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Matthew J. BramleyJames R. Henderson and Jonathan TennysonBrian T. Sutcliffe

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On the Meyer–Botschwina–Burton potential energy surface for H_3^+

Matthew J. Bramley[a)]
Département de Chimie, Université de Montréal, C.P. 6128, Succursale A, Montréal (Québec) H3C 3J7, Canada

James R. Henderson and Jonathan Tennyson[b)]
Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom

Brian T. Sutcliffe
Department of Chemistry, University of York, Heslington, York Y01 5DD, United Kingdom

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In 1986 Meyer, Botschwina, and Burton (MBB) published a systematic and accurate *ab initio* study of the electronic structure of H_3^+.[1] This study contained a number of potential energy surfaces for the molecular ion, including one, the 31 term (one of which merely sets the energy zero), seventh-order 87 GTO corrected surface which had one term adjusted to reproduce the observed H_3^+ bending fundamental. This surface is generally known as the MBB potential and has played an important part in aiding the laboratory and astronomical understanding of this fundamental system. For recent reviews see Refs. 2 and 3.

The surface has also been widely used for rotation-vibration studies of H_3^+ at high energies. During the course of our recent work on this topic,[4,5] it has become apparent that there are two slightly different implementations of the MBB potential energy surface in general use and that this difference is responsible for small disagreements between calculations.

In their paper, MBB give the form of their fitted potential as

$$V=\sum_{n,m,k} V_{n,m,k}S_a^nS_e^{2m+3k}\cos(3k\phi), \quad n+2m+3k\leqslant N, \tag{1}$$

where the $V_{n,m,k}$ are the coefficients determined by fitting and the value of N determines the order of the fit. The coordinates (S_a, S_e, ϕ) are related to the atom–atom distances (R_{12}, R_{23}, R_{31}), by two transformations. The first transformation changes the atom–atom distances to Morse coordinates

$$\widetilde{R}=\left[1-\exp\left(-\beta\frac{R-R_e}{R_e}\right)\right]\Big/\beta. \tag{2}$$

The second transformation is to symmetry-adapted deformation coordinates

$$S_a=(\widetilde{R}_{12}+\widetilde{R}_{23}+\widetilde{R}_{31})/\sqrt{3}, \tag{3}$$

$$S_x=(2\widetilde{R}_{12}-\widetilde{R}_{23}-\widetilde{R}_{31})/\sqrt{6}=S_e\cos(\phi), \tag{4}$$

$$S_y=(\widetilde{R}_{23}-\widetilde{R}_{31})/\sqrt{2}=S_e\sin(\phi). \tag{5}$$

It is possible to express the MBB expansion directly as a function of (S_a, S_x, S_y) instead of (S_a, S_e, ϕ); indeed this expansion is given explicitly by Lie and Frye.[6] In this case useful intermediate parameters in the expansion are[7]

$$S_b^3=S_x^3-3S_xS_y^2, \tag{6}$$

$$S_c^3=S_y^3-3S_yS_x^2. \tag{7}$$

The more widely-used (A) of the two implementations of the MBB potential has been employed by Tennyson and co-workers,[4,8] Whitnell and Light,[9] Bačić and Zhang,[10] and Day and Truhlar,[11] and uses the (S_a, S_x, S_y) coordinates. The problem arises with the two terms with $k=2$ in the expansion (1): $S_e^6\cos(6\phi)$ and $S_aS_e^6\cos(6\phi)$. These terms are related to (S_a, S_x, S_y) via the identity

$$S_e^6\cos(6\phi)=S_b^6-S_c^6. \tag{8}$$

However, we now realize that, in implementation A, the S_c^6 was omitted, and simply S_b^6 and $S_aS_b^6$ were used for the two terms in question. We note that this error does not break the threefold permutational symmetry of the potential.

