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A paradox of grid-based representation techniques: accurate eigenvalues from inaccurate matrix elements

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Abstract   Several approximately variational grid-based representation techniques devised to solve the time-independent nuclear-motion Schrödinger equation share a similar behavior: while the computed eigenpairs, the only results which are of genuine interest, are accurate, many of the underlying Hamiltonian matrix elements are inaccurate, deviating substantially from their values in a variational basis representation. Examples are presented for the discrete variable representation and the Lagrange-mesh approaches, demonstrating that highly accurate eigenvalues and eigenfunctions can be obtained even if some or even all of the Hamiltonian matrix elements in these grid-based representations are inaccurate. It is shown how the apparent contradiction of obtaining accurate eigenpairs with far less accurate individual matrix elements can be resolved by considering the unitary transformation between the representations. Furthermore, the relations connecting orthonormal bases and the corresponding Lagrange bases are generalized to relations connecting nonorthogonal, regularized bases and the corresponding nonorthogonal, regularized Lagrange bases.

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1 Introduction

During the last decades the use of grid-based techniques [1–36] almost revolutionized the variational-type quantum chemical treatment of nuclear motions. Grid-based representation techniques allowed the development of much improved algorithms, in turn yielding more efficient quantum mechanical nuclear motion computations. Application of these algorithms contributed to an improved understanding of (a) highly excited (ro)vibrational states of molecules, [37–56] studied experimentally via high-resolution molecular spectroscopy, and (b) quantum reaction dynamics [12,57–64]. It is generally appreciated that grid-based techniques are not strictly variational. This is due to the fact that the variational principle for the eigenenergies holds if the Hamiltonian matrix elements are evaluated "exactly". This can be achieved either by their analytic computation, corresponding to what is called the variational basis representation (VBR), or by highly accurate numerical procedures, whereby arbitrarily accurate quadrature schemes are employed, as in a finite basis representation (FBR). In more approximate and apparently more useful schemes, like in the discrete variable representation (DVR), [1–4] quadratures and basis functions are entangled and one looses the monotonic convergence of the eigenvalues offered by the variational principle. Nevertheless, the much improved numerical behavior of the DVR more than offsets this inconvenience.

Based on earlier work, [2,3] the DVR technique was introduced to quantum chemistry by Light and co-workers [4,8,14,15] for the efficient variational quantum mechanical treatment of nuclear motions. It has been used in a number of variational computational spectroscopic studies, even to determine full rotational-vibrational spectra of triatomic molecules, involving a large number of converged eigenvalues and eigenvectors [37,38,50,52,53]. It was recognized very early on that the Hamiltonian matrix elements produced by a DVR representation are occasionally inaccurate by a much larger amount than first expected. For example, following criticism by Carter and Meyer [65] on some of the protocols employed in Ref. [37], in 1993 Henderson, Tennyson, and Sutcliffe (HTS) [38] reinvestigated the quadrature approximation of treating the radial singularity during the computation of the vibrational eigenspectrum of H_3^+ by a DVR technique. A numerical observation of HTS was that

$$\widetilde{M}_{\beta,\beta}^{(2)} = 3M_{\beta,\beta}^{(2)} , \tag{1}$$

where $\mathbf{M}^{(2)}$ is the diagonal matrix of r^{-2} over spherical oscillator basis functions [66] evaluated using the DVR approximation and $\widetilde{\mathbf{M}}^{(2)}$ is a symmetric matrix obtained by the usual transformation of the exactly evaluated matrix of r^{-2} to the DVR representation. HTS wrote that this is "*an observation for which we have no explanation*".

The Lagrange-mesh (LM) method, another approximately variational technique for solving the Schrödinger equation, was introduced by Baye and Heenen [16] in 1986. It has been applied to a wide variety of problems in atomic, molecular, and nuclear physics, [19–29] yielding consistently highly accurate results. This accuracy is achieved despite the fact that the Gaussian quadrature approximation employed in

calculating the matrix elements of the potential energy operator and the overlap integrals in a Lagrange basis is not very accurate, as has been demonstrated in a number of numerical investigations, for example by Baye et al. [29]. In relation to the numerical examples studied, these authors stressed [29] that "*the Gauss approximation is far less accurate on individual matrix elements than on energies and wave functions. ...The simplest mesh is the regularized Laguerre mesh with full use of the Gauss approximation. The eigenvalue problem is not generalized and the accuracy is excellent. This might arise from the consistent use of the Gauss approximation in all terms. This striking accuracy remains unexplained.*"

In a recent paper [52] three of us investigated different DVR representations to deal with singularities present in the triatomic vibrational kinetic energy operator given in orthogonal internal coordinates of the two distances—one angle type. It was shown that the quadrature approximation worked almost as well as the exact DVR expressions. This accuracy was observed despite the fact that many of the matrix elements related to the singularity were computed very inaccurately.

