

A Numerical Variational Method for Calculating Accurate Vibrational Energy Separations of Small Molecules and Their Ions*

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Abstract

A combination of known methods have been spliced together in order to calculate accurate vibrational energies and wavefunctions. The algorithm is based on the Rayleigh-Ritz variational procedure in which the trial wavefunction is a linear combination of configuration products of one-dimensional basis functions. The Hamiltonian is that due to Carney and Porter (1976). The kernel of the algorithm consists of the one-dimensional basis functions, which are the finite element solutions of the associated one-dimensional problems.

1. Introduction

There are numerous algorithms (and variants) for solving the one-dimensional nuclear Schrödinger equation, some of which have been compared by Shore (1973*a*) and Malik *et al.* (1980). Perhaps the best known is that due to Numerov (1933) and Cooley (1961). Practical aspects and difficulties associated with this 'shooting' method have been discussed in detail by Cashion (1963), Blatt (1967), Kolos and Wolniewicz (1966), Wicke and Harris (1976) and Johnson (1977). Wicke and Harris (1976) have shown the eigenvalue accuracy to be $O(h^4 k^6)$. Furthermore, the Numerov-Cooley scheme is limited to the computation of one eigenvalue at a time and, moreover, cannot be readily extended to the three-dimensional problem.

Another scheme has been reported by Gordon (1970), where the one-dimensional potential is approximated by a straight line on each interval, thereby yielding analytical solutions that are combinations of Airy functions. The accuracy of the eigenvalue is of $O(h^2)$. Numerical instability limits Gordon's method to the calculation of one solution at a time. A variant of this approach is the scheme proposed by Canosa and Gomes de Oliveira (1970) in which the potential is approximated by a constant function on an interval. Ixaru (1972) showed that the accuracy of the eigenvalues was also of $O(h^2)$. Neither of these methods (which approximate the potential function) readily extends to higher dimensions.

Finite difference methods have a distinct advantage over the previous methods in that they can be easily extended to many dimensions. Basically, the method

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approximates the derivatives of the differential operator by difference quotients. Fox (1957) has summarized several schemes. Keller (1968) has proved that the accuracy of finite difference eigenvalues are to $O(h^2 k^4)$. Truhlar (1972) has applied the finite difference method to one-dimensional vibrational problems, as have Tobin and Hinze (1975). The major difficulty of these methods is the effort involved in improving the accuracy and in trying to compute a sequence of eigenvalues of similar accuracy.

Finite element methods have a more recent history in the study of molecular vibrations. Askar (1975) gave a brief outline of how to apply the finite element method to bound state calculations using linear polynomial basis functions. Nordholm and Bacskey (1976) 'generalised' the method to incorporate a basis of non-overlapping and overlapping sine functions. Shore's (1973*b*) method of cubic splines is a finite element method with a basis of cubic B splines which guarantees a continuous function, first and second derivative. Birkhoff *et al.* (1966) have shown that the eigenvalues are accurate to $O(h^6 k^8)$.

For the multi-dimensional vibrational problem the two reported numerical Rayleigh–Ritz variation algorithms are the finite difference algorithm of Cropek and Carney (1984) and the finite element method of Burton *et al.* (1984*a*, 1984*b*, 1985). Both are *ab initio* methods and have yielded excellent results for the vibrational spacings of small triatomic ions. The present investigation details and extends our solution algorithm which we have successfully applied to the investigation of the vibrational spacings of small D_{3h} molecular ions (see Burton *et al.* 1984*a*, 1984*b*, 1985).

2. Vibrational Schrödinger Solution of D_{3h} Triatomic Molecules

For D_{3h} triatomic molecules, we have adopted the Carney and Porter (1976) normal coordinate Hamiltonian which has the form

$$\hat{H} = \sum_{\alpha=1}^3 \hat{T}_{\alpha} + \hat{T}_l + \hat{U}_w + \hat{V}, \quad (1)$$

where \hat{T}_{α} is the kinetic energy operator, \hat{T}_l the vibrational angular momentum operator, \hat{U}_w the Watson operator and \hat{V} the total electronic potential operator. Our adoption of this Hamiltonian [in preference to (R_1, R_2, R_3) or (R, σ, θ) representations] was due to our initial interest in accurately modelling the low lying vibrational states. For these states, the molecular potential would be expected to be 'nearly' harmonic and so accurate solutions of equation (1) would be expected for a small configurational basis.

