MICHAEL BERBLINGER
CHRISTOPH SCHLIER
JONATHAN TENNYSON
STEVEN MILLER

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II. Comparison with quantum calculations on H_3^+ and HD_2^+

Michael Berblinger and Christoph Schlier

Fakultät für Physik der Universität, Hermann-Herderstrasse 3, D-7800 Freiburg, Germany

Jonathan Tennyson and Steven Miller

Department of Physics and Astronomy, University College London, Gower St., London WC1E 6BT, England

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The semiclassical determination of $N(E;J)$ and $\rho(E;J)$, the specific number and density of quantum states at energy E , and fixed total angular momentum J , by Monte Carlo integration of phase space is compared to recent exact quantum calculations on H_3^+ and HD_2^+ , which yielded lists of up to 900 quantum states for single values of J . This allows for the first time tests of such a procedure to be made *without assuming anything about separability or harmonicity* of the potentials. The excellent agreement between semiclassical and quantum state counts shows that the semiclassical numerical computation is a viable and simple method for the determination of state numbers and densities in small molecules with a precision of the order of 1%. For $J = 0$, the procedure has been extended to state numbers for the different symmetry species occurring in H_3^+ and HD_2^+ .

I. INTRODUCTION

The averaged microcanonical number of quantum states, $N(E;J)$, of a bound molecular system at given energy E and angular momentum J , and its derivative with respect to energy, the density of states $\rho(E;J)$, are important data needed in theories of molecular behavior, especially in the statistical theory of unimolecular decay (e.g., Refs. 1–6). 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, the number of 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 calculation⁷ involving one of the authors of *all* bound quantum states for *one* angular momentum of the molecular ion H_3^+ , for which a very accurate potential energy surface is available.⁸

All practical calculations of $N(E;J)$ are therefore still bound to use approximations. One such approximation is the use of the semiclassical correspondence

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

which correlates the number of quantum states with the volume of classical 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, $d = 2s$ the dimension of phase space.

The computation of Γ itself is nontrivial, since it implies multidimensional integration in a space, which even for a triatomic system has 12 dimensions. One of the best methods to do this is Monte Carlo integration, which has become

more feasible with the advent of fast, inexpensive workstations. This has been discussed in the preceding paper (Ref. 9, henceforth referred to as Paper I), where the following questions were addressed: reduction of the dimension of the integral to four by analytical manipulations; speedup of the Monte Carlo procedure by 1 order of magnitude through the use of quasirandom instead of pseudorandom numbers; and correction of the semiclassical result for the effects of zero point motion. But even if the Monte Carlo integral can be shown to be converged to better than 1%, the question remains: How exact is formula (1), which is only known to hold *asymptotically* for large E , at those energies where we need it? This has been tested in Paper I in a limited way only by comparison with the rigid rotor harmonic oscillator (RRHO) model, which contains neither anharmonic and nonseparable vibrations nor rovibrational coupling.

It is in this paper that we provide the crucial test by comparing the semiclassical numbers of states computed according to Paper I with sufficiently large sets of quantum energies of H_3^+ and HD_2^+ for selected values of the total angular momentum J . Both computations have been done with *exactly* the same potential.⁸ Because of their lightness these systems are strongly quantal and provide the most stringent test of our semiclassical procedure.

In addition, we address a problem arising for molecules of high symmetry: How can one divide the semiclassical number of states into fractions belonging to definite irreducible representations? The necessity to consider also the symmetry species of molecules in the discussion of state-specific bimolecular and unimolecular reactions has been stressed many times by Quack (e.g., Refs. 10–12). The limiting behavior for large E has been derived in these and other papers (e.g., Refs. 13 and 14), and compared with direct state counts of separable models. We derive here a method to compute (still approximate, but) *E-dependent* fractions,

$f(\Gamma)$, which are valid at energies much lower than the infinite energy limit. The formulas are explicitly given for the irreducible representations of groups C_{3v} and C_{2v} , which suffice for the classification of states in H_3^+ and HD_2^+ .

The plan of the paper is thus as follows. Section II gives a short account of the quantum calculations. In Sec. III we discuss the separation of the semiclassical vibrational state count into fractions for the different symmetry species. In Sec. IV we present the comparison with quantum data. We conclude, that—at least for triatomics with a typical potential well—the semiclassical procedure, if it includes the effects of anharmonicity and rotation, i.e., is numerically exact, and after it has been corrected for zero point motion yields state counts which are accurate to 1%.

