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On the advantages of a rectangular matrix collocation equation for computing vibrational spectra from small basis sets

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ABSTRACT

We demonstrate that for calculations of vibrational spectra from small basis sets, a rectangular collocation matrix equation combined with fitting [S. Manzhos and T. Carrington Jr., Can. J. Chem. 87 (2009) 864] is advantageous compared to both a traditional approach where the energies and wavefunctions are found from eigenvectors and eigenvalues of a square matrix and to the method of Boutry et al. [G. Boutry, M. Elad, G.H. Golub, P. Milanfar, SIAM J. Matrix Anal. Appl. 27 (2005) 582] for rectangular matrix pencils. A rectangular matrix equation allows for the use of a small basis set without the loss of information induced by squaring, while fitting the energy insures stability.

1. Introduction

Most numerical methods for solving the vibrational Schrödinger equation represent wavefunctions as linear combinations of basis functions. By various means, it is often possible to find good basis functions, i.e. a small basis with which one can compute the wavefunctions and energies of interest. In general, when one uses good basis functions, it is necessary to choose multidimensional quadrature or collocation points. In this Letter, we make two points: (1) when good basis functions are known, a rectangular eigensolver is sometimes a good tool for calculating energies; (2) for the purpose of solving the Schrödinger equation, the intertwined rectangular eigensolver and optimization method of Manzhos and Carrington [1–3] is better than alternating optimization steps with solution of a rectangular eigenvalue problem.

The vibrational Schrödinger equation $H\psi(\boldsymbol{x}) = E\psi(\boldsymbol{x})$, where $H = T + V(\boldsymbol{x})$, T is the kinetic energy operator (KEO), and V is the potential energy surface in a configuration space $\boldsymbol{x} \in R^d$, is usually solved by expanding the wavefunction ψ in a basis and solving for the coefficients [4]:

$$\psi(\boldsymbol{x}) \approx \sum_{i=1}^{N} c_i \phi_i(\boldsymbol{x}). \tag{1}$$

The most common approach, based on the variational theorem [5], for finding the coefficients involves substituting (1) into the Schrödinger equation and multiplying by a basis function on the left. Potential matrix elements are usually and KEO elements are sometimes evaluated by quadrature. If the quadratures are exact, then as the size of the basis set $\phi_i(\boldsymbol{x})$, $i = 1, \ldots, N$, is increased and approaches completeness, the eigenvalues obtained by solving $Hc = EFc$, where the square matrices H and F are $H_{ij} = \langle\phi_i|H|\phi_j\rangle$ and $F_{ij} = \langle\phi_i|\phi_j\rangle$, approach the exact energies from above [6]. From the eigenvectors c, one determines the wavefunctions. Alternatively, one can aim to satisfy the Schrödinger equation at a set of points $\boldsymbol{x}_i$, $i = 1, \ldots, N$, which results in the so-called collocation equations [7–10].

$$(G + VS)c = Mc = ESc \tag{2}$$

where $G_{ij} = T\phi_j(\boldsymbol{x}_i)$, $S_{ij} = \phi_j(\boldsymbol{x}_i)$, $V_{ij} = V(\boldsymbol{x}_i)\delta_{ij}$, $M = G + VS$. The energies and wavefunctions are determined from solutions of the generalized eigenvalue problem with the matrix pair M, S. Note that the number of points is equal to the number of basis functions. The values of ψ at the points $\boldsymbol{x}_i$ are given by the vector Sc. Because there is no need to use points on a regular mesh the number of required points may be much smaller than it would be if a direct product grid were used. This advantage is particularly effective if adaptable and localized basis functions are used. The collocation approach allows one to avoid explicit integration, but the number of collocation points must be large enough that the quadrature error associated with the points (and some set of weights) is small. If the basis is good, N, the required number of basis functions, is small; nonetheless, to use the collocation method, one must use as many basis functions as points. *Therefore, when standard collocation is used, it is not possible to take full advantage of a good basis.* When it is not possible to find points that are in some sense as good as the basis, the advantage of having a good basis is lost.