Carney and Porter (1976) gave the following expressions for the kinetic energy and vibrational angular momentum operator:

$$\hat{T}_{\alpha} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial S_{\alpha}^2}, \quad (2)$$

$$\hat{T}_l = -\frac{\hbar^2}{2} \left(\frac{S_2 \partial/\partial S_3 - S_3 \partial/\partial S_2}{I_{zz} - \mu(S_2^2 + S_3^2)} \right)^2, \quad (3)$$

where the S_{α} are the symmetry coordinates that satisfy the Eckart (1935) conditions and I_{zz} is a moment of inertia tensor.

As has been pointed out by us elsewhere (see Burton *et al.* 1984*a*), there is an ellipse of singularities associated with large amplitude of vibrations which manifest themselves in the Watson term of the normal coordinate Hamiltonian. By considering only small vibrational amplitudes, we have demonstrated that the Watson term can be effectively replaced by a third-order perturbation expression (see Burton *et al.* 1984*a*). The expression used for \hat{U}_w is given by

$$\hat{U}_w^{(3)} = \frac{\hbar^2}{2\mu} \left\{ \frac{5}{4R_e^2} \left(-1 + \frac{2S_1}{R_e} - \frac{3S_1^2}{R_e^2} + \frac{4S_1^3}{R_e^3} \right) \right\} \\ + \frac{\hbar^2}{2\mu} \left(-\frac{3S_2^2}{R_e^4} - \frac{3S_3^2}{R_e^4} \right) + \frac{\hbar^2}{2\mu} \left(\frac{12S_1 S_2^2}{R_e^5} + \frac{12S_1 S_2^2}{R_e^5} \right), \quad (4)$$

where R_e is the equilibrium bond length.

In the two cases H_3^+ and D_3^+ , the potential used in this study is based on the energy grid constructed from 78 PNO-CI calculations from which is extracted an n th degree Simons-Parr-Finlan force field (see Burton *et al.* 1985), i.e.

$$V(S_1, S_2, S_3) \rightarrow V(\rho_1, \rho_2, \rho_3) = \sum_{\substack{i,j,k \\ i+j+k \leq n}} \alpha_{ijk} \rho_1^i \rho_2^j \rho_3^k, \quad (5)$$

where the variables of the power series are $\rho_i = (R_i - R_e)/R_i$. The R_i are the instantaneous bond lengths and the α_{ijk} are coefficients.

Finite difference and finite element methods are capable of directly solving the multi-dimensional Schrödinger equation. Unfortunately, even for moderate accuracy, a three-dimensional finite element computation would require a mesh size of at least 20 points in each dimension, which would result in matrices of the order 8000×8000 . To demonstrate the accuracy of such a calculation, the mesh would have to be doubled, resulting in matrices well beyond the storage capacity usually available to computer users.

We have followed the usual approach in solving multi-dimensional vibrational problems, i.e. we used the Rayleigh-Ritz method in which the vibrational eigenfunctions are expanded as a linear combination of a configurational product of one-dimensional basis functions. In the case of angular triatomic molecules, the vibrational wavefunctions have the form

$$\bar{\psi} = \sum_{ijk} C_{ijk} \psi_i(S_1) \psi_j(S_2) \psi_k(S_3), \quad (6)$$

where the C are the expansion coefficients and the ψ are the one-dimensional basis functions dependent on coordinate S_i . The eigenfunctions and eigenvalues are determined by applying the variational principle to the undetermined coefficients, which leads to the problem of solving the usual secular equation

$$|H - ES||C| = 0. \quad (7)$$

The simplest approach in constructing the one-dimensional basis functions is to require that they be eigenfunctions of associated one-dimensional Schrödinger equations, i.e.