II. QUANTUM STATE COUNTS FOR H_3^+ AND HD_2^+

Methods for the computation of large ladders of rovibrational states for triatomic molecules have recently been developed by several groups.^{15–17} They vary by starting from different Hamiltonians, using different basis sets, and employing different methods to divide the full calculation into steps in order to circumvent a brute force diagonalization of matrices whose order would be many thousands. H_3^+ and its isotopomers are the ideal playground for these studies, since the molecular potential is well known,⁸ and spectroscopic values for transitions between low lying states can be used to check at least part of the calculation.^{8,18} Further spectroscopic data exist near and above the dissociation limit,^{19,20} but here the computational methods have still to be improved.

In this paper we use the state counts $N(E;J)$ obtained from the quantum energies of H_3^+ and HD_2^+ , which were computed by the group in London. For H_3^+ estimates of all (~ 900) bound states for $J = 0$ have been previously computed^{7,21} using a discrete variable representation (DVR).²² These calculations converged to 10 cm^{-1} for all states below dissociation (assumed to be at 4.885 eV or $39\,400\text{ cm}^{-1}$). Lower levels, i.e., those most critical for our test of the semiclassical corrections, are much better converged.

As yet no DVR computations have been performed on HD_2^+ . Conventional basis set calculations¹⁸ have obtained the $J = 0$ states which lie below the barrier corresponding to linear geometry at about 2 eV . To test further the semiclassical predictions, quantal calculations on rotationally excited HD_2^+ have been executed. These calculations generated long, but still incomplete, lists for $J = 0$ (~ 85 states), $J = 10$ (~ 730 states), and $J = 30$ (~ 175 states). HD_2^+ was selected for these calculations to avoid the symmetry problems encountered with H_3^+ and is discussed below. The calculations were performed using traditional basis sets and a two-step variational procedure,^{23,24} and are similar in spirit to, but more extensive than the ones performed on H_2D^+ .^{23,25} They were done in Jacobi coordinates, which reflect the C_{2v} symmetry of the system, using the TRIATOM²⁶ program suite.

For $J = 0$ the eigenvalues were obtained by diagonalizing a Hamiltonian matrix of dimension 1600 for each sym-

metry. The basis functions were selected using energy ordering.^{24,26} The candidate list of functions was generated from 17 previously optimized¹⁸ Morse oscillatorlike functions for each of the radial coordinates, and Legendre polynomials up to 36th order.

For the $J = 10$ and $J = 30$ calculations the first step assumed that k , the projection of J along the body-fixed z axis was a good quantum number. For HD_2^+ this axis was taken to be along the Jacobi coordinate r . This first step used the same basis and selection criteria as the $J = 0$ calculation. For both $J = 10$ and $J = 30$ with $p = 0$, the second, fully coupled step of the calculation was performed for each symmetry by selecting the 10 000 lowest solutions of the first step calculations, again using energy selection.^{24,26} The $p = 1$ secular matrices [the rotational parity is given by $(-)^{J+p}$] were obtained by dropping the $k = 0$ blocks from the equivalent $p = 0$ matrices.²⁴

It is only possible to diagonalize these large final secular matrix because of their sparseness.²⁴ A calculation with $J = 10$ and $p = 0$ involves 11 separate k blocks, as opposed to 31 for a $J = 30$ calculation. This means that for the same size of the final Hamiltonian matrix, much better coverage of the vibrational space is obtained for the $J = 10$ calculation. We thus obtained reliable estimates for many more $J = 10$ states than $J = 30$ ones, as indicated above.

In HD_2^+ the quantum states have two parity quantum numbers: The reflection behavior in C_{2v} , i.e., whether the vibration belongs to species A_1 or B_2 , and a rotational parity (always zero for $J = 0$). So, the data come out in four (two) lists which have been merged for the comparison, since the phase space volume corresponds to the number of *all* states. Alternatively, we could have compared the state counts for separate species, applying the method of Sec. III to divide $N(E;J)$ into fractions belonging to different symmetry species. But since we seek a smooth approximation to the resulting quantum staircase, it has some advantage to have more states to compare with by merging the lists.

