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AN EFFECTIVE COMPUTATIONAL APPROACH TO THE CALCULATION OF THE VIBRATION–ROTATION SPECTRA OF TRIATOMIC MOLECULES

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The results of some highly accurate non-empirical ro-vibrational calculations on H_2D^+ are reported including some for $J = 30$ which are the first calculations to describe such a highly rotationally excited state. These results are obtained using an improved version of our algorithm. The method used is a variational one and is well adapted to execution on supercomputers. The computational characteristics of the performance the method on the CRAY 1s and the CRAY XMP 48 are given.

1. Introduction

Developments in electronic structure calculations have made possible the construction of accurate potentials, at least for small molecules, and thus opened the way for a variety of fully non-empirical nuclear-motion calculations to which this issue is a testimony. One such problem is the *variational* calculation of molecular vibration–rotation spectra. Early work in this area was performed using the Eckart–Watson Hamiltonian. Pioneers in these developments were Carney and Porter (for a review, see Carney et al. [1]), and Handy and Whitehead [2]. The work to be described here is a development of that variational approach.

Central to the construction of the body-fixed frame in which much of the pioneering work was performed is the assumption of an equilibrium molecular geometry. It has long been recognised (see e.g. Sayvetz [3]) that there are problems when describing large amplitude internal nuclear motions within this assumption. Generally speaking these problems have been addressed only in circumstances where the potential is known to have a very shallow minimum in some direction (as in, for example, free rotation about a single bond). But the problems must become ubiquitous for sufficiently high energy. Modern spectroscopic investigations (see e.g. refs. [4,5]) can probe these regions of high energy. It is therefore clearly important to develop a method of calculating the spectrum which is capable of giving good results both at lower energies where the Eckart–Watson Hamiltonian is usually effective, and at higher energies, where it is liable not to be. There are obvious advantages to formulating a method in terms of a single Hamiltonian, independent of any assumptions about equilibrium geometry, which is effective over the complete range of energies and is adaptable to the details of the potential as revealed by calculation.

Such a Hamiltonian for a triatomic system is described in what follows. An account is given of its use in describing the highly excited rotation–vibration spectrum of H_2D^+.

The states of concern are those for which a clear separation between rotational and vibrational motion is not possible because of the progressive overlap of rotational manifolds belonging to different vibrational

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states. The states are those, therefore, that would probably not be well described in terms of solutions to the Eckart–Watson hamiltonian and our traditional ideas of molecular spectroscopy.

Indeed an initial study [6] for $J \leqslant 20$ suggests that at J of about 25 for H_2D^+ the lowest vibrational excitation should be at a lower energy than the first rotational excitation! It is in order to probe this potentially interesting and unexplored region of the spectrum that we have developed the refined algorithm presented here.

We are thus able to give the first *ab initio* results for a fully coupled triatomic system with $J = 30$.

2. The Hamiltonian

Recently some rather general methods for the construction of Hamiltonians in body-fixed coordinates have been developed [7,8] and in a recent paper [9] it has been shown how to construct a body-fixed Hamiltonian with the desirable properties outlined above for a triatomic molecule, on the basis of these methods.

In order to establish the notation a brief summary of that Hamiltonian will be given here. More details may be found in ref. [9].

A pair of translation-free internal coordinates $\boldsymbol{t}_i$, $i = 1, 2$ are constructed in terms of the lab-fixed coordinates $\boldsymbol{x}_i$, $i = 1, 2, 3$ of the three particles as

$$\boldsymbol{t}_1 = \boldsymbol{x}_3 - \boldsymbol{x}_2, \quad \boldsymbol{t}_2 = \boldsymbol{x}_1 - g\boldsymbol{x}_2 + (g-1)\boldsymbol{x}_3, \quad 0 \leqslant g \leqslant 1. \tag{1}$$

Among the translation-free coordinate sets that have such a form is one in which $\boldsymbol{t}_2$ is the bond-length vector from particle 2 to particle 1, obtained by setting $g = 1$. Also possible is the collision- or scattering-coordinate set in which $\boldsymbol{t}_2$ is the vector from the centre-of-mass of the diatomic 2–3 ($\boldsymbol{t}_1$) to particle 1. In this case

$$g = m_2 m_{\mathrm{d}}^{-1}, \quad m_{\mathrm{d}} = m_2 + m_3 \tag{2}$$

but many more forms are possible.

