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Reply to Comment on: Discrepancies between variationally calculated vibrational energies of H_3^+

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In their Comment Carter and Meyer (CM)[1] analyze discrepancies between calculations performed by us on H_3^+ (Refs. 2–4) and their work on the same systems.[5] For $J=0$ calculations, A_1' energies agree within the convergence limits of the various works, but for A_2' and E' symmetries our work[2,3] gives energies lower than CM's[1,5] for states above the barrier to linearity. CM attribute this discrepancy to our spherical oscillator basis functions. They focus on the behavior of these functions at $R=0$ in scattering coordinates which defines a linear geometry and claim that our use of nonregular functions leads to spurious results at linearity. We dispute this claim.

Maybe regular spherical oscillator functions are a better basis for quasilinear systems. However, in variational calculations a poor basis will always give energies which are too high. Thus, in our first application of a discrete variable representation (DVR) to H_3^+ (Ref. 2) we studied rotationally excited states with $J=1$. We had difficulty converging the rotationally excited levels associated with vibrational states with amplitude at linearity. This problem was almost certainly caused by our use of the same spherical oscillator functions for $J=0$ and $J=1$ calculations.

We remain unclear as to the cause of the difference between CM's calculations and ours. At CM's prompting we performed calculations with all calls to the potential evaluated with $\phi = 0$ in their hyperspherical coordinates. This introduces extra degeneracies which CM's symmetrized basis reproduce exactly. Our calculations give the structure of levels noted by CM: all our odd states had a (quasi)degenerate even counterpart and there were further ($m=0$) even states.

At low energies the splitting between the quasidegenerate odd/even pairs were small but rose rapidly above about 12 000 cm^{-1}. An extreme example was a state at 13 210 cm^{-1} which was split by 47 cm^{-1}. In contrast to the results on the full potential, even states were generally lower than odd one. Tests showed that this splitting was stable to changes in our spherical oscillator basis set, the number of angular DVR points and the size of the final Hamiltonian. The splitting was sensitive to the Morse oscillatorlike functions for the r coordinate.

This sensitivity is due to our Morse-type functions having amplitude at $r=0$ as shown by the presence of grid points with the smallest value of r in our final Hamiltonian. As Morse functions do not behave correctly at the $r=0$ boundary, having amplitude there can cause nonvariational behavior. Removing all points with the smallest value of r from our final basis reduced the splitting by a factor of about 6. In these calculations the odd levels were largely unchanged and the even states were raised above the odd ones.

Calculations with the full H_3^+ potential are less sensitive to the r basis and no grid points with the smallest value of r were ever retained in our final Hamiltonian. We conclude that although our methods are poorly suited to the unphysical $\phi = 0$ calculations, the problems encountered with it do not affect our actual H_3^+ calculations. The difference in behavior is caused by the $\phi = 0$ projection moving geometries with short H–H separations into regions of low potential energy.

We have improved on our previous 3D H_3^+ DVR calculations[3] by retaining $N=4000$ (rather than 3300) contracted functions in our final Hamiltonian. These results show that the calculations behave variationally up to the H_3^+ dissociation limit and are in line with the convergence claims made previously.[3] Table I compares our new results with those of CM and our previous work.

For the recent studies of H_3^+ we have used s wave spherical oscillators (i.e., $l=\alpha=0$). These were chosen while performing 2D quantal and semi-classical calculations on H_3^+ (Ref. 6) because the wave functions had the correct behavior as $R \to 0$. The semiclassical calculations were performed in a domain defined by $-\infty \leqslant R \leqslant +\infty$ and the $\alpha = 0$ spherical oscillators matched semiclassical solutions with odd parity about $R=0$. Spherical oscillators with $\alpha = -1$ were found to match semiclassical results with even parity about $R=0$. As the 2D odd functions have the correct behavior at $R=0$ in 3D these functions were chosen for later work.[2–4]

For our E' states in Table I we tabulate both the results obtained from both even and odd calculations. Of course in a fully converged or properly symmetrized calculation these number should be the same. Inspection of the even results shows that while all our A_1' levels are within 1 cm^{-1} of CM's (their convergence limit), the differences are larger for the E' levels even for our calculations which used "regular" functions approved by CM. These larger differences for E' (and A_2') states can also be seen in the recent calculations of Day and Truhlar,[7] and Bačić and Zhang,[8] although these workers do not see discrepencies on the scale of those found by our odd calculations and in particular the odd $\alpha = 1$ results discussed below.