The problem came to light in work by Bramley and Carrington,[5] who used an independent implementation (B) of the MBB surface expressed in S_a, S_e, ϕ and free of the error. Calculating band origins up to 18 000 cm^{-1} (and using the most recently recommended fundamental constants[12,13]), they reproduced to within 0.1 cm^{-1} the results of Carter and Meyer,[14] which disagree with those of Tennyson and co-workers[4] by as much as 1.5 cm^{-1} in this energy range. On switching to implementation A,[15] and on changing the conversion factor between the unified atomic mass unit and the electron rest mass to the value[16] used consistently in the work of Tennyson and co-workers,[4,8] agreement was obtained with Ref. 4 to within 0.1 cm^{-1}. Two additional conclusions may be drawn: the results of Refs. 4, 5, and 14 are all effectively converged in this energy range with respect to increases in basis size; and Ref. 14 used an implementation of the MBB potential equivalent to B as well as fundamental constants insignificantly different from those of Ref. 12.

To aid future work on this important molecule, the authors (M.J.B. or J.T.) can supply corrected (i.e., implementation B) FORTRAN sources for the MBB potential on request.

[a)] Electronic mail address: bramleym@ere.umontreal.ca.
[b)] Electronic mail address: jt@ib.rl.ac.uk.

[1] W. Meyer, P. Botschwina, and P. G. Burton, J. Chem. Phys. **84**, 891 (1986).
[2] T. Oka, Rev. Mod. Phys. **64**, 1141 (1992).
[3] S. Miller and J. Tennyson, Chem. Soc. Rev. 21, 281 (1992).
[4] J. R. Henderson, J. Tennyson, and B. T. Sutcliffe, J. Chem. Phys. (in press).
[5] M. J. Bramley and T. Carrington, Jr., J. Chem. Phys. (submitted).
[6] G. C. Lie and D. Frye, J. Chem. Phys. **96**, 6784 (1992).
[7] Note that the expressions given for S_b and S_c by Lie and Frye (Ref. 6) are incorrect.
[8] S. Miller and J. Tennyson, Chem. Phys. Lett. **145**, 117 (1988); J. Tennyson and J. R. Henderson, J. Chem. Phys. **91**, 3815 (1989); J. R. Henderson and J. Tennyson, Chem. Phys. Lett. **173**, 133 (1990); J. Tennyson, O. Brass, and E. Pollak, J. Chem. Phys. **92**, 3005 (1990); B. M. Dinelli, S. Miller, and J. Tennyson, J. Mol. Spectrosc. **153**, 718 (1992); J. Tennyson, J. Chem. Phys. (in press).
[9] R. M. Whitnell and J. C. Light, J. Chem. Phys. **90**, 1774 (1989).
[10] Z. Bačić and J. Z. H. Zhang, Chem. Phys. Lett. **184**, 513 (1991); Z. Bačić and J. Z. H. Zhang, J. Chem. Phys. **98**, 3707 (1992).
[11] P. N. Day and D. G. Truhlar, J. Chem. Phys. **95**, 6615 (1991); Q. Zhang, P. N. Day, and D. G. Truhlar, *ibid.* (in press).
[12] *Quantities, Units, and Symbols in Physical Chemistry*, edited by I. M. Mills (Blackwell, Oxford, 1988).
[13] It should be noted that all works quoted here appear to have used *atomic* hydrogen masses consistent with the original work of MBB (Ref. 1).
[14] S. Carter and W. Meyer, J. Chem. Phys. **93**, 8902 (1990); S. Carter and W. Meyer, *ibid.* **96**, 2424 (1991).
[15] In some versions of implementation A, including that used for Ref. 5, a cutoff for atom–atom distances less than $0.7a_0$ has been used. Our tests showed that the differences between band origins calculated with and without this cutoff are insignificant, rising to a maximum of 0.1 cm^{-1} at dissociation.
[16] S. Carter, P. Rosmus, N. C. Handy, S. Miller, J. Tennyson, and B. T. Sutcliffe, Comp. Phys. Comm. **55**, 71 (1989).