For H_3^+ a special problem arises from the fact that, for technical reasons (i.e., the use of Jacobi coordinates), the computation was done like that for HD_2^+ in C_{2v} symmetry, and not in D_{3h} (or C_{3v}) as it should have been. Again, we can merge all states and compare with the full phase space volume. However, it is also important to know how one can partition this number into fractions for the different irreducible representations, since species A_1 is nuclear spin forbidden in the real world, species A_2 has degeneracy four, and species E degeneracy two. (We use a description in terms of group C_{3v} , which is possible since the vibrational motion of triatomics is never odd with respect to reflection at the molecular plane.) This was the incentive to derive the formulas of Sec. III, which allow us to compare with Ref. 7, where the total number of states is given, i.e., that of $A_1 + A_2 + E$ states counting the latter *only once*, and also with the separate quantum state lists, which were obtained by counting pairs of computationally almost degenerate states as species E , the others as A_1 or A_2 depending on their symmetry. Such a decomposition is also vital to any application of the computed density of states to properties such as partition functions, which depend on nuclear spin statistics.

III. NUMBER OF STATES FOR DIFFERENT SYMMETRY SPECIES

The methods discussed up to now allow one to predict the specific number of *all* quantum states, $N(E;J)$. However, in molecules which have point symmetry, one may also ask for the *number of states*, $N(E;J,\Gamma)$, or the fractions,

$$f(E;J,\Gamma) = N(E;J,\Gamma)/N(E;J),$$

of a specific symmetry species Γ . Interest in these numbers may arise, e.g., because selection rules allow only certain species to be reached by dipole radiation, because selection rules have to be obeyed in state-specific reactions,¹⁰⁻¹² or because quantum calculations for comparison have only been done for a certain irreducible representation (as in our case). Explicit limits of $f(E;J,\Gamma)$ for $E \rightarrow \infty$, and E -dependent direct state counts $N(E;J,\Gamma)$ for separable models were discussed in Refs. 10-14. The formulas derived below for $f(E;J=0,\Gamma)$ contain terms down to $O(E^{-2})$, and are thus valid at much lower energies than those given before. For $J > 0$ it is known that the zero order terms in Eqs. (6b) or (13), will remain the same,^{10,13(b)} but additional terms $\propto (B/E)^n$, $n \geq 1$ will appear, as can be deduced from Refs. 11 and 12.

HD_2^+ belongs to symmetry group C_{2v} , and has the three normal modes ν_1 (with classical $J=0$ fundamental 2934 cm^{-1} , vibrational species A_1), ν_2 (2100 cm^{-1} , A_1), and ν_3 (2268 cm^{-1} , B_2). Note that we must distinguish here between the *vibrational* symmetry species, defined if vibration and rotation are separable including, of course, the case $J=0$, and the *rovibrational* species. Note also, that for high lying states of a real molecule with nonseparable anharmonic vibrations, the quanta ν_1 , ν_2 , ν_3 of normal mode excitation are no longer good quantum numbers, whereas the assignments to A_1 or B_2 are.

H_3^+ belongs to symmetry group D_{3h} , it has one normal mode of vibrational species A_1' (3438 cm^{-1}), and one degenerate E' mode (2777 cm^{-1}). Overtones of the latter lead also to species A_2' . Vibrations of species A_1'' , A_2'' , and E'' cannot occur, so we drop the prime in the rest of this paper. In contrast to HD_2^+ and H_2D^+ nuclear spin statistics forbids one *rovibrational* species (A_1) completely. For $J=0$ therefore A_1 states cannot occur at all.

In this section we present formulas for the fractions of states belonging to the different *vibrational* species for the two cases mentioned above, i.e., for triatomics of point groups C_{2v} and D_{3h} . Note that these fractions are *energy dependent*, i.e., we determine not only the constant asymptotic fraction for $E \rightarrow \infty$. The formulas are exact only for uncoupled, harmonic oscillators. For the general case (but still assuming separability of vibration and rotation), we propose as an approximation to use the same fractions as function of the total *number of vibrational states*, $N_{\text{vib}}(E)$, rather than as function of E itself. We feel that this will compensate, at least partially, the effects of coupling and anharmonicity on the number of states below that energy E . This is supported by comparison with the quantum data for $J=0$ within the limits set by their fluctuations (cf. Figs. 5 and 6 below).