There are at least three ways to make good (i.e. small) basis sets. (1) One can diagonalize reduced dimension Hamiltonians and

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retain only a subset of their eigenfunctions. This idea is sometimes called contraction and is often used [11–18]. (2) Unimportant basis functions can be discarded from a direct product basis [19–22]. (3) Parametrized basis functions

$$\psi(\boldsymbol{x}) \approx \sum_{i=1}^{N} c_i \phi_i(\boldsymbol{x}|\lambda_i) \tag{3}$$

where λ_i is a set of parameters, can be optimized [1–3,23]. This can be done by choosing parameters to satisfy the Schrödinger equation at a set of points $\boldsymbol{x}_i$, $i = 1, \ldots, M > N$.

To use good basis functions, it is imperative that one take more points than basis functions. How can this be done efficiently? The standard collocation method is not a good choice, because it requires having as many functions as points. There are two options: (1) use quadrature and the standard approach referred to after Eq. (1); (2) use Eq. (2), but with $M > N$, and solve a rectangular eigenvalue problem.

The most obvious option is quadrature. The simplest quadrature is equivalent to making the rectangular problem square by left-multiplying by the transpose of S (all matrices are assumed to be real),

$$S^T M c = E S^T S c \tag{4}$$

and solving the resulting generalized (but square) eigenvalue problem. This approach is used, for example, by Nakatsuji [24] to solve the electronic Schrödinger equation. In this Letter, this will be referred to as the square approach.

The other option involves solving a rectangular eigenvalue problem, which is unorthodox and unfamiliar. The rectangular eigenvalue problem will not in general have an exact solution. However, if the rectangular eigenvalue problem is a rectangular version of matrix Eq. (2), where matrices M and S are of size $M \times N$, then because it is derived from the Schrödinger equation, it *will* have an exact solution if the basis e.g. $\phi_i(\boldsymbol{x}|\lambda_i)$ is good enough. On the contrary, to the extent that wavefunctions of interest are not linear combinations of the basis functions, because the basis is not large enough or because the parameters λ_i are non-optimal (we refer to such a basis as incomplete), only an approximate solution exists that minimizes a given error measure. In Ref. [25], Boutry et al. introduced a method to find approximate solutions of a rectangular eigenvalue problem. They look for matrices M_0, S_0 for which Eq. (2) does have an exact solution and which are as close as possible to the original matrices M, S.

Ideally, one would not only solve a rectangular eigenvalue problem but also optimize basis set parameters. In Ref. [1], Manzhos and Carrington (MC) introduced an approach that fits parameters of a small basis and E to solve the Schrödinger equation and showed that it can be used to compute spectra of small molecules from very small basis sets (dozens of functions) [1–3]. They used a rectangular collocation matrix Eq. (2). E and c were fitted to minimize the residual $Mc - ESc$ in the least-squares sense.

One of the purposes of this Letter is to demonstrate that rectangular approaches are, in some cases, better than the square approach. A second purpose of this Letter is to compare, for the purpose of solving the Schrödinger equation, alternating optimization steps with solution of a rectangular or square eigenvalue problem and the intertwined optimization rectangular eigensolver – MC method. Doing so, we demonstrate that rectangular methods enable one to use efficiently the information contained in $M > N$ points $\boldsymbol{x}_i$ to optimize basis functions.

In Section 2, we briefly describe the methods of MC [1] and of Boutry et al. [25] and show their relation. In Section 3, we give numerical results. Section 4 concludes.

2. Methods

As explained in the Introduction, one can solve the Schrödinger equation using a pre-determined basis and more collocation points than basis functions, provided there is some way of solving the resulting rectangular eigenvalue problem. One way to do this is with the method of Boutry et al. [25]. It approximates E, c of the rectangular matrix equation $Mc = ESc$ with exact solutions of $M_0 c = E S_0 c$, where M_0, S_0 differ from M, S by a minimal (in the least-squares sense) perturbation. Boutry et al. have shown that such a solution minimizes the residual

$$R = \frac{\|(M - ES)c\|_2^2}{1 + |E|^2}. \tag{5}$$

For given matrices M, S, i.e. for a given basis, and a given c, E is found as the '+'-root of the quadratic equation

$$c^T (S^T + E M^T)(M - ES)c = 0. \tag{6}$$

For a given E, c is found as the right singular vector corresponding to the smallest singular value of the matrix $(M - ES)$. The process is repeated until E and c are self-consistent. The solution of Eq. (6) is

$$E = \frac{-c^T S^T S c + c^T M^T M c + \sqrt{(c^T S^T S c - c^T M^T M c)^2 + 4(c^T M^T S c)^2}}{2 c^T M^T S c}. \tag{7}$$

Note that the equations of Boutry et al. ignore units and possibly different scales of the matrices M, S and of E. In practice, it is possible to find a self-consistent solution that is a good solution to the Schrödinger equation, only if the basis is nearly complete. In that case, there is no need to scale the matrices so that they are dimensionless before applying the approach of Boutry et al.