Whatever the precise choice made for g, a suitable set of rotation-free internal coordinates is r_1 the length of $\boldsymbol{t}_1$, r_2 the length of $\boldsymbol{t}_2$ and θ the angle between $\boldsymbol{t}_1$ and $\boldsymbol{t}_2$. The body-fixed frame may be defined by placing the z-axis along $\boldsymbol{t}_1$ (or $\boldsymbol{t}_2$), and requiring the other coordinate to remain in the positive x-half on the x–z plane defined by the three particles. The body-fixed axis system is chosen to be right-handed. Making such choices the body-fixed Hamiltonian may be written down and its form is given in full in ref. [9]. On both physical and computational grounds it is appropriate to regard this Hamiltonian as working on a manifold of function of the form:

$$r_1^{-1} r_2^{-1} \Psi_{mnkj}^{J}(r_1, r_2) \Theta_{jk}(\theta) \,|\, JMk\rangle. \tag{3}$$

Here $|\, JMk\rangle$ is a standard angular momentum eigenfunction in the Euler angles for the rotation of the molecule as a whole and $\Theta_{jk}(\theta)$ is an associated Legendre polynomial in the Condon and Shortley phase convention [10]. The total energy of the system does not depend on M, the component of total angular momentum along the space-fixed z-axis. So without loss of generality one can consider only the ordinary angular eigenfunctions $|\, Jk\rangle$.

The body-fixed Hamiltonian is allowed to operate on functions of the form (3) and the results are multiplied from the left by $(\Theta_{j'k'} \,|\, Jk'\rangle)^*$ followed by integrations over the Euler angles and θ. This leads to an effective Hamiltonian which determines $\Psi_{mnkj}^{J}(r_1, r_2)$. The choice of form made for the radial functions in (3) is equivalent to incorporating the radial part of the Jacobian into the operator so that subsequent radial integrations are over $\mathrm{d}r_1$, $\mathrm{d}r_2$. It results in an effective Hamiltonian which is manifestly Hermitian. The form of the Hamiltonian is

$$\hat{H} = \hat{K}_{\mathrm{V}}^{(1)} + \hat{K}_{\mathrm{V}}^{(2)} + \hat{K}_{\mathrm{VR}}^{(1)} + \hat{K}_{\mathrm{VR}}^{(2)} + V, \tag{4}$$

where

$$\hat{K}_{\mathrm{V}}^{(1)} = \delta_{j'j}\delta_{k'k}\left[-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r_1^2} - \frac{\hbar}{2\mu_2}\frac{\partial^2}{\partial r_2^2} + \frac{\hbar^2}{2}j(j+1)\left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right)\right], \tag{5}$$

$$\begin{aligned}\hat{K}_{\mathrm{V}}^{(2)} = & -\frac{\hbar^2}{\mu_{12}} d_{jk}\delta_{j'j+1}\delta_{k'k}\left(\frac{\partial}{\partial r_1} - \frac{(j+1)}{r_1}\right)\left(\frac{\partial}{\partial r_2} - \frac{(j+1)}{r_2}\right) \\ & -\frac{\hbar^2}{\mu_{12}} d_{j-1,k}\delta_{j'j-1}\delta_{k'k}\left(\frac{\partial}{\partial r_1} + \frac{j}{r_1}\right)\left(\frac{\partial}{\partial r_2} + \frac{j}{r_2}\right),\end{aligned} \tag{6}$$

