

Potential optimized discrete variable representation

Julián Echave and David C. Clary

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

Received 2 December 1991; in final form 18 December 1991

A new discrete variable representation (DVR) is proposed where the eigenstates of one-dimensional reference Hamiltonians are used to obtain the DVR localized basis functions. The method is applied to two model vibrational problems, the two- and three-dimensional Hénon–Heiles potentials, for which it is found to be much more efficient than the usual DVR and distributed Gaussian basis methods.

1. Introduction

A very powerful way of solving the Schrödinger equation consists of expanding the wavefunctions in a basis of localized functions of the coordinates and solving the resulting matrix equations. The distributed Gaussian basis approach (DGB) uses Gaussian functions localized around coordinate points conveniently placed [1]. The Gaussian functions are not orthogonal, therefore it is necessary to diagonalize the overlap matrix and there may be overcompleteness problems. Another localized basis approach is the so-called discrete variable representation (DVR) [2] method. In this the localized functions are approximate eigenfunctions of coordinate operators and they are orthogonal.

The DVR was proposed by Harris, Engerholm and Gwinn in 1965 [3]. It was first used as a convenient method to calculate potential matrix elements [3–5]. In the 80s it was given new impetus when Light and co-workers generalized it and applied it to a number of interesting quantum mechanical problems [1,6–8]. Recently it has been applied successfully in several important problems including the vibration of highly excited triatomic molecules [9–11], van der Waals molecules [12,13] and time-independent reactive scattering [14,15]. It has also been extended to time-dependent problems [16].

The DVR localized functions are obtained from the diagonalization of coordinate matrices calculated using suitable primitive basis sets. The DVR

Hamiltonian matrix is easy to obtain, and there are many manipulations that one can do to reduce the size of the final matrix that needs to be diagonalized. The most straightforward is to discard functions that are in regions where the potential energy is too large. There are also more powerful contracting techniques, such as the use of the ray-eigenvector basis of Bačić and Light [7,8], that we will discuss later.

The primitive basis functions are usually chosen to be polynomials of a function of the coordinate, because then the DVR potential energy matrix is approximately diagonal, the approximation being of Gaussian accuracy [4]. This condition limits the choice of primitive basis. In most cases considered in literature the basis functions do not have information about the potential energy surface. A useful way of reducing the size of basis sets to be used in multidimensional problems is to diagonalize convenient one-dimensional Hamiltonians and use the eigenfunctions obtained to treat the multidimensional problem [17,18]. In this Letter we use these eigenfunctions to obtain the DVR localized functions.

In section 2 we present a potential-optimized DVR (PO-DVR) where the DVR points are placed according to the potential energy surface. In section 3 we apply this method to two simple model vibrational problems and we compare with usual DVR and DGB calculations. Further comments and conclusions can be found in section 4.

2. Theory

We are interested in the solution of the Schrödinger equation for a general multidimensional Hamiltonian

$$H = H_0 + V(x, y, \dots), \quad (1)$$

where H_0 contains the kinetic energy term and may include part of the potential energy. $V(x, y, \dots)$ is the part of the potential energy not considered in H_0 . The methods considered in this Letter are basis set methods in which a suitable basis set is chosen, the matrix representing the Hamiltonian is calculated and diagonalized to obtain energies and stationary states. The number of functions to use depends on the properties of the basis used, on the number of energy levels one wants to calculate and on the accuracy required.

2.1. Discrete variable representation

The DVR is a localized basis set method where the basis functions are constructed as follows. First one chooses primitive one-dimensional basis sets

$$\{\phi_l(x), l=1, 2, \dots, N_x\}, \quad \{\psi_m(y), m=1, 2, \dots, N_y\}, \quad \dots \quad (2)$$