Does one expect solving the rectangular eigenvalue problem always to give better solutions to the Schrödinger equation than solving the square eigenvalue problem? If E and ψ *are* solutions of $H\psi(\boldsymbol{x}) = E\psi(\boldsymbol{x})$, then $\|\psi\|^2 \|H\psi\|^2 = \|\psi H \psi\|^2$, which can be written in matrix form as

$$c^T S^T S c c^T M^T M c = (c^T M^T S c)^2. \tag{8}$$

Therefore, if a wavefunction can be exactly represented as a linear combination of basis functions, Eq. (7) becomes

$$E = \frac{c^T M^T M c}{c^T M^T S c} \tag{9}$$

which is the same as the E obtained from Eq. (4):

$$E = \frac{c^T S^T M c}{c^T S^T S c} \tag{10}$$

due to Eq. (8). That is, if the basis is complete, the rectangular and square matrix equations are equivalent.

In the method of MC [1], energies are not obtained by applying the Boutry algorithm to solve the rectangular eigenvalue problem obtained by representing wavefunctions in a fixed basis set. Instead, the energies are fitting parameters, and they and the basis functions are optimized simultaneously. The iterative solution of the rectangular eigenvalue problem is intertwined with the optimization of the basis parameters. The residual (11) of a rectangular collocation matrix equation

$$R = \frac{1}{L} \sum_{k=1}^{L} \frac{\|(M - E_k S)c_k\|^2}{E_k^2 \|S c_k\|^2}, \tag{11}$$

is minimized by simultaneously fitting basis set parameters λ_i and E. The most straightforward way to optimize basis functions would require solving, using the algorithm of Boutry et al. a rectangular

problem for a sequence of different sets of parameters. Rectangular eigenvalues of the final rectangular eigenvalue problem, corresponding to the final basis parameters, would be the final energies. Instead, MC simultaneously optimize basis parameters and L energies. For each level, and for a given value of E, the coefficients c are elements of the right singular vector corresponding to the smallest singular value of the matrix $(M - ES)$, as in the method of Boutry et al. This singular vector is the eigenvector corresponding to the smallest eigenvalue of $(M - ES)^T(M - ES)$. For a fixed and nearly complete basis, minimizing the residual of Eq. (11) and minimizing the residual of Eq. (5) give similar results for the numerical values of E_k that we used. The ideas are general, but MC have used Gaussian-like basis functions [23,26–29],

$$\phi_i(\boldsymbol{x}|\lambda_i) = \prod_{j=1}^{d} \frac{b_{ij}}{\sqrt{\pi}} \exp(-b_{ij}^2(w_{ij} - \boldsymbol{x}_j)^2) \tag{12}$$

with the ratio of b_{ij} for different j fixed to the ratio of corresponding coordinate ranges. Each basis function therefore has $d + 1$ parameters $\lambda_i = \{b_i, w_{ij}\}$, $j = 1, \ldots, d$. Initially, the widths b_i and positions w_{ij} are given values within physically motivated ranges, but are otherwise random (see Ref. [3] for details). In applications of the method reported so far, the final fitted energies are almost equal to those obtained from Eq. (10) and Eq. (9) with the final optimized basis. For example, in the application to the vibrational spectrum of the water molecule, the difference between the fitted E and E of Eq. (10) was an order of magnitude smaller than the overall accuracy of the solution when using about $N = 30$ basis functions and $M = 1500$ points [3]. This near equality means that the MC method does find an optimal set of parameters of a near-complete basis. A term proportional to $\sum_{k=1}^{L}\left(E_k^{fit} - E_k^{Eq.(10)}\right)^2$ can be added to the residual of Eq. (11) to improve convergence [3] (this term was not used in the tests of the following section).

