quantal calculation. Full smooth line: absolute value of Whitten–Rabinovitch correction, dashed: Haarhoff correction [Eq. (22)].

$$\Delta_{\rm WR} = N_{\rm scl} - N_{\rm wr} = N_{\rm scl}(E' + 1)^{-2} \cdot \frac{s}{6.467} \cdot \beta_{\rm WR}. \tag{23}$$

So, we feel that Haarhoff's treatment gives an explanation of what happens, while the fact that his series diverges enforces the use of *ad hoc* approximations like those of Whitten and Rabinovitch. Figure 3 shows some of the aforementioned differences for HD_2^+ in $J = 0$.

The insight gained from meditating Fig. 2 shows also that the problem *cannot* be solved by omitting from the integral that part of phase space, in which any vibrational mode has a classical energy below its zero point energy. This was proposed recently as a correction in quasiclassical trajectory calculations, where problems of zero point motion do also exist.[39,40] But one can show that this procedure applied to the phase space integral of harmonic oscillators yields nothing else as the expression

$$N(E) = \frac{(E - E_z)^s}{s!\Pi\omega_i}, \tag{24}$$

which is clearly defective (see Sec. IV). This sheds some doubt on whether the procedure promoted in Refs. 39 and 40 will really help.

The implementation of the Whitten–Rabinovitch correction in our case leaves still several choices.

Method (a): Take the function $N_{\rm vibrot}(E;J)$ from Eq. (20), and replace E by $E - \beta w(E')E_z$, where E' is still $(E - E_z)/E_z$ as in Eq. (2). This means that the energy scale is shifted in the final semiclassical result.

Method (b): Replace E by $E - \beta w(E')E_z$ *only* in the *vibrational* state count, Eq. (3), which is one of the factors in the integrand of formula (20), but leave the other factor, the rotational density, unchanged. In this case the convolution, Eq. (20), must be done numerically. Since $\rho_{\rm rot}(E;J)$ has a singularity, this procedure has to be done by convoluting $\rho_{\rm vib}$ with $N_{\rm rot}$ instead of $N_{\rm vib}$ with $\rho_{\rm rot}$.

In both cases, β and E_z are computed from the classical *vibrational frequencies*, $\omega_i(J)$, *of the rotating molecule* taken at the minimum of $V_{\rm eff}$. In this way we take care of the centrifugal distortion of the molecule. We do *not*, of course, use $\beta_{\rm rot} = \beta \cdot (s + (1/2)r)/s$, which was suggested to correct for rotation in microcanonical or canonical ensembles of s oscillators and r rotors, which include all possible values of J.[1,2,18] In our case this would mean using $\beta_{\rm rot} = \frac{4}{3} \cdot \beta$, since the M degeneracy is not counted. With this $\beta_{\rm rot}$ the Whitten–Rabinovitch correction is by far overdone in a fixed J ensemble! Playing around with the value of β, we found that small ($< 10\%$) changes can lead to *slight* improvements of the semiclassical result in certain ranges of E', but after some experimentation found those insignificant enough to stay with the original Eq. (4b).

Our final addition to the Monte Carlo program concerns the implementation of method (b) above in the realistic case, where vibration and rotation are no longer separable, and therefore the convolution [Eq. 20)] cannot be explicitely done. The Whitten–Rabinovitch correction must now be performed *within* the Monte Carlo sampling. To do this, we have also to *define* which part of the energy belongs to vibration and which to rotation, since both are coupled by Coriolis terms. We define

$$E_{\rm vib} = T_{\rm kin} + V(R,r,\gamma) - V(R_0,r_0,\gamma_0), \tag{25}$$

where $V(R_0,r_0,\gamma_0)$ is the potential minimum of the rotating molecule, which is somewhat higher than the absolute minimum due to the centrifugal distortion associated with $J > 0$. This definition of $T_{\rm kin}$ corresponds to the one given recently by Jellinek.[41] The Whitten–Rabinovitch function $w(E')$ is then determined with the argument

$$E'_{\rm vib} = \frac{E_{\rm vib} - E_z(J)}{E_z(J)}, \tag{26}$$

and the numerator of the integrand in Eq. (13) replaced

$$(E - T_{\rm rot} - T_{\rm tum} - V)^{3/2}$$
$$\rightarrow [E - T_{\rm rot} - T_{\rm tum} - V - \beta w(E'_{\rm vib})E_z]^{3/2}. \tag{27}$$

This results in a shift in the energy scale for $T_{\rm kin}$, Eq. (11), and, consequently, also for $E_{\rm vib}$, Eq. (25), which is the desired result. The difference between methods (a) and (b) vanishes for $J = 0$, and increases with J, since this moves an increasing part of the energy into rotation.