From these one obtains the new basis functions

$$|x_\lambda\rangle = \sum_{l=1}^{N_x} \mathbf{T}_{\lambda l}^x \phi_l(x), \quad |y_\mu\rangle = \sum_{m=1}^{N_y} \mathbf{T}_{\mu m}^y \psi_m(y), \quad \dots \quad (3)$$

where $\mathbf{T}^x, \mathbf{T}^y, \dots$ are the matrices that diagonalize the coordinate matrices $\mathbf{X}, \mathbf{Y}, \dots$ that represent the coordinate operators x, y, \dots (or functions of them) in the representation defined by (2). Note that $|x_\lambda\rangle$ is the function corresponding to the eigenvalue x_λ of \mathbf{X} , etc. It turns out that these functions are localized around their eigenvalues and because of the Hermiticity of the coordinate matrices they are orthogonal. The DVR basis is the direct product basis $\{|x_\lambda y_\mu \dots\rangle = |x_\lambda\rangle |y_\mu\rangle \dots\}$. Because these functions are localized we can introduce a parameter V_{\max} and truncate the basis set to the functions with $V(x_\lambda, y_\mu, \dots) < V_{\max}$.

Usually, the primitive basis sets (2) are chosen so that the matrix elements of the H_0 term in (1) are

easy to calculate (e.g. diagonal). The matrix representing this operator in the DVR, $\mathbf{H}_0^{\text{DVR}}$ is then easily calculated with the help of (3). **Because of the localized nature of the basis functions the potential energy matrix is considered to be diagonal:**

$$\langle x_\lambda y_\mu \dots | V | x_{\lambda'} y_{\mu'} \dots \rangle = V(x_\lambda, y_\mu, \dots) \delta_{\lambda\lambda'} \delta_{\mu\mu'} \dots \quad (4)$$

Once obtained, the Hamiltonian matrix is diagonalized using standard methods. It is important to note at this point that while $\mathbf{H}_0^{\text{DVR}}$ is evaluated exactly, \mathbf{V}^{DVR} is only approximately diagonal. The accuracy of this approximation depends on the primitive basis used (eq. (2)) and on the way the localized basis functions (3) are obtained from it (i.e. on the coordinate functions diagonalized). As discussed in section 1, if the primitive basis consists of polynomials of a certain function of the coordinate and the matrix representing this function is diagonalized to obtain the DVR localized functions (3), then the approximation (4) is of Gaussian accuracy [4].

2.2. Potential-optimized discrete variable representation method

The forms and positions of the DVR localized basis functions depend on the properties of the primitive basis sets (2). In order to obtain localized functions that have some information about the potential energy surface we propose to use in (2)

$$\{\phi_l^{\text{PO}}(x), l=1, 2, \dots, N_x^{\text{PO}}\}, \quad \{\psi_m^{\text{PO}}(y), m=1, 2, \dots, N_y^{\text{PO}}\}, \quad \dots \quad (5)$$

where PO stands for potential optimized and $\phi_l^{\text{PO}}(x), \psi_m^{\text{PO}}(y), \dots$ are the eigenstates of conveniently designed one-dimensional reference Hamiltonians $H_{\text{ref}}^x, H_{\text{ref}}^y, \dots$,

$$H_{\text{ref}}^x \phi_l^{\text{PO}}(x) = \epsilon_l^x \phi_l^{\text{PO}}(x), \quad H_{\text{ref}}^y \psi_m^{\text{PO}}(y) = \epsilon_m^y \psi_m^{\text{PO}}(y), \quad \dots \quad (6)$$

We then use these to obtain localized functions $\{|x_\lambda\rangle^{\text{PO}}, \{|y_\mu\rangle^{\text{PO}}, \dots$ as explained above. For further reference we call this the PO-DVR method.

It could seem that using this method we lose the advantage of easy calculation of the $\mathbf{H}_0^{\text{DVR}}$. This is not so, because we can solve (6) using the usual DVR basis functions so that eventually we express our new

PO-DVR basis functions in terms of the primitive basis functions (2). Thus we can see this method as transforming from the primitive basis sets (2) to localized basis sets $\{|x_\lambda\rangle^{\text{PO}}\}$, $\{|y_\mu\rangle^{\text{PO}}\}$, ... that have some information about the potential energy surface. These PO-DVR basis functions are then used as explained in the paragraphs following (3). Note, that in general (5) will not be polynomials of any function of the coordinate. Therefore approximating the potential matrix by a diagonal matrix (eq. (4)) is not of Gaussian accuracy. However, it is known that it is a very good approximation [3,19], and we did not find any problems in the cases where we applied the method.