It is possible to use MC-type ideas to solve the rectangular eigenvalue problem associated with a *fixed* basis. This is done by not fitting the basis parameters, choosing the energy to minimize the residual (or equivalently taking it from Eq. (10)), obtaining c as the eigenvector corresponding to the smallest eigenvalue of $(M - ES)^T(M - ES)$, and iterating to self-consistency. This yields a modified version of the Boutry algorithm for solving a rectangular eigenvalue problem. This is denoted BEGM-MC (the authors' initials). When the basis is not good enough to provide an excellent representation of a particular wavefunction, the approximate energies and wavefunctions one obtains from the MC, Boutry or BEGM-MC, and square methods may be different. In the next section, we shall compare these methods for a fixed basis. We also compare (1) the MC method, (2) combining the optimization of basis parameters and Boutry's method for solving the rectangular problem, and (3) the optimization of parameters combined with the squared approach for solving the Schrödinger equation. The goal is to determine which methods allow one to solve the Schrödinger equation using a small basis.

3. Numerical tests and discussion

All methods were tested on an uncoupled potential representing the vibrations of H_2O. For the purpose of comparing the rectangular solvers and for the purpose of assessing their usefulness for solving the Schrödinger equation, the absence of coupling is unimportant. Previous calculations have demonstrated that the coupling does not degrade the accuracy of the MC method [2,3]. We used the anharmonic uncoupled approximation to the potential energy surface (PES) that was introduced in Ref. [3]. First, the equilibrium structure ($V = 0$), harmonic normal mode frequencies and normal coordinates were computed using DFT [30]. Second, DFT energies were computed on normal coordinate slices extending to a maximum energy $V_{max} = 20\,000\ cm^{-1}$. Third, the potential slices thus obtained were fitted to sixth-order polynomials. The PES was defined as

$$V_{unc}(Q) = \sum_{i=1}^{d} V_i^{slice}(Q_i), \tag{13}$$

where Q_i are mass-weighted normal mode coordinates, and $V_i^{slice}(Q_i)$ are the polynomial fits. The PES slices are shown in Figure 1. This 3D PES was then sampled at 3000 random points as described in Ref. [3]. In each calculation, half of the points, randomly chosen from the full set of 3000, were used to fit, and the other points were used as a test set. The residuals we report were computed at points in this test set. The reader is referred to Ref. [3] for details. The Schrödinger equation was solved using $T = -\frac{1}{2}\sum_{i=1}^{d}\frac{\partial^2}{\partial Q_i^2}$. We compute the ZPE and the levels with one quantum of excitation in each normal mode. In Ref. [3], the algorithm of Manzhos and Carrington was used to compute the same four levels on a fully coupled DFT PES as well as on the same uncoupled PES used here with a similar accuracy of about $1\ cm^{-1}$. For the purpose of comparing the three methods, we chose the uncoupled PES because it allowed us to obtain the exact, reference energies by the Runge–Kutta method [31] applied to each slice. These energies and corresponding transition frequencies are listed in Table 1. All calculations were done using Matlab [32].

In the first set of tests, we compare the accuracy of the energies obtained with a fixed basis size. In the previous section, we have demonstrated that if the basis is good enough, identical results will be obtained from the square approach and the rectangular methods. If the basis is not large enough to represent accurately the wavefunctions of interest, the results obtained with the square and rectangular methods will differ. We use a Gaussian basis of the form of Eq. (12) whose parameters have been optimized by the MC method, but N is not large enough to give accurate energies. Absolute errors and residuals are shown in Figures 2 and 3. All results are averaged over basis sets optimized from different sets of starting parameters. This gives more representative data than would be obtained from a single basis set. In certain runs with $N = 10$–20 basis functions, the squaring method and the method of Ref. [25] gave very poor solutions to the Schrödinger equation. Such runs were excluded from the average. It is clear that when the basis is small and incomplete, the MC method gives the most stable results. It is able to provide a realistic solution with very small N where the other methods fail: four levels are computed with an accuracy of several cm^{-1} using only 10 basis functions. As the basis approaches completeness ($N > 20$), all methods give