A. C_{2v}

The normal modes are A_1, A_1, B_2 . We treat first a single vibration of species B_2 , and add the other vibrations by convolution: $N(\nu_2, \nu_3) = \rho(\nu_2) \otimes N(\nu_3)$, $N(\nu_1, \nu_2, \nu_3) = \rho(\nu_1) \otimes N(\nu_2, \nu_3)$. For a B_2 -vibration every odd overtone (including the fundamental) has species B_2 , every even overtone species A_1 . If one draws the staircases for the numbers $N(\nu_3, A_1)$ and $N(\nu_3, B_2)$ one finds that they are interpolated by the smooth functions

$$N(\nu_3, A_1) = \frac{v+1}{2} \quad \text{and} \quad N(\nu_3, B_2) = \frac{v}{2}. \quad (2)$$

So the fractions are

$$\begin{aligned} f(\nu_3, A_1) &= \frac{N(\nu_3, A_1)}{N(\nu_3, A_1) + N(\nu_3, B_2)} = \frac{v+1}{2v+1} \\ &= \frac{1}{2} \cdot \frac{1+1/v}{1+1/2v} \approx \frac{1}{2} \cdot \left(1 + \frac{1}{2v} + \dots\right), \\ f(\nu_3, B_2) &= \frac{N(\nu_3, B_2)}{N(\nu_3, A_1) + N(\nu_3, B_2)} = \frac{v}{2v+1} \\ &= \frac{1}{2} \cdot \frac{1}{1+1/2v} \approx \frac{1}{2} \cdot \left(1 - \frac{1}{2v} + \dots\right), \end{aligned}$$

and their ratio is

$$r(\nu_3) = \frac{v}{v+1} = 1 \cdot \frac{1}{1+1/v} \approx 1 \cdot \left(1 - \frac{1}{v} + \dots\right). \quad (3)$$

What looks like a harmless correction becomes a large effect, when we fold in the two A_1 vibrations. To this effect we have to convolute *on the energy scale*

$$N(\nu_2, \nu_3) = \int_0^E dE' N(\nu_3)(E') \rho(\nu_2)(E-E'), \quad (4)$$

where $N(\nu_3)$ is either

$$N(\nu_3, A_1) = \frac{E}{2\omega_3} + \frac{1}{4}, \quad \text{or} \quad N(\nu_3, B_2) = \frac{E}{2\omega_3} - \frac{1}{4}, \quad (5)$$

and $\rho(\nu_2)$ is $1/\omega_2$, and further to convolute with $\rho(\nu_1) = 1/\omega_1$. The final result for three harmonic oscillators is

$$N(\nu_1, \nu_2, \nu_3) = \frac{E^3}{6\omega_1\omega_2\omega_3} \cdot \frac{1}{2} \cdot \left(1 \pm \frac{3\omega_3}{2E}\right), \quad (6a)$$

i.e.,

$$f(E; \Gamma) = 1 \pm \frac{3\omega_3}{2E}, \quad (6b)$$

where the $+$ sign is for species A_1 , the $-$ sign for B_2 . The ratio of state numbers at energy E is therefore

$$\begin{aligned} r(\nu_1, \nu_2, \nu_3) &= \frac{N(\nu_1, \nu_2, \nu_3, B_2)}{N(\nu_1, \nu_2, \nu_3, A_1)} = \frac{E/\omega_3 - 3/2}{E/\omega_3 + 3/2} \\ &\approx 1 - 3 \cdot \frac{\omega_3}{E} + \frac{9}{2} \cdot \left(\frac{\omega_3}{E}\right)^2 + \dots \quad (7) \end{aligned}$$

for large E . This is a massive correction to the asymptotic $r=1$; the value $r=0.9$ is, e.g., only reached for $E=28.5 \cdot \omega_3$.

As we said there is no unambiguous way to apply this result to real molecules. We propose to express Eq. (6) in the

N scale [$N = N(A_1) + N(B_2)$] using Eq. (8), which holds for harmonic oscillators

$$E = (6\omega_1\omega_2\omega_3N)^{1/3} = a\omega_3N^{1/3} \quad (8)$$

with $a = (6\omega_1\omega_2/\omega_3^2)^{1/3}$. (We will drop the ν 's from now on.) From Eq. (6) we then arrive at the fractions

$$f(A_1) = \frac{N(A_1)}{N(A_1) + N(B_2)} = \frac{1}{2} \cdot \left(1 + \frac{3}{2aN^{1/3}}\right), \quad (9a)$$

and

$$f(B_2) = \frac{N(B_2)}{N(A_1) + N(B_2)} = \frac{1}{2} \cdot \left(1 - \frac{3}{2aN^{1/3}}\right), \quad (9b)$$

and their ratio

$$r = \frac{N(B_2)}{N(A_1)} = \frac{a \cdot N^{1/3} - 3/2}{a \cdot N^{1/3} + 3/2}. \quad (10)$$

We postpone the comparison with computed quantum states until Sec. IV, and treat first our second example.