In the following sections, especially in Sect. 2, the high accuracy of some of the grid-based methods is explored. In Sects. 3–5 explanations are provided to the above-mentioned observations. Furthermore, in Sect. 4 some relations fundamental for standard, orthonormal Lagrange bases are generalized to nonorthogonal, regularized Lagrange bases.

2 On the accuracy of DVR matrix elements

It is important to stress at the outset that in all DVR computations, with or without nonvariational behavior in the eigenvalues, the computed matrix elements of coordinate operators are inexact. This can be shown perhaps most simply for the following one-dimensional test case.

Consider the eigenvalue equation $\hat{H}^{HO}\Psi = \epsilon\Psi$ with $2\hat{H}^{HO} = -d^2/dq^2 + q^2$, and form its DVR by employing the N Gauss–Hermite DVR basis functions defined in Ref. [67] and related to the N-point Gauss–Hermite quadrature and the first N eigenfunctions of the harmonic oscillator Hamiltonian $\hat{H}^{HO}$. To obtain the DVR the matrix elements of the kinetic energy operator as well as those of the overlap matrix are calculated exactly by analytical formulae [16,19,67]. The matrix elements of the potential energy operator are calculated approximately by employing the N-point Gauss–Hermite quadrature resulting in a diagonal potential energy matrix with diagonal elements $V_{ii} = q_i^2/2, \quad i = 1, 2, \ldots, N$, where q_i denotes the ith Gauss–Hermite quadrature point [67]. If the potential energy matrix is calculated in the DVR basis exactly, one finds that it is no longer diagonal. It has nonzero off-diagonal elements $V_{ij} = 1/4, i \neq j$, and even the diagonal elements $V_{ii} = q_i^2/2 + 1/4$ differ from those obtained by the Gaussian quadrature approximation [67]. Clearly, the Hamiltonian matrix in the approximate DVR deviates substantially from that in the VBR, corresponding to calculating all matrix elements exactly in the DVR basis. Yet, by solving the approximate DVR matrix eigenvalue equation all but the highest eigenvalue is obtained with very high precision [9]. This contradiction can be resolved as follows.

The N DVR basis functions can be related to the first N eigenfunctions of the harmonic oscillator by an orthogonal transformation matrix $\mathbf{T}$ [2,3,8,9,31]. The orthogonal transformation of the DVR matrix eigenvalue equation by $\mathbf{T}$ results in a new matrix eigenvalue equation leading to the same eigenvalues as the DVR. This new matrix representation can be also obtained [3,8,31] by using the first N eigenfunctions of the harmonic oscillator as basis functions, when the matrix elements of the kinetic energy operator are calculated exactly, and those of the potential energy operator are calculated by the N-point Gauss–Hermite quadrature. This representation is called the finite basis representation (FBR). The FBR and the DVR are equivalent representations in the sense that they lead to the same eigenvalues. Since an N-point Gaussian quadrature gives exact result for any integrand which is a polynomial of degree less than or equal to $2N-1$, [68] all but the NNth element in the FBR of the harmonic oscillator Hamiltonian are exact. This and the equivalence of the FBR and DVR explain why the DVR gives highly accurate eigenvalues and eigenfunctions in spite of the inaccuracy of the DVR matrix elements.

3 Explanation of the observation of HTS

The numerical observation of HTS mentioned in the Introduction can be explained as follows. The exact matrix elements to the operator $x^{-1} = r^{-2}$ in a DVR basis based on generalized Laguerre polynomials $L_n^\gamma(x)$, with $\gamma > 0$, can be obtained analytically by the approach described in Ref. [67] as

$$(x^{-1})_{i,j} = \delta_{ij}\frac{\gamma+1}{\gamma x_i} + (1-\delta_{ij})\frac{1}{\gamma\sqrt{x_i x_j}} \tag{2}$$

From this expression Eq. (1) follows immediately once noted that HTS set $\gamma = 1/2$ in Table 4 of Ref. [38].