$$\hat{K}_{\mathrm{VR}}^{(1)} = \delta_{k'k'}\delta_{j'j'}\frac{\hbar^2}{2\mu_1 r_1^2}\left(J(J+1) - 2k^2\right) - \delta_{j'j}\frac{\hbar^2}{2\mu_1 r_1^2}\left(\delta_{k'k+1}C_{Jk}^{+}C_{jk}^{+} + \delta_{k'k-1}C_{Jk}^{-}C_{jk}^{-}\right), \tag{7}$$

$$\begin{aligned}\hat{K}_{\mathrm{VR}}^{(2)} = & \,\delta_{k'k+1}\delta_{j'j+1}\frac{\hbar^2}{2\mu_{12}}C_{Jk}^{+}\frac{a_{jk}}{r_1}\left(\frac{(j+1)}{r_2} - \frac{\partial}{\partial r_2}\right) + \delta_{k'k+1}\delta_{j'j-1}\frac{\hbar^2}{2\mu_{12}}C_{Jk}^{+}\frac{b_{jk}}{r_1}\left(\frac{j}{r_2} + \frac{\partial}{\partial r_2}\right) \\ & + \delta_{k'k-1}\delta_{j'j+1}\frac{\hbar^2}{2\mu_{12}}C_{Jk}^{-}\frac{a_{j-k}}{r_1}\left(\frac{(j+1)}{r_2} - \frac{\partial}{\partial r_2}\right) + \delta_{k'k-1}\delta_{j'j-1}\frac{\hbar^2}{2\mu_{12}}C_{Jk}^{-}\frac{b_{j-k}}{r_1}\left(\frac{j}{r_2} + \frac{\partial}{\partial r_2}\right).\end{aligned} \tag{8}$$

V is the full potential, if it is expressed by means of the Legendre expansion

$$V(r_1, r_2, \theta) = \sum_{\lambda} V_{\lambda}(r_1, r_2) P_{\lambda}(\cos\theta) \tag{9}$$

then integrating over θ gives

$$V = \sum_{\lambda j} \delta_{kk'} g_{\lambda}(j', j, k) V_{\lambda}(r_1, r_2), \tag{10}$$

where the Gaunt coefficient in (10) is

$$g_{\lambda}(j', j, k) = (-1)^k\left[(2j'+1)(2j+1)\right]^{1/2}\begin{pmatrix} j' & \lambda & j \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} j' & \lambda & j \\ -k & 0 & k \end{pmatrix} \tag{11}$$

using the conventional notation [11] for the 3-j symbols.

In the above expressions the embedding is for z along $\boldsymbol{t}_1$. To obtain the expressions for z along $\boldsymbol{t}_2$ it is simply necessary to interchange r_1 and r_2 and μ_1 and μ_2. The auxilliary quantities are defined as follows

$$d_{jk} = \left[(j-k+1)(j+k+1)/(2j+1)(2j+3)\right]^{1/2}, \tag{12}$$

$$a_{jk} = \left[(j+k+1)(j+k+2)/(2j+1)(2j+3)\right]^{1/2}, \tag{13}$$

$$b_{jk} = \left[(j-k)(j-k-1)/(4j^2-1)\right]^{1/2}, \tag{14}$$

$$C_{jk}^{\pm} = \left(j(j+1) - k(k\pm 1)\right)^{1/2}. \tag{15}$$

The effective operator is diagonal in J and no explicit reference is made to this. Otherwise the

Kronecker deltas show the coupling within the rotational and the angular manifolds. The reduced masses in the expressions are given by

$$\mu_1^{-1} = m_2^{-1} + m_3^{-1}, \quad \mu_2^{-1} = m_1^{-1} + g^2 m_2^{-1} + (1-g)^2 m_3^{-1}, \quad \mu_{12}^{-1} = g\left(m_2^{-1} + m_3^{-1}\right) - m_3^{-1}, \tag{16}$$

and it is easily seen that when collision coordinates are chosen μ_{12}^{-1} becomes zero and thus $\hat{K}_{\mathrm{V}}^{(2)}$ and $\hat{K}_{\mathrm{VR}}^{(2)}$ vanish.