$$\begin{aligned} \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dS_1^2} + V(S_1, 0, 0) \right) \psi_i &= \lambda_i \psi_i, \\ \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dS_2^2} + V(R_e, S_2, 0) \right) \psi_j &= \mu_j \psi_j, \\ \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dS_3^2} + V(R_e, 0, S_3) \right) \psi_k &= \nu_k \psi_k. \end{aligned} \quad (8)$$

As a result of such a construction, Burton *et al.* (1984*b*) have demonstrated that (if the inter-mode coupling terms are small) a configuration list determined from an excited-energy criterion yields a more compact wavefunction compared with a basis selection criterion based on node counting. Hence, our configuration list is determined by the cut-off criterion

$$E_{\max} \geq \lambda_i + \mu_j + \nu_k. \quad (9)$$

Correct to second order, the Watson term has no inter-mode coupling (see Burton *et al.* 1984*a*). Its inclusion in equation (8) would only marginally alter the one-dimensional eigenvalues, since for the three-dimensional problem H_3^+ the Watson term generally increases the vibrational energy level by 27.46 cm^{-1} . Nevertheless, it would introduce a mass-dependent contribution to the one-dimensional potential energy terms and so perhaps improve the compactness of the vibrational wavefunctions. This has not yet been investigated.

3. One-dimensional Finite-element Method

The eigenvalues and eigenfunctions of the one-dimensional problems given by equation (8) are the stationary points and values of the Rayleigh quotient. As one can choose a linear expansion of the trial function u in terms of some basis functions ϕ , the Rayleigh quotient can be put into the form

$$R(c) = c^T A c / c^T B c, \quad (10)$$

where $c^T = (c_1, c_2, \dots, c_N)$ are the free parameters and where

$$A_{ij} = \langle \phi'_i, \phi'_j \rangle + \langle \phi_i, V \phi_j \rangle, \quad B_{ij} = \langle \phi_i, \phi_j \rangle. \quad (11)$$

If the basis functions are non-orthogonal then the stationary values of equation (10) are given by the generalised eigenvalue problem

$$A c = \lambda B c. \quad (12)$$

The Rayleigh–Ritz finite element methods (FEM) are distinctive, because of the choice of local basis functions. The local nature of the finite element basis functions require the definition of boundaries and corresponding meshes. The FEM basis functions are a piecewise approximation to the true eigenfunction and so each finite element basis is only non-zero on the few adjacent mesh intervals. As many of the overlap integrals over the basis functions are zero, both global matrices **A** and **B** are

sparse and banded. The matrix \mathbf{B} is not diagonal since the basis functions are not orthogonal. An excellent account of FEM and their construction in solving equations (such as equation 8) has been given by Strang and Fix (1973).

Usually in FEM, the basis functions are low degree polynomials. The Hermite cubic polynomials have a distinct advantage as basis functions, since they are constructed by imposing continuity, not only on u^h , but also on its first derivative; i.e. both function value v and first derivative value v' are shared by the cubic in the next interval (see Strang and Fix 1973). The overall local approximation u^h on the interval $0 \leq x \leq h$ is

$$u^h(x) = v_0 \phi_1(x) + v'_0 \phi_2(x) + v_h \phi_3(x) + v'_h \phi_4(x). \quad (13)$$

The cubic basis functions are determined by imposing the conditions that each function and first derivative values are zero or one at the boundaries, i.e. the Hermite cubics have form

$$\begin{aligned} u^h &= a_0 + a_1 x + a_2 x^2 + a_3 x^3, \\ \phi_1(x) &= 2x^3/h^3 - 3x^2/h^2 + 1, & \phi_2(x) &= x^3/h^2 - 2x^2/h + x, \\ \phi_3(x) &= -2x^3/h^3 + 3x^2/h^2, & \phi_4(x) &= x^3/h^2 - x^2/h. \end{aligned} \quad (14)$$