We would like to summarize the PO-DVR in algorithmic form:

(1) Choose convenient primitive basis sets $\{\phi_l(x), l=1, \dots, N_x\}$, $\{\psi_m(y), m=1, \dots, N_y\}$, ...

(2) Obtain the corresponding DVR basis functions $|x_\lambda\rangle$, $|y_\mu\rangle$, ...

(3) Using the DVR basis functions solve the one-dimensional effective equations (6) to obtain new basis sets $\{\phi_l^{\text{PO}}(x), l=1, \dots, N_x^{\text{PO}}\}$, $\{\psi_m^{\text{PO}}(y), m=1, \dots, N_y^{\text{PO}}\}$, ... In our numerical calculations we choose $N_x^{\text{PO}}, N_y^{\text{PO}}$ so that the energy of the states included is less than certain energy cut-offs $E_{\text{max}}^x, E_{\text{max}}^y$, ...

(4) Obtain PO-DVR basis functions $|x_\lambda\rangle^{\text{PO}}, |y_\mu\rangle^{\text{PO}}$, ...

(5) Discard functions such that the potential is greater than a potential-energy cut-off V_{max} .

(6) Calculate and diagonalize the PO-DVR Hamiltonian matrix.

2.3. Ray-eigenvector contraction procedure

There is a way of contracting the size of a DVR Hamiltonian matrix that has to be diagonalized [7,8]. In our localized basis function notation this procedure consists of using the so-called ray-eigenvector (REV) basis set

$$\{\phi_{\lambda n}(x, y, z, \dots) = |x_\lambda\rangle \xi_n^\lambda(y, z, \dots)\}, \quad (7)$$

where $\xi_n^\lambda(y, z, \dots)$ are the eigenfunctions of the $(n-1)$ -dimensional ray Hamiltonians $H^2(y, z, \dots) = H(x_\lambda; y, z, \dots)$. Only functions with energies smaller than a certain energy cut-off E_{ray} are used. For further reference we call this the DVR-REV method.

This contraction procedure can also be applied to contract the PO-DVR Hamiltonian, giving place to a PO-DVR-REV method.

3. Numerical results

In this section we apply the PO-DVR to two model vibrational problems that have been treated using the DGB method [1]. We compare the convergence properties of the PO-DVR with other DVRs and with the DGB.

3.1. Two-dimensional Hénon-Heiles potential

We first consider the 2D Hénon-Heiles Hamiltonian

$$H = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + V_{\text{2DHH}}(x, y), \quad (8)$$

where

$$V_{\text{2DHH}}(x, y) = \frac{1}{2}(x^2 + y^2) + \sqrt{0.0125}(x^2y - \frac{1}{3}y^3). \quad (9)$$

We use the primitive basis sets

$$\left\{ \cos\left(\frac{l\pi x}{2L}\right); \sin\left(\frac{(l+1)\pi x}{2L}\right); l=1, 2, \dots, N_x \right\},$$

$$\left\{ \cos\left(\frac{m\pi y}{2L}\right); \sin\left(\frac{(m+1)\pi y}{2L}\right); m=1, 2, \dots, N_y \right\} \quad (10)$$

(where we set $L=10$ to cover the region of interest) to obtain the DVR basis of size $N_x \times N_y$ that we truncate keeping functions with $V < V_{\text{max}}$ only. We also use the DVR-REV procedure in which we diagonalize the 1D ray Hamiltonians for each of the DVR x -points keeping ray-eigenvectors with energies smaller than E_{ray} , as explained in section 2.3. To obtain the PO-DVR localized basis set we use the reference Hamiltonians

$$H_{\text{ref}}^x = -\frac{1}{2} \frac{\partial^2}{\partial x^2} + \min[V_{\text{2DHH}}(x, y); y],$$

$$H_{\text{ref}}^y = -\frac{1}{2} \frac{\partial^2}{\partial y^2} + V_{\text{2DHH}}(x=0, y), \quad (11)$$

where $\min[f(x, y, z, \dots); y, z, \dots]$ stands for "vary y, z, \dots to find the minimum for a given value of x ". Using eigenstates of (11) with energies smaller than E_{\max}^x and E_{\max}^y , respectively, we obtain the PO-DVR basis functions and discard the ones with $V > V_{\max}$.