It should be noticed that the form of the Hamiltonian (4) is such that no singularities arise when $\theta = 0$ or π so that linear configurations of the particles are accommodated for all g without special provision.

3. The method

Previous experience [12–18] has shown that the trial functions Ψ_{mnkj}^{J} can be very effectively chosen as products of ortho-normal Morse-oscillator-like functions, $H_n(r_1)$. If the parameters of these functions are optimised then it does not prove necessary to allow for any dependence on J, k or j. Details of the choice of these functions and of the analysis for the calculation of their matrix elements over the effective Hamiltonian can be found in ref. [9]. Details of the actual computational schemes used in matrix element evaluation can be found in refs. [19,20].

The complete trial wave function is taken to be a linear combination of functions like (3), with the radial functions Ψ_{mnkj}^{J} realised as products $H_n(r_1)H_m(r_2)$. If, however, such a trial function is used directly with the complete Hamiltonian to perform fully coupled rotation–vibration calculations, the problem rapidly becomes intractable for large J, since every function of the internal coordinates must, in principle, be associated with $2J + 1$ rotational functions.

Actually, the increase is not quite so fast as this in a triatomic since planar symmetry can be used to separate the problem into two parts each of dimension $J + p$ where $p = 0$ and 1. The $p = 0$ states are conventionally designated e and while the $p = 1$ are called f. The parity of each of these parts is given by $(-1)^{J+p}$. Even so the rapid increase of problem size with J has limited calculations of this type to J values of 4 or less.

Recently, however, the authors have developed a two-step approach [6,9,21] involving a second variational step. This seems to be very effective in achieving high accuracy for high J states while keeping the problem tractable.

The procedure is similar to the one used by Chen et al. [22] in calculations on H_2O using the Eckart–Watson Hamiltonian. It is based on the observation that for many systems the potential is such that an internal coordinate system can be chosen in such a way that k (the projection of J along the body-fixed z-axis) is nearly conserved. It is thus possible to obtain reasonable approximate solutions to the full problem simply by solving the problem specified by

$$\hat{H}_k = \hat{K}_{\mathrm{V}}^{(1)} + \hat{K}_{\mathrm{V}}^{(2)} + \delta_{k'k}\hat{K}_{\mathrm{VR}}^{(1)} + V \tag{17}$$

for each k value of interest.

In (17) $\delta_{k'k}\hat{K}_{\mathrm{VR}}^{(1)}$ signifies the first term in (7). It is often said that $\hat{H}_k$ is formed by the neglect of off-diagonal Coriolis interactions. The solutions to the full problem are then expressed in terms of the solutions to the problems specified by (17).

The method can lead to savings if not all the solutions are required to converge the low lying states of the full problem. In addition the resulting full secular problem has a sparse structure which can be utilised computationally.

The linear variational solution to $\hat{H}_k$ with eigenvalue ϵ_{ki} for fixed J can be written (cf. (3)) as

$$|ki\rangle = \sum_{j,m,n} c^{J,k,i}_{j,m,n} H_n(r_1) H_m(r_2) \Theta_{jk}(\theta) \,|\, Jk\rangle \tag{18}$$

and the matrix elements of the full Hamiltonian are then

$$\langle k', i' \,|\, \hat{H} \,|\, k, i\rangle = \delta_{k'k}\delta_{i'i}\epsilon_{ki} + \delta_{k',k\pm 1}\left\langle k', i'\middle| \hat{K}^{(1)}_{\mathrm{VR}} + \hat{K}^{(2)}_{\mathrm{VR}} \middle| k, i\right\rangle, \tag{19}$$

where $\hat{K}^{(1)}_{\mathrm{VR}}$ consists of the remaining terms of (7) not used in (17). The off-diagonal matrix elements that form the second term in (19) can be evaluated by transforming matrix elements over the original basis functions.

The first step in the calculation is the solution of a series of secular problems specified by the $\hat{H}_k$. This is, technically, the same process as solving a pure $J = 0$ vibrational problem but in the present case, the terms from $\hat{K}^{(1)}_{\mathrm{VR}}$ in $\hat{H}_k$ effectively modify the pure potential so that it depends on J and k. For a given J it is sufficient to solve $J + 1$ such problems (rather than $2J + 1$) because $\hat{H}_k$ contains terms only in k^2.