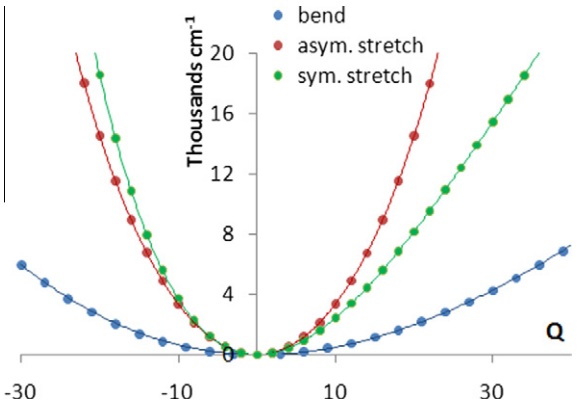

Figure 1. Slices of water PES along normal coordinates. The dots are DFT values, and the lines are sixth-order polynomial fits.

Table 1
Energy levels and corresponding transition frequencies in cm^{-1} for the anharmonic uncoupled potential of water, obtained with the Runge–Kutta algorithm.

Level	E	ν
ZPE	4513.6	N/A
ZPE + asym. stretch	8387.2	3873.6
ZPE + sym. stretch	8062.5	3548.9
ZPE + bend	6088.5	1574.9

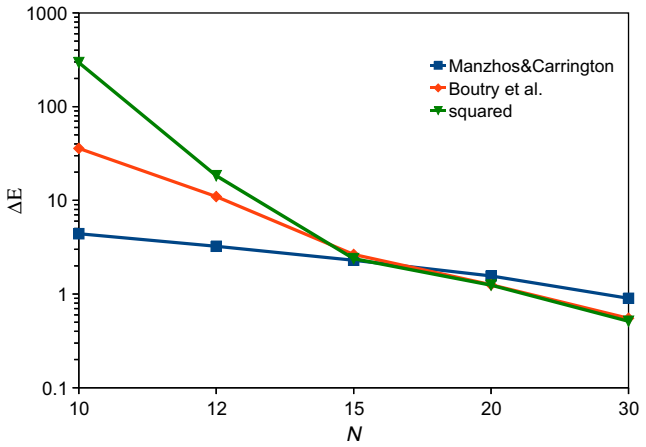

Figure 2. Mean absolute error in energy over the four levels listed in Table 1 of the three methods for different basis set sizes, in cm^{-1}. Basis parameters are optimized with the method of Manzhos and Carrington. The numbers are averages of 10 calculations differing by random initial parameter values and random potential points. The connecting lines are to guide the eye.

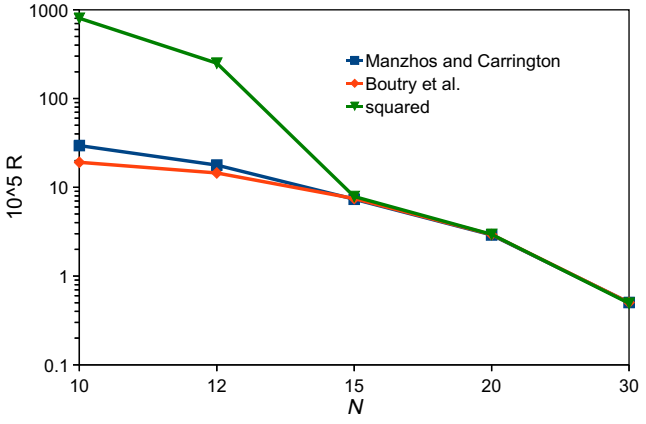

Figure 3. Mean residual over the four levels listed in Table 1 of the three methods for different basis set sizes. Basis parameters are optimized with the method of Manzhos and Carrington. The numbers are averages of 10 calculations differing by random initial parameter values and random potential points. The connecting lines are to guide the eye.

very similar results. At $N = 30$, all three methods achieve an accuracy of less than 1 cm^{-1}. The squaring method outperforms, closely followed by the method of Boutry et al. The underperformance of the method of MC largely disappears if the term $\sum_{k=1}^{L}(E_k^{fit} - E_k^{Eq.(10)})^2$ is added to the residual for minimization. The MC method is therefore an effective means of extracting good energies from a small and incomplete basis of good functions.