IV. RESULTS AND DISCUSSION

Our main results for the RRHO model are presented in Figs. 4 and 5. The parameters (cf. Table I) are those of HD_2^+ with $J = 10$ and 30, respectively. We show the staircase corresponding to the quantum energies, the uncorrected semiclassical state count, the same numbers corrected after methods (a) and (b), and finally the overkill by subtracting the full zero point energy, which is erroneously sometimes considered to be the correct zeroth order formula. One observes, that the semiclassical, Whitten–Rabino-

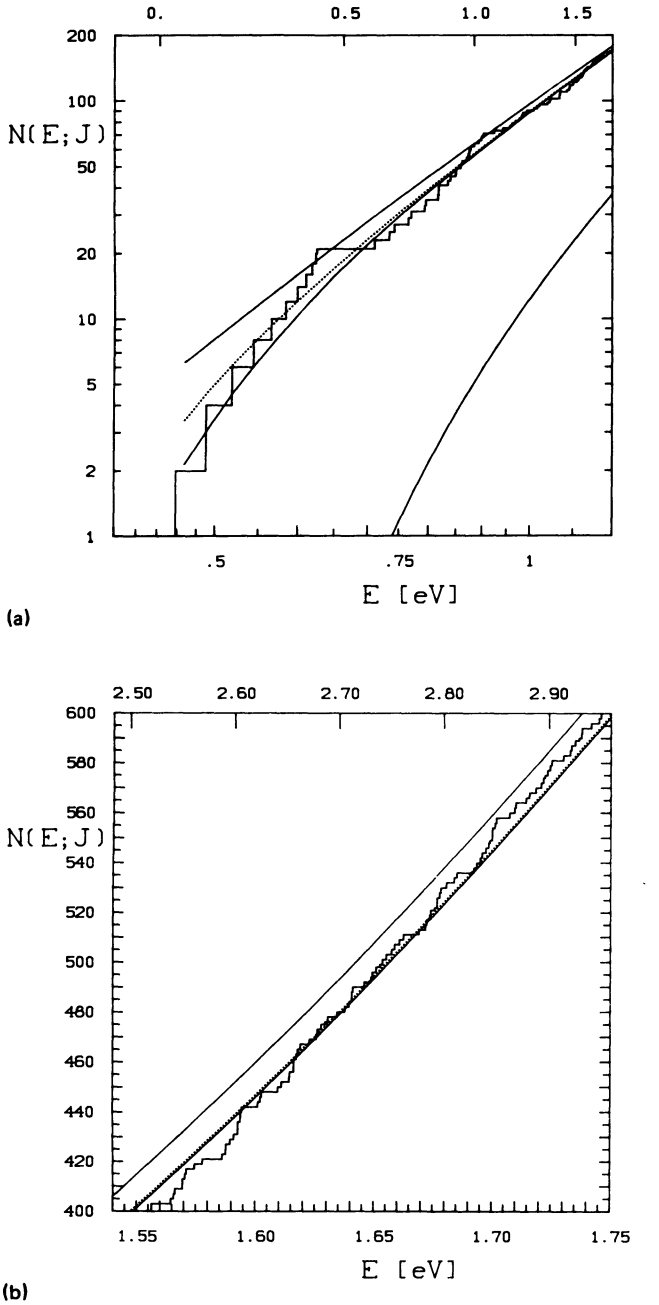

FIG. 4. Quantal state count (staircase) and its different semiclassical approximations for a RRHO model of HD_2^+ in state $J = 10$. The smooth lines are from top to bottom: (1) Uncorrected semiclassical phase space volume in units of h^4; (2, dotted) corrected after method (a) of the text, i.e., the full energy is used for correction; (3) corrected after method (b), where only the vibrational part of the energy is taken to compute the correction; and (4) only shown in Fig. 4(a), corrected by subtracting the full zero point energy.