Generally, equations (13) and (14) are arranged in the matrix equation form,

$$\mathbf{a} = \mathbf{h}\boldsymbol{\phi}, \quad (15)$$

where

$$\begin{aligned} \mathbf{a} &= (a_0, a_1, a_2, a_3)^T, & \boldsymbol{\phi} &= (v_0, v'_0, v_h, v'_h)^T, \\ \mathbf{h} &= \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ -3/h^2 & -2/h & 3/h^2 & -1/h \\ 2/h^3 & 1/h^2 & -2/h^3 & 1/h^2 \end{vmatrix}. \end{aligned}$$

In the one-dimensional problem, the finite elements are just the subintervals that divide the domain $[a, b]$. The wavefunction is approximated on each interval $h_i = x_{i+1} - x_i$ by a combination of the Hermite cubics that span that interval.

The integrals of the global matrices \mathbf{A} and \mathbf{B} are computed by means of element \mathbf{K}_1 (stiff) and \mathbf{K}_0 (mass) matrices respectively, where (see Strang and Fix 1973)

$$\int_0^h (u^h)'^2 = \boldsymbol{\phi}^T \mathbf{K}_1 \boldsymbol{\phi}, \quad \int_0^h (u^h)^2 = \boldsymbol{\phi}^T \mathbf{K}_0 \boldsymbol{\phi}. \quad (16)$$

The element matrices are generated in terms of the interval length and their values are incorporated into the global matrices \mathbf{A} and \mathbf{B} by overlapping the v_h and v'_h contributions of one interval with the v_0 and v'_0 of the next. The boundary conditions $u(a) = u(b) = 0$ are imposed on the trial solution resulting in the deletion of the two basis functions from the expansion set, so that the first and last blocks are of order 3×3 .

The contributions to the potential function integrals of the **A** matrix are evaluated by Gaussian quadrature on each interval, i.e.

$$\int_0^h \phi_i(x) V(x) \phi_j(x) dx = D_{ij} = \sum_{k=1}^n w_k \phi_i(x_k) \phi_j(x_k) V(x_k), \quad (17)$$

where a six-point quadrature scheme is employed on each interval.

The element matrix **K**₀ is positive definite which results in a global positive definite **B** matrix; **B** is by definition symmetric. The **K**₁ element matrix is indefinite leading to an indefinite **A** matrix, which is symmetric because the Hamiltonian is hermitian. Both **A** and **B** are large (typically of order 200×200) but they are also sparse since only elements (*i, i*) to (*i, i+3*) need to be computed. To take advantage of the sparse nature of the matrices, a solution of the generalised eigenvalue problem has been developed by Doherty (1981) called the incomplete Choleski conjugate gradient (ICCG) method. The **B** matrix is iteratively factored into **LL**^T by a Cholesky elimination and the eigenvalues of **L**⁻¹**A**(**L**⁻¹)^T are computed using the QR algorithm (see Francis 1961). The sequence of conjugate gradient reduction steps reorient the initial random orthogonal vectors to the minimising direction and so hasten their convergence. The advantage of the ICCG method is that the sparseness of the **A** and **B** matrices is retained in the **L** matrices because of the use of the iterative Choleski factorisation technique of Meijerink and Van Der Vorst (1977). Hence, the computer storage capacity required is very much reduced.

It is a well-known feature of Rayleigh–Ritz numerical calculations that the higher eigenvalues become increasingly inaccurate. It has been shown by Birkoff *et al.* (1966) that the finite element eigenvalues λ_k are accurate to $O(h^6 k^8)$ and that the eigenfunctions are correct to $O(h^{4-s} k^4)$ in the *s* derivative. Clearly there is a strong dependence on *k*.

Many methods have been discussed to improve the accuracy of the higher eigenvalues. For example, Paine (1979) proved that in a finite difference approximation, the usual finite difference estimates of eigenvalues to $O(h^2 k^4)$ can be improved to at least a uniform $O(h^2 k)$ by simple kinetic energy corrections. The method of Paine *et al.* (1981) is in fact useful in FEM as is demonstrated below.