B. D_{3h}

The first incentive to tackle the problem of this section came from the fact that the quantum states of H_3^+ were computed by the UCL group not in point symmetry D_{3h} , but like HD_2^+ in C_{2v} .⁷ As a consequence, the classification of states in the correct group could only be done by identifying E states as (computationally only near) degenerate pairs of A_1 and B_2 states. This procedure is limited to levels where the computational error is well below the average level spacing. In order to estimate the total number of states for each species, therefore, in Ref. 7 the asymptotic statistical fractions were used.

The calculation of fractions similar to those of Eqs. (9) and (10) is a little more involved here than in C_{2v} , since the overtones of the degenerate E mode have a more complicated species behavior. We first treat the case of a single E -mode excited to quantum level v_2 . Using for the first 12 overtones the formulas given in Ref. 27, and then applying induction, one can compute the “staircase” functions for the numbers of states for each species. The following polynomials interpolate these in such a way, that *on the average* they pass at half-height through the steps. (The cumulative error vanishes on every third step.) One obtains

$$N_2(A_1) = \frac{(v_2 + 1)^2}{12} + \frac{v_2 + 1}{4} + \frac{1}{9}, \quad (11a)$$

$$N_2(A_2) = \frac{(v_2 + 1)^2}{12} - \frac{v_2 + 1}{4} + \frac{1}{9}, \quad (11b)$$

$$N_2(E) = \frac{(v_2 + 1)^2}{3} - \frac{2}{9}. \quad (11c)$$

Their sum is $(v_2 + 1)^2/2$ or $(E/\omega_2)^2/2$ as semiclassically expected for a two-dimensional oscillator.

We now have to include mode ν_1 . The species of any excited state of ν_2 will not change if ν_1 quanta of ν_1 (of species A_1) are also excited. Therefore, we can again use simple convolution to derive our result. We get

$$N(A_1) = \frac{1}{36} \frac{E^3}{\omega_1\omega_2^2} + \frac{1}{8} \frac{E^2}{\omega_1\omega_2} + \frac{1}{9} \frac{E}{\omega_1}, \quad (12a)$$

$$N(A_2) = \frac{1}{36} \frac{E^3}{\omega_1\omega_2^2} - \frac{1}{8} \frac{E^2}{\omega_1\omega_2} + \frac{1}{9} \frac{E}{\omega_1}, \quad (12b)$$

TABLE I. Numbers of states for different symmetry species of H_3^+ in $J = 0$ at $E = 4$ eV ($32\,262\text{ cm}^{-1}$) and $E = 4.8849$ eV ($39\,399\text{ cm}^{-1}$, the nominal dissociation energy) computed in different approximations. Energies are measured from the bottom of the well. The zero point energy is 0.5410 eV (4363.5 cm^{-1}).

Energy and type of calculation	C_{2v}		D_{3h}	“all”, i.e., $A_1 + A_2 + E$	A_1	A_2	E
	Even	Odd	$A_1 + A_2 + 2E$				
$E = 4.00$ eV							
Semiclassical ^a	310	257	567	380	122	70	188
Quantal ^b	312	260	572	399 ^b	104 ^c	87 ^c	191 ^c
				364 ^d			
				381 ^e			
Assigned ^f				393	134	80	179
$E = 4.8849$ eV							
Semiclassical ^a	684	593	1277	853	260	170	424
Quantal ^b	680	596	1276	879 ^b	227 ^c	199 ^c	425 ^c
				823 ^d			
				851 ^e			

^a Data computed from phase space volume, corrected for zero point effects, multiplied by the fractions given in Eqs. (14), and rounded to integers.

^b Data computed after Ref. 7 in symmetry group C_{2v} , and partitioned as explained there, i.e., $N(\text{all states}) = N(\text{even}) + \frac{1}{2}N(\text{odd})$.

^c Computed from the asymptotic fractions: $N(A_1) = \frac{1}{2}N(\text{even})$, $N(A_2) = \frac{1}{2}N(\text{odd})$, and from $N(E) = \frac{1}{2}\{N(\text{even}) + N(\text{odd})\}$. Note from Eqs. (14) that for $N(E)$ the asymptotic value is approached much earlier than for $N(A_1)$ or $N(A_2)$.