A appropriate sub-set of these solutions may then be used in the secondary variational step. To form the full matrix elements it is simply necessary to perform a two-index transformation with the coefficients of (18) over the original matrix elements and the secular problem may then be solved.

As is seen from the form of (19), the secondary secular equation can be stored as a vector of diagonal elements ϵ_{ki} and a rectangular matrix $\mathbf{O}^k$ of off-diagonal elements. If the N lowest eigenfunctions of $\hat{H}_k$ are used for each k then $\mathbf{O}^k$ contains the N^2 dimensional block linking $|ki\rangle$ to $|k + 1, i'\rangle$. There are $J - p$ such blocks so the storage is approximately a factor J less than that of storing the full matrix.

In the present calculations on H_2D^+ scattering coordinates with z along the scattering (r_2) axis are an appropriate choice for the potential expansion. Such a coordinate choice also provides an extra element of symmetry in any AB_2 system because here the Gaunt coefficients in the Legendre expansion (10) vanish unless $j + j' + \lambda$ is even. This decouples the j-odd (o or ortho) and j-even (e or para) functions.

In scattering coordinates $\hat{K}^{(2)}_{\mathrm{VR}}$ vanishes and $\hat{K}^{(1)}_{\mathrm{VR}}$ simplifies so that

$$O^k_{i'i} = C^+_{J,k} \sum_{j,m,n} \sum_{j',m',n'} C^+_{jk}\delta_{j'j}\delta_{m'm}\left\langle H_{n'}\middle| \frac{1}{2\mu_2 r_2^2} \middle| H_n\right\rangle c^{Jki}_{jmn} c^{Jk+1i'}_{jmn'}. \tag{20}$$

The expression like (20) in the case of an arbitrary choice of g is not quite so simple, for it contains extra loops that arise as a consequence of matrix elements off-diagonal in j and m as well as n. It is nevertheless, like (20), a form ideally suited to vectorisation with the innermost loops over i and i'.

The programs to realise the method are written for a CRAY machine and designed to take maximum advantage of its vector capabilities. More technical details of the implementation may be found in the published program suite [20] and in ref. [21].

In the present work attention will be concentration on a strategy for effective choice of an appropriate sub-set of solutions to $\hat{H}_k$ for the solution of the full problem in the large J case. This problem is important as calculations of the highest J discussed here lie on the edge of what is achievable with present day supercomputers.

4. The calculations

The potential used in the calculations on H_2D^+ was that of Meyer et al. [23]. This potential was obtained by means of a sequence of full CI calculations with an extensive Gaussian basis set and is the most accurate non-empirical potential currently available.

Table 1
Computational characteristics of one- and two-step calculations on a CRAY XMP-48 of the 20 lowest ro–vibrational states of H_2D^+ ($J = 4$, $p = 0$, j even)

	One-step	Two-step	
		first step	second step
Dimension of largest secular problem	1500	300	1500
Storage required (words)	2377979	211979	543372
Matrix construction time (cpu s)	1.80	1.16	24.30
Matrix diagonalisation time (cpu s)	241.37	13.40	42.26
Total time (cpu s)	243.17		81.12
Maximum storage (words)	2377979		543372

To establish the utility of the two-step variational procedure and to provide a computational context, some timings and storage requirements are shown in table 1. The calculations to which the table refers are for the 20 lowest ro–vibrational states of H_2D^+ with $J = 4$ for the symmetry block ($p = 0$, j even).