To more clearly demonstrate the problem at hand, let us consider the simplest one-dimensional problem in which the potential is zero on the interval [0, 1] and the eigenfunctions are subject to the usual boundary conditions, i.e. $u(0) = u(1) = 0$. The exact solutions to this problem are well known and are given by

$$\lambda_k = (k\pi)^2, \quad u_k(x) = (2)^{0.5} \sin k\pi x. \quad (18)$$

Table 1 contains the error of the finite element approximations using a coarse mesh of eight equal finite elements and a six-point quadrature scheme. Table 1 clearly indicates that the error in the eigenvalue rapidly escalates. In fact, this error may be viewed as a kinetic energy correction; that is, if the zero potential is replaced by a harmonic box potential [i.e. $V(x) = \lambda - x^2$ within 0 to 1], then the addition of the correction term to the eigenvalues of the latter problem yields solutions which are more in keeping with a much finer grid. This is also clearly demonstrated in Table 1 where the difference between the corrected eigenvalues and those of the refined grid is less than 0.04 for $k = 15$. In fact, it can be demonstrated that the eigenvalues

Table 1. Eigenvalue FEM solutions to one-dimensional problems

k	Zero potential ^A ($\lambda_{\text{FEM}} - \lambda_{\text{EXACT}}$)	Harmonic box potential ^B	
		FEM' ($n = 8$)	FEM ($n = 80$)
1	0.00000113	10.15116404	10.15116403
2	0.00025070	39.79939302	39.79939300
3	0.00521909	89.15434203	89.15434246
4	0.04115627	158.24395807	158.24396178
5	0.19280393	247.07148059	247.07150069
6	0.65904492	355.63763624	355.63774578
7	1.83540261	483.94186153	483.94296510
8	8.34531833	631.98728454	631.98727697
9	10.31309209	799.77196216	799.77074085
10	21.8031644	987.29362633	987.29340236
11	44.37983578	1194.55551205	1194.55530601
12	86.79137032	1421.55698659	1421.55650745
13	159.37394846	1668.29871549	1668.29708348
14	257.96868640	1934.78390444	1934.77714250
15	314.75074476	2221.03891373	2220.99683625

^A The exact solutions are given by equation (18). The number of finite elements defined on the domain is $n = 8$.

^B The FEM represents the finite element eigenvalues without any correction, whereas FEM' represents the finite element solution with the correction of note A added to the respective eigenvalues. The number of finite elements defined on the domain is given in parentheses. The potential is harmonic only on the interval $[0, 1]$.

Table 2. One-dimensional eigenvalues (in a.u.) for normal modes of H_3^+

The potential used is the fifth order Simon-Parr-Finlan fit (see Burton *et al.* 1985) yielding $V_{\min} = -1.34286$ a.u. All results have been computed using a six-point quadrature scheme

k	S_1^A		S_2^B		S_3^C	
	FEM	Extrap. ^D	FEM	Extrap. ^D	FEM	Extrap. ^D
1	-1.33404	-1.33404	-1.33566	-1.33566	-1.33556	-1.33556
2	-1.31873	-1.31873	-1.32351	-1.32351	-1.32283	-1.32283
3	-1.30387	-1.30387	-1.31186	-1.31186	-1.30991	-1.30991
4	-1.28946	-1.28946	-1.30091	-1.30091	-1.29683	-1.29683
5	-1.27548	-1.27548	-1.29098	-1.29098	-1.28363	-1.28363
6	-1.26192	-1.26192	-1.28260	-1.28260	-1.27034	-1.27034
7	-1.24875	-1.24876	-1.27645	-1.27646	-1.25697	-1.25697
8	-1.23598	-1.23599	-1.27143	-1.27143	-1.24356	-1.24358
9	-1.22358	-1.22360	-1.26600	-1.26608	-1.23013	-1.23017
10	-1.21154	-1.21157	-1.25988	-1.26039	-1.21675	-1.21679

^A Interval over the range $[-1, 2]$ with the mesh over 28 intervals: 4×0.125 , 16×0.0625 , 4×0.125 , 4×0.25 .