The ratio of 3 introduced in Eq. (1) and made apparent in Eq. (2) is not unique to the spherical oscillator DVR basis with $\gamma = 1/2$. In a recent study [52] we employed Bessel-DVR functions [69] defined as

$$\chi_i(r) = (-1)^{i+1}\frac{r_i\sqrt{2r}}{r^2 - r_i^2} J_{1/2}(Kr), \quad i = 0, 1, 2, \ldots, N-1, \tag{3}$$

where $J_{1/2}(Kr)$ is a Bessel function of the first kind and $K = N\pi/R^{\max}$. The set of Bessel grid points is defined as $r_i = (i+1)\pi/K$; thus, all the grid points are in the interval $0 < r_i \leq R^{\max}$, where $R^{\max}$ is a free parameter used to define the range of the r coordinate. When employing the Bessel-DVR basis the analytic matrix elements of the r^{-2} operator are obtained as

$$(r^{-2})_{i,j} = (-1)^{i+j}\left(3r_i^{-2}\delta_{ij} + \frac{2}{r_i r_j}(1-\delta_{ij})\right), \tag{4}$$

whereas the standard DVR approximation provides a diagonal matrix with elements

$$(r^{-2})_{i,j} \simeq r_i^{-2} \delta_{ij}. \tag{5}$$

Eqs. (4) and (5) clearly show that an observation similar to that of HTS holds analytically for the Bessel-DVR basis, as well. Although the analytic matrix representations of r^{-2} with the spherical oscillator and the Bessel DVR bases, Eqs. (2) and (4), respectively, show a considerable formal similarity, the actual grid points and thus the numerical matrix elements are, of course, different.

Note, finally, that the inaccuracy of the matrix elements of coordinate operators (Sect. 2) does not explain the breakdown of a DVR calculation when a singularity is present (Sect. 5).

4 The accuracy of the Lagrange-mesh method

The Lagrange-mesh (LM) method is a subset of the DVR methods [8,9,15,31,32,67] for which the Lagrange conditions provide high accuracy. In the particular case of a truncated standard orthogonal polynomial basis and the corresponding Gaussian quadrature grid the DVR and the LM methods are identical. This identity and a simple analysis of the accuracy of the Gauss–Hermite DVR of the harmonic oscillator eigenvalue equation help elucidating the reasons behind the high accuracy of the eigenvalues and eigenfunctions resulting from a Lagrange-mesh representation.

Similar arguments can be applied to explain the high accuracy of the Lagrange-mesh method in the case of more complicated Hamiltonians, whenever the Lagrange-mesh and DVR methods are identical, i.e., in the case of orthogonal polynomial bases and the associated Gaussian quadrature grids. When the DVR and Lagrange-mesh methods are different, which happens, for instance, for the case of the nonorthogonal polynomial bases studied in Ref. [29], the analyis may be generalized as follows.

Let the basis sets and the quadrature in which the FBR and LM representations are to be formed be defined. Therefore, the task is to find the transformation matrix relating the two basis sets and to check the accuracy of the matrix elements in the FBR. If the transformation matrix is invertible, the FBR and LM representations are equivalent, that is they lead to the same eigenvalues. If, in addition to this a sufficient number of the Hamiltonian and overlap matrix elements in the FBR are accurate, then accurate results will be obtained by using either representation. The transformation from the FBR to the Lagrange-mesh representation spreads the error localized on only a small number of matrix elements in the FBR to all the matrix elements in the Lagrange-mesh representation, but the accuracy of the approximating eigenvalues and eigenfunctions remains the same as that in the FBR. A worked-out example should make these general arguments transparent.