Table 2
Rotational term values for H_2D^+ in cm^{-1}

Level	Ground state				ν_2			ν_3			ν_1	
	exp.		theory		exp.	theory		exp.	theory		exp.	theory
	[25]	this work	[16]	[24]	[23]	this work	[16]	[23]	this work	[16]	a)	this work
1_{01}	45.70	45.68	45.63	45.80	40.82	40.77	40.6	48.53	48.53	48.6	45.69	45.66
1_{11}	60.03	60.02	59.96	60.19	52.92	52.89	52.6	67.36	67.37	67.8	58.02	57.97
1_{10}	72.46	72.43	72.37	72.62	72.55	72.52	72.5	73.88	73.87	74.0	70.82	70.77
2_{02}	131.66	131.59	131.46	131.97	112.49	112.37	111.9	142.33	142.30	142.6	130.82	130.76
2_{12}	138.86	138.81	138.67	139.22	116.87	116.75	116.1	155.61	155.63	156.4	136.39	136.31
2_{13}	175.94	175.86	175.70	176.36	173.50	173.37	173.3	177.04	176.98	177.0	174.65	174.53
2_{21}	218.66	218.62	218.42	219.29	209.59	209.52	209.2	233.03	233.03	233.9	211.36	211.29
2_{20}	223.86	223.81	223.61	224.50	221.19	221.13	221.1	234.14	234.12	234.8	217.33	217.15
3_{03}	251.42	251.32	251.06	252.07		209.42	208.8	275.29	275.24	275.8	248.81	248.70
3_{13}	254.07	253.97	253.69	254.73	210.82	210.60	209.7	283.15	283.12	284.2	250.46	250.46
3_{12}	326.17	326.01	325.71	327.00		314.20	314.0	328.82	328.68	328.6	324.58	324.41
3_{22}	354.78	354.68	354.34	355.81		333.41	332.9	374.83	374.78	375.7	178.82	347.23
3_{21}	376.34	376.20	375.87	378.32	374.40	374.19	374.3	381.89	381.78	382.0	291.49	371.25
3_{31}	458.35	458.23	457.84	459.89	445.58	445.47	445.1	485.38	485.38	487.1	442.41	442.26
3_{30}	459.84	459.76	459.32	461.37		450.33	450.1	485.35	485.35	487.0	444.35	444.20
4_{04}		402.31	402.31			333.99	333.4	441.90	441.80	442.6	398.12	397.97
4_{14}	403.69	403.53	403.08		334.32	334.28	334.2	439.93	440.09	442.0	398.59	398.40
4_{13}	516.16	515.93	515.44		484.92	484.56	484.0	525.04	524.79	524.6	512.65	512.40
4_{23}		531.16	530.65			492.22	491.8	559.03	558.89	560.1		523.05
4_{22}	581.39	581.24	580.70		582.74	582.12	582.0		580.19	579.9		577.55
4_{32}		645.41	644.78			624.63	624.4		673.52	675.0		629.91
4_{31}		654.32	653.70			624.63	624.4		674.28	675.4		641.22
4_{41}		778.59	777.80			759.31	758.9		823.25	826.0		750.45
4_{40}		778.93	778.14			760.80	760.3		823.19	825.9		750.95
Band origin					2205.88	2206.25	2207.9	2335.44	2334.99	2335.0	2737.00	2992.96

[a] Inferred from table 1 of ref. [27] using the ν_0 levels of ref. [25].

In the first column are presented the results of solving the full 1500 dimensional secular problem directly for the lowest 20 eigenvalues. The second two columns give the results of the two-step method to accomplish the same end, that is *all* the intermediate functions generated in the first step were used in the second. The results of the two processes should therefore be the same and in fact are, to within the tolerance of the iterative diagonalizer used in the second step.

It is seen that not only does the two-step procedure require much less store but that it is also quicker than the one-step procedure. Much bigger savings are made if fewer functions are used in the second step. The same results can in fact be obtained in the example shown in table 1 with only 800 functions chosen in the second step, with a consequent saving of about half the store and a drop in total time to 28.76 s.

In the calculations whose characteristics are shown in table 1, 300 basis functions were used in the solution of the $\hat{H}_k$ problem for all values of k.