We have also performed calculations with $\alpha = +1$ spherical oscillators in the R coordinate. According to CM these oscillators have the correct regular behavior at $R=0$ for odd parity calculations. In these calculations we kept

TABLE I. Comparison of H_3^+ band origins quoted by CM[1] in cm^{-1}. Our results are tabulated as differences in cm^{-1} from CM's. For E' states we tabulate, respectively, even and odd parity levels. Our results were obtained using spherical oscillator functions with $\alpha = 0$ except for the columns marked * which used $\alpha = 1$ functions.

S	CM (Ref. 5)	$N = 3300$ (Refs. 3 and 4)	$N = 4000$	$N = 3300$*	S	CM (Ref. 5)	$N = 3300$ (Refs. 3 and 4)		$N = 4000$		$N = 3300$*	
A_1'	13 705.9	−0.4	−0.5	43.3	A_2'	13 747.4	−0.7		−0.7		−0.7	
	14 186.0	−0.4	−0.5	2.7		15 179.0	−0.9		−0.9		−1.1	
	14 662.7	0.0	0.0	0.3		15 951.0	−1.1		−1.1		−1.4	
	14 886.3	0.7	0.6	2.0		16 579.0	−2.2		−2.3		−4.3	
	14 938.5	0.3	0.3	0.5		17 077.4	−1.0		−1.0		−1.9	
	15 061.5	−0.3	−0.3	10.1		17 671.5	−1.0		−1.1		−1.5	
	15 157.7	0.1	−0.1	32.0		17 806.9	−4.1		−4.1		−11.1	
	15 867.6	0.1	0.0	3.1		17 846.0	−4.6		−4.7		−14.3	
	15 908.9	0.1	−0.1	5.3		18 316.9	−1.5		−1.6		−3.2	
	16 195.0	0.4	−0.3	10.0		18 867.0	−2.1		−2.2		−3.6	
	16 443.6	−0.2	−0.3	0.4		19 175.1	−4.9		−4.9		−15.1	
	16 694.3	−0.4	−0.4	6.4	E'	13 681.5	−0.4,	−0.6	−0.6,	−0.6	14.0,	−0.6
	17 060.8	0.1	0.0	3.6		15 325.0	−0.4,	−0.6	−0.6,	−0.6	2.4,	−0.9
	17 272.8	−0.2	−0.3	10.5		16 546.8	−1.3,	−2.7	−1.3,	−2.7	0.9,	−6.6
	17 428.1	0.3	0.1	5.6		16 909.5	−0.3,	−0.7	−0.3,	−0.7	4.4,	−1.7
	17 585.3	0.4	0.3	2.4		17 440.7	−0.5,	−1.7	−0.7,	−1.7	6.0,	−2.9
	17 679.9	0.8	0.6	4.2		17 691.0	0.1,	−0.8	−0.1,	−0.9	8.1,	−2.4
	17 745.0	−0.5	−0.7	30.7		17 849.3	−1.1,	−3.4	−1.3,	−3.4	1.2,	−3.5
	18 226.1	0.1	−0.2	17.7		17 957.1	−1.0,	−1.2	−1.1,	−1.2	4.5,	−1.4
	18 358.6	0.2	0.0	5.0		18 209.1	0.3,	−1.2	0.0,	−1.3	8.1,	−2.6
	18 454.0	0.0	−0.2	83.1		18 345.4	0.1,	−0.6	0.0,	−0.7	4.8,	−1.1
	18 582.8	0.1	−0.1	15.2		18 568.3	−1.1,	−1.9	−1.2,	−2.0	12.6,	−3.1

all other parameters unchanged from $\alpha = 0$ calculations quoted above. As can be seen from Table I, the $\alpha = 1$ functions give *lower* energies for our odd states and higher energies for the even (A_1') states. This is in line with our expectations and with CM's observation that $\alpha = 1$ oscillators are the appropriate basis functions for the odd parity states. These observations do not resolve the discrepancy between the H_3^+ calculations but do support our view that it is not due to our spherical oscillator functions.

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