In table 1 we show converged results for the highest 22 vibrational energy levels calculated using PO-DVR. The symmetry assignments are done by comparison with the results of ref. [1], because we do not symmetry-adapt our basis sets. Because the primitive basis sets (10) are used in one-dimensional calculations, their size does not affect much the overall CPU time. We could then make N_x and N_y very large to ensure convergence with respect to these parameters. However, because we want to compare with DVR and DVR-REV where these parameters do have a large effect on the CPU time, we did calculations with increasing values of $N_x = N_y$. We still have three parameters that affect the size of the final Hamiltonian matrix: E_{\max}^x , E_{\max}^y , and V_{\max} . We used $E_{\max}^x = E_{\max}^y = E_{\max}$ and $V_{\max} = \beta E_{\max}$. Using $\beta = 1.2$ we performed calculations for increasing values of E_{\max} until results were converged to the desired accuracy.

Fig. 1 shows the number of basis functions required with different methods as a function of the global error, calculated by averaging the absolute errors of the energies of the highest levels, shown in

Table 1

Highest energy levels of the 2D Hénon-Heiles potential calculated using PO-DVR with $N_x = N_y = 55$, $E_{\max} = 30$, $\beta = 1.2$. Eight decimal places are shown of which we underline the ones not converged (based on the comparison with the energies calculated using $E_{\max} < 30$). The symmetry assignments are done by comparison with results of ref. [1].

State	Energy	State	Energy
23 E	11.15164330	11 A ₂	12.27719166
15 A ₁	11.16025775	18 A ₁	12.33377986
9 A ₂	11.32523125	29 E	12.48020130
24 E	11.38300716	30 E	12.71162360
25 E	11.53351158	19 A ₁	12.74818280
16 A ₁	11.74951826	31 E	12.76142735
10 A ₂	11.75229694	12 A ₂	13.03206043
17 A ₁	11.96607998	20 A ₁	13.07698414
26 E	11.96807864	32 E	13.08119146
27 E	12.06503857	13 A ₂	13.08687270
28 E	12.20570248	33 E	13.23324215

2D Hénon-Heiles Potential

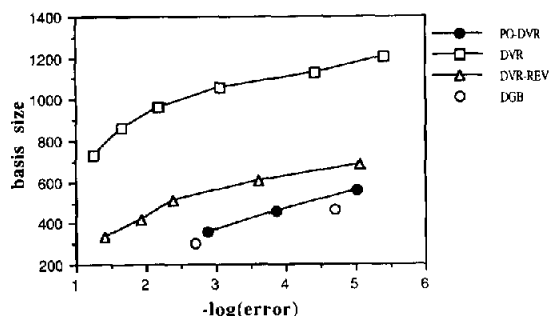


Fig. 1. Number of basis functions as a function of the global error for the 2D Hénon-Heiles potential. The parameters are: PO-DVR: $N_x = N_y = 47$; $E_{\max} = 16, 18$ and 20 ; $V_{\max} = \beta E_{\max}$ with $\beta = 1.2$. DVR: $N_x = N_y = 47$; $V_{\max} = 14, 16, 18, 20, 22, 24$. DVR-REV: $N_x = N_y = 47$; $E_{\max} = 24, 26, 28, 30, 32$; $V_{\max} = 28$. DGB: Basis sets C and E of ref. [1].

table 1. We can see that the PO-DVR requires less functions than the DVR-REV and much less than the DVR. The basis sizes for PO-DVR and DGB are of the same order. We have performed some calculations using a PO-DVR-REV technique, but the cpu time was greater than for the PO-DVR. This was due to the extra-time required to perform the transformation between the PO-DVR and PO-DVR-REV representations, that compensated the reduction in the dimension of the basis set.