^B Interval over the range $[-1, 3]$ with the mesh over 28 intervals: 4×0.125 , 16×0.0625 , 4×0.125 , 3×0.25 , 1.25 .

^C Interval over the range $[-1.5, 1.5]$ with the mesh over 28 intervals: 3×0.25 , 0.125 , 20×0.0625 , 0.125 , 3×0.25 .

^D Richardson extrapolation based on doubling the mesh size to 56 intervals.

with the kinetic energy correction are more in keeping to an accuracy of $O(\hbar^6 k^6)$ (see Hamilton 1983). The above study not only suggests where the major error in the FEM procedure occurs, but also suggests an alternative avenue in securing more accurate high energy eigenvalues.

In order to construct the basis functions for the H_3^+ and D_3^+ vibrational problem, the use of the kinetic energy correction was deemed not to be the preferable route, since there was no clear connection to a corresponding accuracy of the eigenfunctions. Hence, the route taken was to focus on refining the grid.

The choice of endpoints requires careful consideration as the eigenfunctions are forced to zero at the endpoints. Moreover, if the endpoints are chosen far beyond the region in which the wavefunction has converged then it will not only significantly increase the computation time but also it might produce a three-dimensional domain which goes beyond the realistic behaviour of physical motion of the molecule. For example, typical ranges for S_1 , S_2 and S_3 are $[-1, 2]$, $[-1, 3]$ and $[-1.5, 1.5]$ respectively (see Hamilton 1983). To determine the mesh, the range was subdivided into a coarse mesh with constant spacing and then selectively refined over each subinterval to ensure that the highest eigenvalue required had converged to some tolerance. Table 2 gives a mesh for each coordinate and the corresponding eigenvalues of the respective one-dimensional problems (see equation 8). Table 2 also gives the Richardson extrapolated results, which further demonstrates that for such a mesh the basis functions have converged.

4. Integral Evaluation for the Three-dimensional Problem

There are basically only three types of integrals that need to be evaluated in the three-dimensional vibrational problem spanned by a FEM basis set: integrals involving the position operator (or dot products thereof), integrals involving a first derivative operator (or dot products thereof), and integrals involving the potential energy operator. The second derivative of the kinetic energy operator reduces to a dot product of first derivatives, because by using integration by parts on the interval, the boundary conditions ensure that the function is zero at the endpoints of the interval. Hence, we have

$$\langle \psi_1, \hat{T}_\alpha \psi_j \rangle = -(\hbar^2/2\mu) \langle \psi'_1, \psi'_j \rangle. \quad (19)$$

In the case of global basis functions it does not matter if one performs the integration by parts since the functions themselves have sufficient continuity. However, in the case of piecewise or local basis functions, using integration by parts lifts the condition of the continuity of the second derivative at the nodes. [The latter is satisfied using cubic B splines (see Strang and Fix 1973).]

The evaluation of these integrals is based on the element stiff matrix (see equation 16). Hence, the global integrals are evaluated by assembling a similar matrix to \mathbf{A} (i.e. \mathbf{A}') and then performing the usual matrix multiplication $\mathbf{c}^T \mathbf{A}' \mathbf{c}$.

An examination of integrals involving the Watson operator (see equation 4) reveals that they reduced to one-dimensional integrals which involve the position operator (or dot products thereof). Those integrals involving the \hat{T}_l operator (see equation 3) reduced to one-dimensional integrals involving the first derivative operator, position operator or dot products thereof. All the integrals involving the \hat{T}_α , \hat{T}_l and $\hat{U}_w^{(3)}$ operators are evaluated using a six-point Gauss–Legendre quadrature scheme. When

spanned by a configurational basis, the integrals are weighted by the appropriate one-dimensional Kronecker deltas (see the Appendix).