We have also tested the rectangular and square methods with fixed bases (i.e. matrices) of variable quality by starting with an optimized basis determined with the MC method and perturbing it by adding random noise to the basis parameters,

$$\lambda_i^A = \lambda_i + Ar, \tag{14}$$

where A is the noise amplitude, and components of r are in the range $[-0.5–0.5]$. We tested perturbing only the positions, perturbing only the widths, and perturbing both. The behavior in all cases was the same. We therefore report results obtained by perturbing both according to Eq. (14). In Figures 4 and 5, we plot the mean absolute error in E and the residual vs. the noise amplitude. In this test, we cannot directly compare the method of Manzhos and Carrington, which simultaneously optimizes basis parameters and the energy, with methods that only solve an eigenproblem. Instead, the results of BEGM-MC are shown which self-consistently solves the rectangular matrix equation with fixed matrices. The squaring method is the most stable, while the methods of BEGM-MC and of Boutry gave poor solutions even at a small noise amplitude. The stability of the squaring method can be related to the fact that the multiplication by the transpose effectively averages out the noise. In conclusion, if the basis is good enough for the square method to provide a good solution, that solution is the most stable to perturbation, but this is of limited utility.

In the final, and most important, set of tests we compared three methods of optimizing basis parameters and therefore solving the Schrödinger equation. Two of the approaches use a standard Levenberg-Marquard method and solve an eigenvalue problem for each set of trial basis parameters. The first of these two solves a rectangular eigenvalue problem with the method of Boutry et al. The second solves the square eigenvalue problem of Eq. (4). The third approach is the MC method. If one's purpose is to solve the Schrödinger equation and not merely to solve a general rectangular eigenvalue problem, then this is the most important test. If optimization + Boutry were as good as MC, it would be preferable because MC have an additional fitting parameter, E, and this increases the fitting cost. We find that only the MC method is able to optimize the basis and hence to solve the Schrödinger equation. For these tests, we use basis sizes $N = 10–30$. For the squaring method, we minimized the sum of eigenvalues corresponding to the energies in Table 1 [23,33]. For the method of Boutry et al., the residual of Eq. (11) was minimized. Both methods failed to find basis parameters that yield good solutions to the Schrödinger equation. Figure 6 helps explain why this happens. We plot the sum of eigenvalues of Eq. (4) corresponding to the energies of fitted levels during the

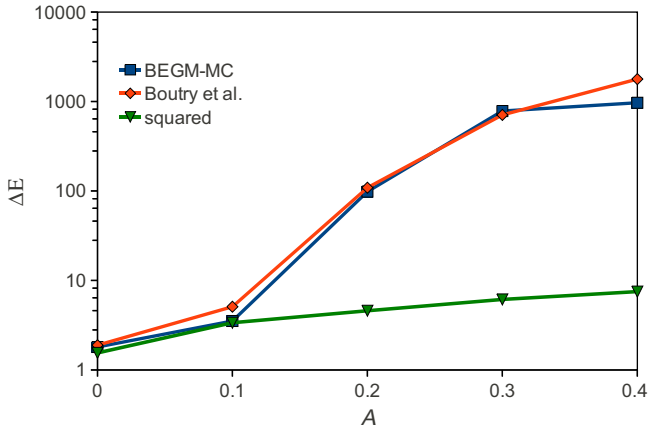

Figure 4. Mean absolute error in energy over the four levels listed in Table 1of the three methods for different perturbations to optimized basis parameters (A in Eq. (14)) for $N = 20$, in cm^{-1}. Basis parameters are optimized with the method of Manzhos and Carrington. The numbers are averages of 10 calculations differing by random noise. The connecting lines are to guide the eye.

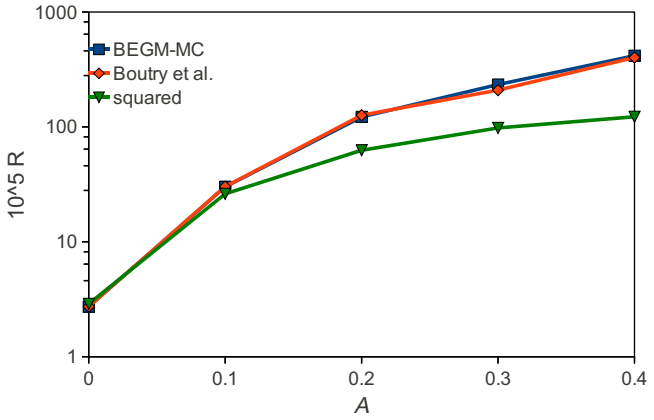

Figure 5. Mean residual over the four levels listed in Table 1 of the three methods for different perturbations to optimized basis parameters (A in Eq. (14)) for $N = 20$, in cm^{-1}. Basis parameters are optimized with the method of Manzhos and Carrington. The numbers are averages of 10 calculations differing by random noise. The connecting lines are to guide the eye.