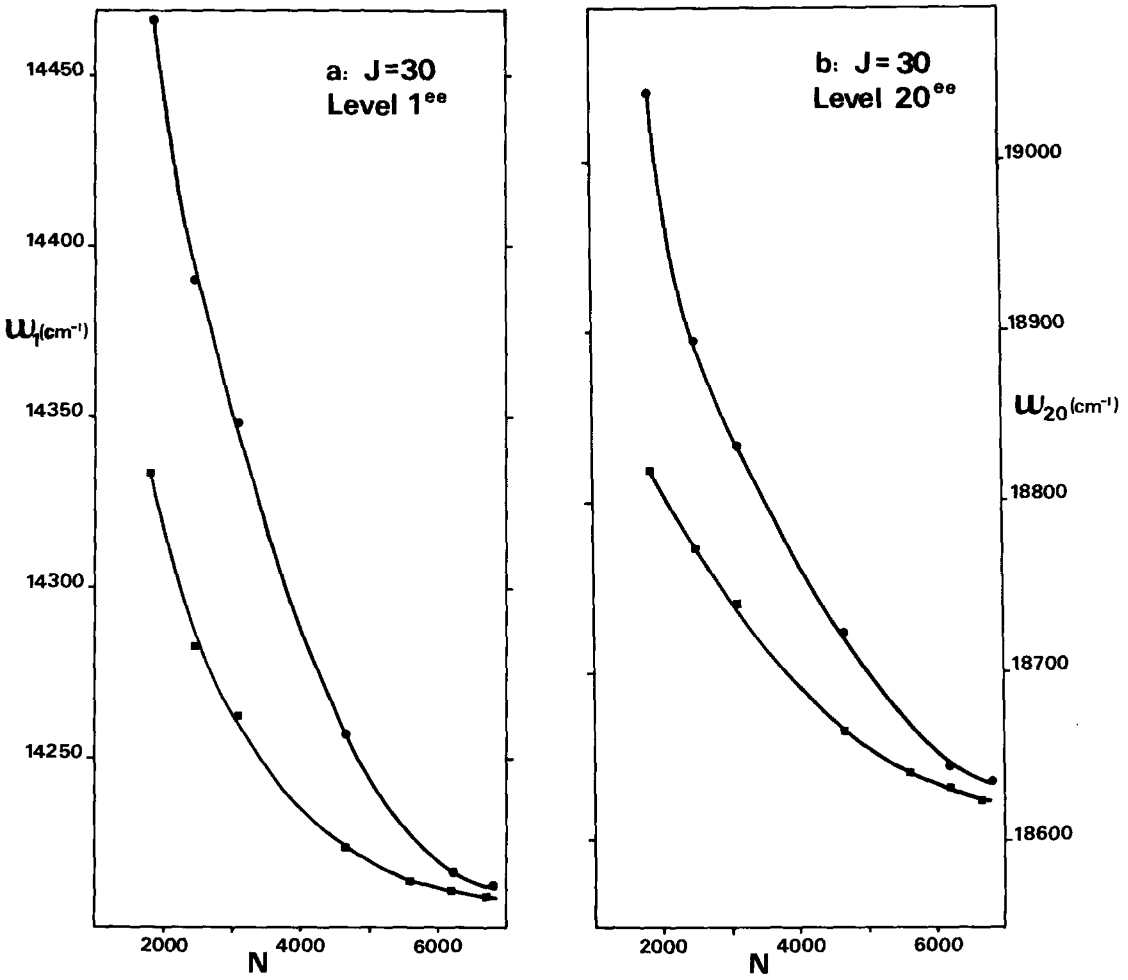

Fig. 1. The convergence of the energy levels 1^{ee} and 20^{ee} for the $J = 30$ state of H_2D^+ as a function of the total number of basis functions N used in the second step of two-step calculation. The points ● represent calculations carried out selecting equal numbers, N, of basis functions for each k level. The points ■ represent calculations which select the basis functions for the second step on the criterion of lowest energy (energy selection).

It should be noted that, although it is not of central concern here, this present approach gives results as good as, if not superior to the Eckart–Watson approach in such low J calculations. This is evidenced by the quality of the rotational constants obtained in earlier work [16] on H_2D^+, and in the material presented in table 2.