3.2. Three-dimensional Hénon-Heiles potential

For the 3D Hénon-Heiles Hamiltonian

$$H = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} - \frac{1}{2} \frac{\partial^2}{\partial z^2} + V_{3DHH}(x, y, z), \quad (12)$$

where

$$V_{3DHH}(x, y, z) = \frac{1}{2}(x^2 + y^2 + z^2) - 0.1(xy^2 + 0.1x^3 + yz^2 + 0.1y^3). \quad (13)$$

We used the primitive basis sets (10) for x and y , and

$$\left\{ \cos\left(\frac{n\pi z}{2L}\right); \sin\left(\frac{(n+1)\pi z}{2L}\right); n = 1, 2, \dots, N_z \right\} \quad (14)$$

for z . The reference Hamiltonians

$$\begin{aligned}
H_{\text{ref}}^x &= -\frac{1}{2} \frac{\partial^2}{\partial x^2} + V_{\text{3DHH}}(x, y=0, z=0), \\
H_{\text{ref}}^y &= -\frac{1}{2} \frac{\partial^2}{\partial y^2} + V_{\text{3DHH}}(x=0, y, z=0), \\
H_{\text{ref}}^z &= -\frac{1}{2} \frac{\partial^2}{\partial z^2} + V_{\text{3DHH}}(x=0, y=0, z) \quad (15)
\end{aligned}$$

were diagonalized in the usual DVR representation to obtain the basis sets (3). Using the eigenstates with energies smaller than E_{max}^x , E_{max}^y , E_{max}^z , respectively, we calculated the localized PO-DVR basis functions. Further contraction was achieved by discarding functions with $V > V_{\text{max}}$.

In this 3D case, it turned out to be much more convenient to use a PO-DVR-REV technique. For each of the PO-DVR x-points, we diagonalized the two-dimensional ray Hamiltonians using the PO-DVR basis functions for y and z truncated according to $V < V_{\text{max}}$. We then utilized ray-eigenvectors with energies smaller than E_{ray} . For each value of E_{max}^x , we used increasing values of E_{ray} . For a given E_{ray} we set $E_{\text{max}}^y = E_{\text{max}}^z = \alpha E_{\text{ray}}$ and $V_{\text{max}} = \beta E_{\text{ray}}$. In trial calculations we found that good values for α and β were $\alpha = 0.8$, $\beta = 1.4$.

Table 2 shows converged results for the first 20 energy levels of the 3D Hénon-Heiles potential calculated with the PO-DVR-REV method. Fig. 2 shows the number of basis functions for PO-DVR and PO-

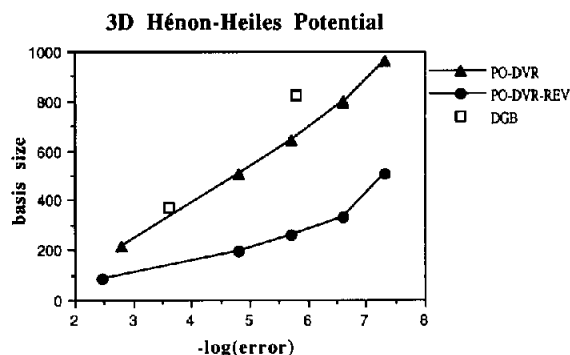


Fig. 2. Number of basis functions as a function of the global error for the 3D Hénon-Heiles potential. The parameters are: PO-DVR-REV: $N_x = N_y = N_z = 47$; $E_{\text{max}}^x = 8$; $E_{\text{ray}} = 10, 11, 12, 13, 14$; $E_{\text{max}}^y = E_{\text{max}}^z = \alpha E_{\text{ray}}$ with $\alpha = 0.8$; $V_{\text{max}} = \beta E_{\text{ray}}$ with $\beta = 1.4$. PO-DVR: $N_x = N_y = N_z = 47$; $E_{\text{max}}^x = 8$; $E_{\text{max}}^y = E_{\text{max}}^z = 8, 8.8, 9.6, 10.4, 11.2$; $V_{\text{max}} = \beta E_{\text{max}}$ with $\beta = 1.75$. DGB: Basis sets C and F of ref. [1].

DVR-REV as a function of the global error, calculated by averaging the absolute errors of the energies of the 20 states of table 2. Two points corresponding to different DGB basis sets used in ref. [1] are also shown. We can see that the PO-DVR-REV basis is very good, requiring 3 to 4 times less basis functions than the DGB to achieve a desired accuracy.

4. Conclusions

We have developed an easy to program and very efficient potential-optimized discrete variable representation in which the points are optimized for the potential energy surface. This is done using primitive basis sets of eigenfunctions of convenient one-dimensional reference Hamiltonians. We applied the method to two model vibrational problems to compare with the usual DVR and with DGB. For the 2D Hénon-Heiles potential we needed less basis functions than the usual DVR and of the same order as the DGB. For the 3D Hénon-Heiles potential, due to the possibility of contracting the basis using the ray-eigenvector procedure, the number of functions was much smaller than for the DGB.