^d Computed as $N(\text{all states}) = \frac{1}{2}N(\text{even}) + N(\text{odd})$, an alternative to b.

^e Computed as $N(\text{all states}) = \frac{2}{3}\{N(\text{even}) + N(\text{odd})\}$, which is the best asymptotic approximation in view of Eqs. (14).

^f Quantal data from Ref. 7 assigned by counting near degenerate even and odd states as E states.

$$N(E) = \frac{1}{9} \frac{E^3}{\omega_1 \omega_2^2} - \frac{2}{9} \frac{E}{\omega_1}, \quad (12c)$$

which sums to $E^3/6\omega_1\omega_2^2$ as it should. Finally, the fractions of the species are

$$f(A_1) = \frac{1}{6} + \frac{3}{4} \frac{\omega_2}{E} + \frac{2}{3} \frac{\omega_2^2}{E^2}, \quad (13a)$$

$$f(A_2) = \frac{1}{6} - \frac{3}{4} \frac{\omega_2}{E} + \frac{2}{3} \frac{\omega_2^2}{E^2}, \quad (13b)$$

$$f(E) = \frac{2}{3} - \frac{4}{3} \frac{\omega_2^2}{E^2}. \quad (13c)$$

Again, the correction to the asymptotic value for the A_1 and A_2 states is large, e.g., 90% of the asymptotic value is only reached at $E \approx 45 \cdot \omega_2$. The correction to the E state is smaller, since it has no term $\propto 1/E$; see also Table I. We apply Eqs. (13) to the real molecule by setting $E = (6\omega_1\omega_2^2 N)^{1/3} = a\omega_2 N^{1/3}$ to convert to the N scale, and identifying N with the semiclassical number of states, $N_{\text{sc}}(E)$, of the real molecule. This leads to

$$f(A_1) = \frac{1}{6} + \frac{3}{4a} N^{-1/3} + \frac{2}{3a^2} N^{-2/3}, \quad (14a)$$

$$f(A_2) = \frac{1}{6} - \frac{3}{4a} N^{-1/3} + \frac{2}{3a^2} N^{-2/3}, \quad (14b)$$

and

$$f(E) = \frac{2}{3} - \frac{4}{3a^2} N^{-2/3}. \quad (14c)$$

It is in this form with $a = (6\omega_1/\omega_2)^{1/3}$ that the fractions have been applied in the following section.

IV. RESULTS AND DISCUSSION

Quantum state counts from the calculations described in Sec. II are the yardstick for measuring the accuracy of the semiclassical numbers of states, which were generated from Monte Carlo integrated phase space volumes, and corrected for zero point effects as described in Paper I. The intramolecular potential for both calculations was identical. Except for the semiclassical replacement of J by $J + (1/2)$ and $|J|$ by $\sqrt{J(J+1)}$ in the phase space integrals, and the correction for zero point motion, nothing has been adapted or fitted.

We first show results in which phase space and quantum states have not been partitioned according to symmetry species. Figure 1 shows the results for H_3^+ in $J=0$. The staircase of all quantum states (including the forbidden A_1 states, and counting the E states twice) is plotted against energy E , measured from the bottom of the effective (i.e., J dependent) potential well. (For the A_2 states alone see Fig. 6.) The reduced energy scale

$$E' = \frac{E - E_z}{E_z} \quad (15)$$

(E_z is the zero point energy) is also indicated. The semiclassical result is shown with and without correction. One sees that the correction improves the agreement systematically. Better resolution is obtained in Fig. 2, which shows the differences between semiclassical and quantum counts. Apply-

FIG. 1. Numbers of quantum states for H_3^+ , $J=0$ vs energy E (lower scale), and reduced energy E' [Eq. (15)] (upper scale). The staircase gives the quantum result, the upper smooth curve the semiclassical result without correction, the lower one the corrected semiclassical result. In (a) we show at the lower right also the so-called "classical" approximation (e.g., Ref. 1), in which the full zero point energy is subtracted. Note that (a) has a logarithmic scale.

ing the correction leaves a mean difference of the order of one count in 900 at about 4.7 eV. The steep increase of ΔN above 4.9 eV seems to indicate a systematic deviation of the quantum state count due to loss of convergence near the first dissociation limit (assumed to be 4.885 eV in the quantum calculations⁷).