vitch corrected state counts are very accurate. Of course, they are smooth, and cannot follow the quantum step structure. As expected, the best fit is obtained with method (b); this is most clearly visible for $J = 30$. Note that the absolute amount of correction is much larger for $J = 30$ than for $J = 10$. This can be understood by observing that to first order (i.e., in the limit that B_{eff} is small compared to the ω's) the main effect of rotation is a multiplication of the vibrational state count by $2J + 1$, smeared out by the convolution, Eq. (11a).

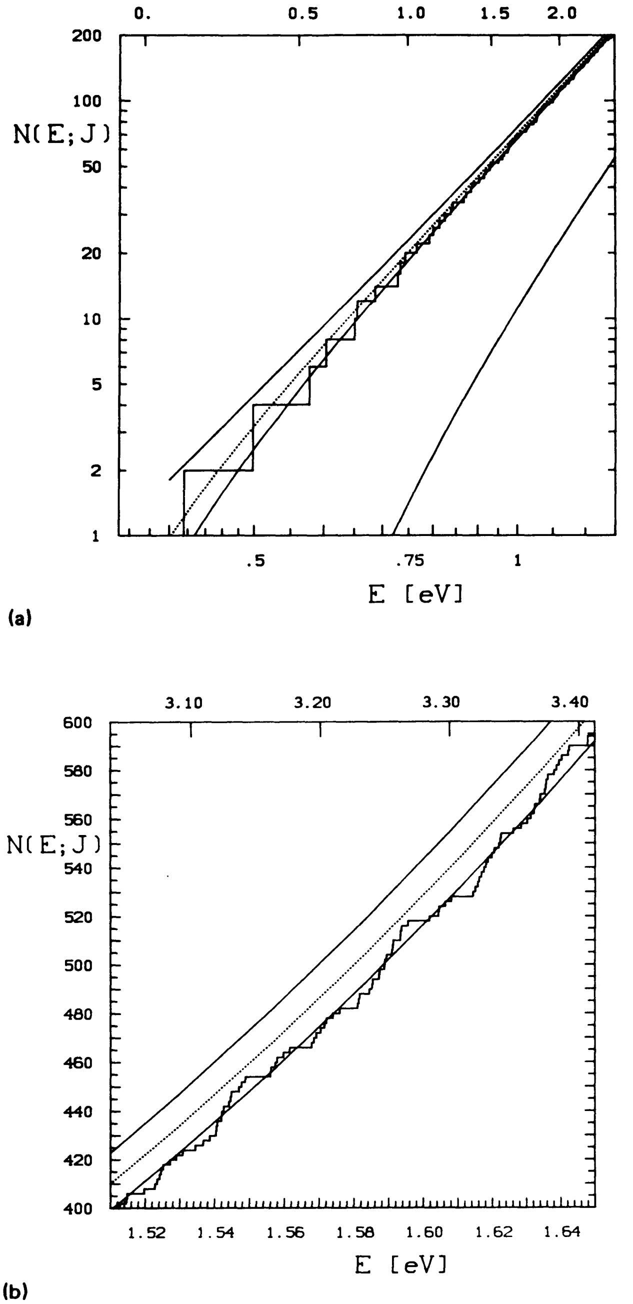

FIG. 5. Same as Fig. 4 but with $J = 30$. The difference between methods (a) and (b) is most obvious in Fig. 5(b).

As mentioned above, there is still some possibility that one may find a substitute for the formula of Whitten and Rabinovitch, which is somewhat better. But we did not want to repeat their work. Moreover, the *crucial* test must be against *quantum* states of rotating, anharmonic, nonseperable systems. The only such system with a sufficient number of computed quantum states is H_3^+ and its isotopomers.[7,42,43] We present and comment this comparison in the following paper.[27] It confirms the conclusion, which we can draw from this paper limited to RRHO molecules, that for small systems with known intramolecular potential very precise, *J*-specific numbers and densities of states can be computed semiclassically with reasonable effort.

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