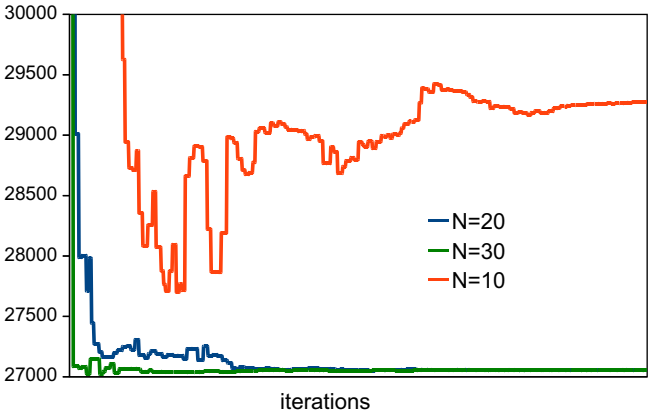

Figure 6. The sum of eigenvalues of Eq. (4) during the iterations of the method of Manzhos and Carrington for different basis sizes, in cm^{-1}.

iterations of the MC method. The convergence to the target value is non-uniform, which is of course due to the fact that the initial basis is far from complete. This causes Boutry iterations to diverge. Optimization with the Boutry and square methods works poorly due to the fact that the quantity being minimized does not vary monotonically; the optimization can get lost. In the method of MC, the energy is a fitting parameter that is allowed to vary within a window, typically ±10 cm^{-1} [2,3]. This stabilizes the initial stages of the fit. Without this, the optimization can fail if the calculation starts with a basis which is far from optimal.

If the basis is large enough, here more than about 20, the eigenvalues obtained from the square method are closest to the true solution for any set parameters λ_i. It might seem counter-intuitive that the method that possesses the best accuracy every step of the way cannot build a solution. Yet this is not surprising considering that for a fixed basis, it is possible to determine N coefficients but not $N(d+1)$ parameters from an $N \times N$ matrix. The information needed to determine the parameters is contained in $M > N$ points but is lost during squaring. One might still hypothesize that there exists a path in the parameter space of monotonically decreasing $\sum_i E_i$ which is not taken by our fit shown in Figure 6, but the fact that trace minimization fails to find a solution allows us to rule that possibility out.

4. Conclusion

It is sometimes possible to parameterize basis functions used to solve the vibrational Schrödinger equation so that for some choice of the parameters, a small number of functions make a basis good enough to compute accurate energy levels. When this is the case, one needs a means of optimizing the parameters. Because the basis is small, using the same number of quadrature/collocation points as basis functions gives poor results. It is not possible to use standard collocation with more points than basis functions, so one is forced to use either the square method (Eq. (4)) or to deal with a rectangular eigenvalue problem with matrices of size $M \times N$, $M > N$. We have shown that optimization combined with both the square method and the rectangular eigensolver of Boutry et al. [25] are not as good as the method of Manzhos and Carrington.

As the basis approaches completeness, all three methods converge to similar results. Although the squared problem is the most accurate with a fixed basis that is large enough, we show in this Letter that optimization with the method of MC is better. We demonstrated that when using a small number of Gaussian-like basis functions, a careful optimization of the basis parameters to build a near-complete basis is needed to achieve good results. Only the method of Manzhos and Carrington could build such an optimized basis. We also showed that for small but optimized basis sets, fitting to determine the rectangular eigenvalues is better than either the original method of Boutry et al. [25] or the square method.

We have shown that an accuracy of about 5 cm^{-1} for four low-lying vibrational levels of H_2O can be achieved with only 10 basis functions using the method of Manzhos and Carrington [1–3] on a model three-dimensional anharmonic potential. We believe therefore that the rectangular collocation method described here and in Refs. [1–3] combined with a small set of adaptable basis functions (not necessarily of Gaussian type) is a promising route to minimize the computational cost of vibrational calculations.

Acknowledgements

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