Consider the one-dimensional Hamiltonian

$$\hat{H} = -\frac{d^2}{dx^2} + \frac{l(l+1)}{x^2} + V(x), \tag{6}$$

where $l = 0, 1, \ldots,$ and $V(x)$ is a potential energy function. Let the nonorthogonal, regularized basis be

$$\hat{\varphi}_n(x) = xL_n(x)e^{-x/2}, n = 0, 1, \ldots, N - 1, \qquad (7)$$

where $L_n(x)$ is the nth normalized Laguerre polynomial. The related regularized Lagrange–Laguerre basis is

$$\hat{f}_i(x) = \frac{x}{x_i}f_i(x) = (-1)^i x_i^{-1/2} \frac{xL_N(x)}{x - x_i}e^{-x/2}, \quad i = 1, 2, \ldots, N, \qquad (8)$$

where

$$f_i(x) = (-1)^i x_i^{1/2} \frac{L_N(x)}{x - x_i}e^{-x/2}, \qquad (9)$$

and x_i is the ith zero of the Nth Laguerre polynomial. This is one of the examples studied numerically, with various choices of $V(x)$, in Ref. [29].

The FBR and the LM representations of $\hat{H}$ are formed in the $\hat{\varphi}$ and $\hat{f}$ bases, respectively, by employing the N-point Gauss–Laguerre quadrature, whose quadrature points are just the x_is and the quadrature weights are defined as

$$\lambda_i = e^{x_i} \left[x_i \left(\frac{dL_N(x)}{dx} \right)^2_{x=x_i} \right]^{-1}, \qquad (10)$$

when calculating matrix elements of $V(x) + l(l + 1)x^{-2}$ and the overlap integrals. The matrix elements of the operator $-d^2/dx^2$ are calculated exactly by employing analytical formulae in both representations.

The basis functions $\hat{\varphi}_n(x)$ are polynomials of degree $n + 1$ multiplied by the weight function $\exp(-x/2)$. The basis functions $\hat{f}_i(x)$ are polynomials of degree N multiplied by the weight, since

$$\frac{xL_N(x)}{x - x_i} = x \prod_{j=1; j \neq i}^{N} (x - x_j). \qquad (11)$$

The Gaussian quadrature approximation to the centrifugal term gives the exact matrix elements [29]. Therefore, it suffices to check the accuracy of the quadrature approximation to the matrix elements $\langle \hat{\varphi}_m | V | \hat{\varphi}_n \rangle$ and $\langle \hat{f}_j | V | \hat{f}_i \rangle$.

The polynomial degree of the relevant integrands is $m + n + 2 + deg(V(x))$ and $2N + deg(V(x))$, respectively, where $deg(V(x))$ denotes the degree of the polynomial best approximating $V(x)$ in the range of configuration space of interest. Since the number of Gaussian quadrature points is N and $2N - 1 < 2N + deg(V(x))$, none of the matrix elements in the Lagrange-mesh representation can be exact. In contrast, with a given $deg(V(x))$ and a sufficiently large N, $m + n + 2 + deg(V(x)) \leq 2N - 1$

can occur for certain values of m and n (recall that $m, n = 0, 1, \ldots, N - 1$) and a number of matrix elements in the FBR can be exact.

As to the overlap matrix elements, one must consider the integrals $\langle \hat{\varphi}_m | \hat{\varphi}_n \rangle$ and $\langle \hat{f}_j | \hat{f}_i \rangle$. Since $2N > 2N - 1$, none of the matrix elements of the overlap matrix in the Lagrange-mesh representation can be exact. On the contrary, all elements but the diagonal element $m = n = N - 1$ of the overlap matrix are exact in the FBR, since $m + n + 2 \leq 2N - 1$ for all allowed values of m and n, save the case $m = n = N - 1$.

In the particular example $V(x) = x^2$ considered in Ref. [29], most of the matrix elements of $V(x)$ and the overlap matrix are exact in the FBR, whereas there are no exact matrix elements in the corresponding LM representation. The numerical results presented in Ref. [29] show that the Lagrange-mesh representation gives highly accurate results. This may be unexpected if one simply considers the numerical [29] and the above analytical results on the accuracy of matrix elements of the Lagrange-mesh representation. Were the FBR and LM representations equivalent, they would lead to the same eigenvalues. This would readily explain the "unexpected" accuracy of eigenpairs calculated by the Lagrange-mesh representation, since most of the matrix elements in the FBR have been shown to be exact, and thus the FBR leads to eigenpairs of high accuracy. To show the equivalence of the two representations it suffices to find the matrix transforming from the Lagrange basis $\hat{f}$ to the $\hat{\varphi}$ basis.