The potential energy integrals have the form,

$$\int dz \psi_k \psi_{k'} \cdot \int dy \psi_j \psi_{j'} \cdot \int dx \psi_i \psi_{i'} \cdot V(x, y, z), \quad (20)$$

where x, y, z are equivalent to S_1, S_2, S_3 for the H_3^+ problem. In order to evaluate this integral, a numerical quadrature scheme is required to replace the integral by a discrete sum over particular quadrature points. A Gauss-Legendre quadrature scheme using six points along each coordinate becomes computationally intractable for even a small configuration list. Furthermore, such a scheme samples the potential function in the classically forbidden regions where the one-dimensional eigenfunctions should be very close to zero, but are not, due to the imperfections of the FEM method. This results in a divergent integral.

Even though a promising optimised quadrature scheme for matrix eigenfunctions of general anharmonic potentials has recently come to our attention (see Schwenke and Truhlar 1984), we have adopted the Harris, Engerholm and Gwinn (HEG) (1965) integration scheme to evaluate the three-dimensional potential integrals over the finite element basis. The HEG scheme requires the computation of an X matrix, the elements of which have the form

$$X_{ij} = \int_a^b \psi_i(x) \cdot x \cdot \psi_j(x) dx. \quad (21)$$

For the finite element method, these integrals may be computed exactly over each element using the methods described above. A typical integral on the interval $0 \leq x \leq h$ over the finite basis $\phi_i (i = 1, 4)$ of equation (14) is

$$\int_0^h \phi_i(x) \cdot x \cdot \phi_j(x) dx = \phi^T (K_2 + a_h K_0) \phi, \quad (22)$$

where ϕ is defined in equation (15), K_0 is the element matrix defined by equation (16) and

$$a_h = a + \sum_{i=1}^{l-1} h_i$$

is the left end of the l interval position in the total range $[a, b]$ with unequal mesh spacings h_l ($l = 1, \dots, L$). The element matrix K_2 is given by

$$K_2 = h^2 \begin{vmatrix} 3/35 & h/60 & 9/140 & -h/70 \\ h/60 & h^2/280 & h/60 & -h^2/280 \\ 9/140 & h/60 & 2/7 & -h/28 \\ -h/70 & -h^2/280 & -h/28 & h^2/168 \end{vmatrix} \quad (23)$$

The 4×4 element matrix resulting from equation (22) is combined into a large K matrix ($2L \times 2L$) from which the X matrix of equation (21) is computed as

$$X_{ij} = \psi_i^T K \psi_j, \quad (24)$$

where ψ_i are the coefficients of the i th eigenfunction.

The HEG method is readily extended to many dimensions (see Endres 1967). For the three-dimensional problem, three matrices are diagonalised in order to enable the potential integral to be evaluated. The three-dimensional potential integral matrix is then given by

$$V(X, Y, Z) = C_z C_y C_x V(\Lambda, \Omega, \Gamma) C_x^T C_y^T C_z^T \\ = \sum_{l=1}^L C_{kl} C_{k'l} \sum_{m=1}^M C_{jm} C_{j'm} \sum_{n=1}^N C_{in} C_{i'n} V(\lambda_{nn'}, \omega_{mm'}, \nu_{ll'}), \quad (25)$$

where, for example, C_x is determined from the matrix equation $C_x^T X C_x = \Lambda$ (see Hamilton 1983).