It should be mentioned that in the case of vibrational problems, such as the ones considered here, one can use harmonic oscillator functions as primitive basis sets [20] and the convergence of DVR

Table 2

Energies for lowest 20 states of the 3D Hénon-Heiles potential calculated using PO-DVR-REV with $N_x = N_y = N_z = 47$, $E_{\text{max}}^x = 7.0$, $E_{\text{ray}} = 15.09$, $\alpha = 0.8$, $\beta = 1.4$. Eight decimal places are shown of which we underline the ones not converged (based on the comparison with the energies calculated using the same E_{max}^x but lower E_{ray} and calculations with $E_{\text{max}}^x = 10.0$). The symmetry assignments are done by comparison with results of ref. [1]

State	Energy	State	Energy
1A	1.49388975	8A	4.36246633
2A	2.47041786	4B	4.37333155
1B	2.47996173	9A	4.39593489
3A	2.49168459	5B	4.41909342
4A	3.42714282	10A	4.42935669
2B	3.43827646	11A	4.45122546
5A	3.45388584	6B	4.45262411
6A	3.47192175	12A	4.47208896
3B	3.48408013	7B	4.48245730
7A	3.48631241	13A	4.48258834

and DVR-REV would probably be much better. However such basis sets might not be appropriate for more complicated potential energy surfaces. It is for these cases that we expect the PO-DVR approach to be particularly useful. Indeed, we are currently implementing it as part of a four-atom reactive scattering code and we expect the PO-DVR method to have many other useful applications in spectroscopy and dynamics calculations.

Acknowledgement

This work was supported by the Science and Engineering Research Council.

References

- [1] I.P. Hamilton and J.C. Light, *J. Chem. Phys.* 84 (1986) 306.
- [2] J.C. Light, I.P. Hamilton and J.V. Lill, *J. Chem. Phys.* 82 (1985) 1401.
- [3] D.O. Harris, G.G. Engerholm and W.D. Gwinn, *J. Chem. Phys.* 43 (1965) 1515.
- [4] A.S. Dickinson and P.R. Certain, *J. Chem. Phys.* 49 (1968) 4209.
- [5] D. Cropek and G.D. Carney, *J. Chem. Phys.* 80 (1984) 4280.
- [6] Z. Bačić and J.C. Light, *Ann. Rev. Phys. Chem.* 40 (1989) 469.
- [7] Z. Bačić and J.C. Light, *J. Chem. Phys.* 85 (1986) 4594.
- [8] Z. Bačić and J.C. Light, *J. Chem. Phys.* 86 (1987) 3065.
- [9] J.R. Henderson, S. Miller and J. Tennyson, *J. Chem. Soc. Faraday Trans.* 86 (1990) 1963.
- [10] M. Mladenović and Z. Bačić, *J. Chem. Phys.* 93 (1990) 3039.
- [11] C. Leforestier, *J. Chem. Phys.* 94 (1991) 6388.
- [12] S.E. Choi and J.C. Light, *J. Chem. Phys.* 92 (1990) 2129.
- [13] J. Mladenović and Z. Bačić, *J. Chem. Phys.* 94 (1991) 4988.
- [14] D.E. Manolopoulos and R.E. Wyatt, *Chem. Phys. Letters* 152 (1988) 23.
- [15] Z. Bačić, J.D. Kress, G.A. Parker and R.T. Pack, *J. Chem. Phys.* 92 (1990) 2344.
- [16] J.T. Muckerman, *Chem. Phys. Letters* 173 (1990) 200.
- [17] S. Carter and N.C. Handy, *Mol. Phys.* 57 (1986) 175.
- [18] P.F. Endres, *J. Chem. Phys.* 47 (1967) 798.
- [19] S. Kanfer and M. Shapiro, *J. Phys. Chem.* 88 (1984) 3964.
- [20] S. Maluendes, G. Arteca, F.M. Fernández and E.A. Castro, *Mol. Phys.* 45 (1982) 511.