The central computational problem for the high J case is how to choose a suitable set of functions from the first variational step to yield a tractable secular problem in the second step. If it is assumed that solutions from all the $J+1$ Hamiltonians $\hat{H}_k$ are going to contribute equally to the solution of the full problem then it is natural to choose the lowest N solutions from each problem ordered accordingly to increasing $\epsilon_{k,i}$, $i = 1, 2, \ldots, N$. If this is done then the dimension of the secular problem in the second step is $(J+1-p)N$. In a typical calculation the basis set size for the first step is of order 200 to 700 and the size N is of order 10 to 300.

Sufficient solutions are taken of the second variational step to cover the rotational manifold of the first three or four vibrational states, the position of the vibrational states being determined by $J=0$ calculations.

Table 3
Energies [a] for $J = 30$ levels 1^{ee} to 20^{ee}

Level	Selection on $N_k = 220$ 6820 basis functions CRAY 1s	Selection on lowest 6650 basis functions from full 1st step CRAY 1s	Selection on lowest 9300 basis functions from full 1st step CRAY-XMP 48
1	14217.74	14209.93	14195.41
2	15243.77	15217.67	15161.05
3	15879.00	15874.32	15853.41
4	16154.82	16109.94	16033.34
5	16499.08	16483.84	16464.54
6	16790.24	16764.59	16678.90
7	16942.48	16890.59	16833.93
8	17166.17	17144.37	17116.07
9	17381.84	17347.99	17251.24
10	17583.72	17523.16	17463.74
11	17678.46	17673.65	17644.02
12	17789.63	17746.25	17691.96
13	18044.75	18005.52	17884.08
14	18075.24	18045.52	18012.66
15	18116.05	18081.25	18032.07
16	18259.05	18206.86	18163.53
17	18471.65	18423.94	18365.71
18	18481.83	18467.65	18386.08
19	18629.05	18560.99	18499.32
20	18644.39	18623.52	18548.50
T_c [b] (s)	749.73	717.79	419.44
T_d [c] (s)	773.66	502.27	1736.85
T_{TOT} (s)	1523.39	1222.06	2156.29
STORE (words)	1740158	1714641	3304118

[a] Energies in cm^{-1} relative to ground state of $J = 0^e$.

[b] T_c: computer time required to construct secular matrix.

[c] T_d: computer time required to diagonalise matrix and obtain lowest 20 eigenvalues, for CRAY 1s runs, and lowest 47 eigenvalues, for CRAY-XMP 48 run.

An alternative mode of selection is however possible. In this the maximum size of the secondary secular problem is determined in advance and the functions selected from the solutions of the first step as a whole, without reference to their k value, in order of increasing energy. The block structure on k arising from (19) is, of course, kept for computational efficiency and the choice means that the blocks will now be rectangles of varying sizes.

Table 3 compares results obtained using both methods of selection in the Cray 1s computer at ULCC, using maximum allowed storage of 1.8 million words. Column 3 contains our "best" results, calculated on the Cray XMP 48 at the Rutherford-Atlas Laboratory, using the second method of basis function selection. Fig. 1 shows graphically the convergence of two particular energy of levels (1 and 20) to their "true" value as the size of the secondary secular problem is increased, using both methods of basis set selection.

It is seen that it is more economical to use the energy selection from the first step as a whole. Although fewer (6650 as against 6820) basis functions are used in the comparable Cray 1s runs, the method which selects from the first step as a whole consistently gives results closer to the best results available from the Cray-XMP 48. We note that the procedures used by Chen et al. [22] and others (e.g. ref. [24]) are not easily adapted to this energy selection criterion as their expansion functions used in the second step are degenerate on k.

The results given in table 3 represent the first fully coupled calculations on a system with J as high as 30. These calculations are thus approaching the challenging domain ($J = 30$–45) which appears to be probed by the remarkable, but still poorly understood, experiments of Carrington and co-workers [4,5].

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