For this $J=0$ example all absolute differences are small numbers. For $J>0$ they grow by a factor somewhat less

FIG. 2. Difference ΔN between the semiclassical number of states and the number of quantum states for H_3^+ in $J = 0$ vs E and E' . Upper trace and left scale: taken with uncorrected semiclassical $N(E)$. Lower trace and right scale: with corrected $N(E)$.

than, but of the order of $2J + 1$. Larger differences occur therefore for $J = 10$ and 30 , where we have quantal energies from HD_2^+ . Figures 3 and 4 show some sample data. It is obvious that the Whitten–Rabinovitch correction improves the agreement between quantum and semiclassical state numbers appreciably, and that the application of the correction to the vibrational part of the energy only, called method (b) in Paper I is superior to the simpler method (a), in which the total energy is shifted. Only Fig. 4(b) for $J = 30$ shows some residual difference, which may indicate, that the correction is still too small. Another possibility is a large fluctuation (note that due to so much energy bound in rotation the vibrational excitation is small here). An unambiguous decision would need more computed quantum states.

Results for specific symmetry species are shown in Figs. 5 and 6. The first shows the ratio of quantum states of species A_1 and B_2 for HD_2^+ , $J = 0$ compared to the result of Eqs. (7) and (10). There is a clear tendency for Eq. (10) to give the better fit, especially at high E , though one would like to have a few more computed quantum states for an unambiguous decision.

Figure 6 shows the number of states function, $N(E)$, of the lowest A_2' states of H_3^+ in $J = 0$. They were obtained from the quantum calculation done in symmetry C_{2v} (Ref. 7) by looking for near degeneracies between A_1 and B_2 states, and assigning those almost coinciding as E states in D_{3h} . Their number is compared here with the semiclassical $N(E)$ from Paper I multiplied by the fraction $f(A_2')$ from Eq. (14b). The agreement is rewarding, even though one sees the limits of the method of classifying E states from near energy coincidences at the upper end of the energy scale. A

(a)

(b)

FIG. 3. Similar to Fig. 1 for HD_2^+ in $J = 10$. The curves corrected after method (a) of Paper I are shown, they practically coincide with those from method (b).

more precise estimate for the total number of states (i.e., A_1 plus A_2 states plus E states counted singly) below an energy of 4.885 eV (which is the assumed dissociation energy measured from the bottom of the H_3^+ well to the lowest level of $\text{H}_2 + \text{H}^+$), which was given as 881 in Ref. 7 is now 853 ± 2 states. A breakdown of the semiclassical state numbers at $E = 4.00$ and 4.885 eV is given in Table I.

Let us stress again that this is the first test of the numerical virtues of semiclassically computing the number of states for a system, which is more realistic than a nonrotating mod-

(a)

(b)

FIG. 4. Similar to Fig. 1 for HD_2^+ in $J = 30$. The smooth curves are from top: uncorrected semiclassical, corrected after method (a) of Paper I, corrected after method (b); in (a) at the lower right also the so-called classical approximation.

el of uncoupled harmonic oscillators. It is possible, because quantum ladders of a length, which makes such a comparison meaningful, have been computed for the first time for any molecule. The agreement obtained is, indeed, gratifying. It shows that, given the potential, the calculation of hundreds or thousands of quantum states only to get a correct state density will not be necessary. Though the results apply immediately only to H_3^+ and its isotopomers, one expects them to hold at least for the broad class of "normal," chemi-

FIG. 5. Ratio of number of states of species B_2 to that of species A_1 for HD_2^+ in $J = 0$ vs energy E and reduced energy E' . The true ratio of quantum states jumps at every new state. The dashed curve implements Eq. (7), the dotted one Eq. (10) identifying N with the continuous semiclassical $N(E)$.

cally bound triatomic molecules. In addition, there is no reason to believe that floppy triatomics or other polyatomics will behave much differently. The bottleneck in the precise determination of quantum state counts and state densities will, obviously, always be the knowledge of the intramolecular potential. Without that knowledge one will always be

FIG. 6. Number of states of species A_2 for H_3^+ in $J = 0$. The staircase is the quantum result determined (Ref. 7) from the C_{2v} calculations as described in the text, the smooth curve the corrected semiclassical result multiplied with the fraction, $f(A_2)$, Eq. (14b).

constrained to the use of approximations of the RRHO type modified by well known—but not so well proven—corrections for anharmonicity and similar effects.

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