Table 3. Eigenvalues (in cm^{-1}) from a $2 \times 2 \times 2$ calculation using the HEG quadrature scheme

The notation $2 \times 2 \times 2$ means that the lowest two one-dimensional eigenfunctions along each coordinate were selected to form the CI list. The notation $n \times n \times n$ for the quadrature gives the number of points along each coordinate

5×5×5 quad.	10×10×10 quad.	20×20×20 quad.
4418.21	4418.38	4418.38
7003.28	7005.21	7005.22
7005.39	7005.59	7005.59
7899.79	7903.71	7903.74
9782.47	9784.17	9784.18
10760.22	10765.13	10765.17
10816.37	10824.34	10824.41
14441.18	14451.32	14451.44

In this scheme it is difficult to anticipate how many one-dimensional functions to include since they define the maximum number of quadrature points at which the potential integrals are evaluated. Table 3 shows the eigenvalues obtained from a $2 \times 2 \times 2$ calculation for 5, 10 and 20 quadrature points per dimension. It would appear that the low lying eigenvalues have converged for 10 quadrature points per dimension for matrix elements involving the first two eigenfunctions in each dimension. However, for high energy vibrational eigenfunctions a 20 point quadrature scheme is required (see Burton *et al.* 1984*a*, 1984*b*, 1985). This is consistent with the analysis of Cropek and Carney (1984).

5. Conclusions

For the triatomic hydrogen cation, the accuracy of the above multi-dimensional vibrational method has been demonstrated in a number of investigations (see Burton *et al.* 1984*a*, 1984*b*, 1985). In particular, it has been demonstrated that the bottleneck in accuracy of the lowest lying vibrational intervals is not due to the imperfections of the algorithm, but due to the inaccuracy of the force fields (see Burton *et al.* 1985). It is hoped that with the new generation of CI potential surfaces (see Burton 1980; Dykstra 1984) the emphasis will once again focus on the vibrational/rotational algorithms.

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Appendix

We present the one-dimensional integrals to be evaluated in the three-dimensional problem, where the suffixes i, j, k indicate a sole dependence on the S_1, S_2, S_3 coordinates respectively:

\hat{T}_a integrals—basic form:

$$\langle \psi, \hat{T}_a \psi \rangle = -\frac{\hbar^2}{2\mu} \delta_{jj'} \delta_{kk'} \int \psi_i \psi_i'; \quad (\text{A1})$$

\hat{T}_l integrals

$$\begin{aligned} \langle \psi, \hat{T}_l \psi \rangle = & -\frac{\hbar^2}{2\mu} \int \frac{\psi_i \psi_{i'}}{\mu(R_e + S_1)^2} \{ \int \psi_j S_2^2 \psi_{j'} \int \psi_k \psi_{k'}'' \\ & + \int \psi_k S_3^2 \psi_{k'} \int \psi_j \psi_{j'}'' - \delta_{kk'} \int \psi_j S_2 \psi_{j'}' - 2 \int \psi_j S_2 \psi_{j'}' \int \psi_k S_3 \psi_{k'}' \\ & - \delta_{jj'} \int \psi_k S_3 \psi_{k'}' \}; \end{aligned} \quad (\text{A2})$$

\hat{U}_w integrals

$$\begin{aligned} \langle \psi, \hat{U}_w^{(3)} \psi \rangle = & \delta_{jj'} \delta_{kk'} \left\{ \int \psi_i \frac{5\hbar^2}{8\mu R_e^2} \left(-1 + \frac{2S_1}{R_e} - \frac{3S_1^2}{R_e^2} + \frac{4S_1^3}{R_e^3} \right) \right\} \psi_{i'} \\ & - \delta_{ii'} \delta_{kk'} \frac{3\hbar^2}{2\mu R_e^4} \int \psi_j S_2^2 \psi_{j'} - \delta_{ii'} \frac{3\hbar^2}{2\mu R_e^4} \int \psi_k S_3^2 \psi_{k'} \\ & + \delta_{jj'} \frac{6\hbar^2}{\mu R_e^5} \left(\int \psi_i S_1 \psi_{i'} \int \psi_k S_3^2 \psi_{k'} \right) + \delta_{kk'} \frac{6\hbar^2}{\mu R_e^5} \left(\int \psi_i S_1 \psi_{i'} \int \psi_j S_2^2 \psi_{j'} \right). \end{aligned} \quad (\text{A3})$$

Note that for the \hat{T}_a and \hat{T}_l integrals all second derivatives are reduced to first derivatives by using integration by parts.