The standard Lagrange–Laguerre basis functions $f_i(x)$ can be expressed as [16]

$$f_i(x) = \lambda_i^{1/2} \sum_{n=0}^{N-1} \varphi_n(x_i) \varphi_n(x), \tag{12}$$

where

$$\varphi_n(x) = e^{-x/2} L_n(x). \tag{13}$$

Substitution of Eqs. (12) and (10) into the defining equation, Eq. (8), of the regularized Lagrange–Laguerre functions gives

$$\hat{f}_i(x) = \frac{1}{x_i} \sum_{n=0}^{N-1} T_{ni} \hat{\varphi}_n(x), \tag{14}$$

where

$$T_{ni} = \left[x_i \left(\frac{dL_N(x)}{dx} \right)^2_{x=x_i} \right]^{-1/2} L_n(x_i). \tag{15}$$

Since T_{ni} is just the nith element of the N by N orthogonal matrix $\mathbf{T}$ transforming between standard Gauss–Laguerre DVR and the corresponding Laguerre polynomial

basis functions, Eq. (14) can be inverted to obtain

$$\hat{\varphi}_n(x) = \sum_{i=1}^{N} T_{ni} x_i \hat{f}_i(x).$$ (16)

Therefore, representations of an eigenvalue equation formed in the $\hat{\varphi}$ and $\hat{f}$ bases are equivalent and lead to the same eigenvalues, regardless of the approximation invoked when calculating the matrix elements, and regardless of the fact that the approximation may give accurate matrix elements with one of the basis sets while failing to give accurate matrix elements with the other.

The relationship between the regularized basis functions $\hat{f}_i$ and $\hat{\varphi}_n$ of Eqs. (14) and (16), respectively, can be rewritten as

$$\hat{f}_i(x) = \frac{1}{x_i^2} \lambda_i^{1/2} \sum_{n=0}^{N-1} \hat{\varphi}_n(x_i) \hat{\varphi}_n(x)$$ (17)

and

$$\hat{\varphi}_n(x) = \sum_{i=1}^{N} \lambda_i^{1/2} \hat{\varphi}_n(x_i) \hat{f}_i(x).$$ (18)

These equations suggest the following generalization of the equations relating orthonormal bases and the corresponding Lagrange bases to nonorthogonal, regularized bases.

Let $\varphi_n(x), n = 0, 1, \ldots, N-1$ be a truncated orthonormal basis satisfying the equations

$$\sum_{n=0}^{N-1} \varphi_n^*(x_i) \varphi_n(x_j) = \lambda_i^{-1} \delta_{ij}$$ (19)

$$\sum_{i=1}^{N} \lambda_i \varphi_n^*(x_i) \varphi_m(x_i) = \delta_{nm},$$ (20)

with grid points $x_i, i = 1, 2, \ldots, N$, and where superscript $*$ denotes complex conjugation, δ_{ij} and δ_{nm} denote Kronecker-delta symbols, and λ_i is defined by Eq. (19) when $i = j$. Furthermore, let $\hat{\varphi}_n(x) = r(x)\varphi_n(x)$ be a nonorthogonal set of functions obtained by multiplying $\varphi_n(x)$ with a function $r(x)$, requiring only that the regularizing function $r(x)$ satisfies $r(x_i) \neq 0, \ i = 1, 2, \ldots, N$. Then, the equations

$$\hat{f}_i(x) = \frac{1}{r^2(x_i)} \lambda_i^{1/2} \sum_{n=0}^{N-1} \hat{\varphi}_n^*(x_i) \hat{\varphi}_n(x),$$ (21)

define nonorthogonal, regularized Lagrange functions. Remarkably, the reverse relationship has exactly the same form as that of the corresponding relation of orthonormal bases, i.e.,

$$\hat{\varphi}_n(x) = \sum_{i=1}^{N} \lambda_i^{1/2} \hat{\varphi}_n(x_i) \hat{f}_i(x). \tag{22}$$

5 On the DVR of essential singularities

In many practical applications, e.g., during the computation of the energy levels of Coulombic systems, [19,36] energy levels of the spherical oscillator, [52] quantum dynamics studies, [35] and (ro)vibrational spectra of molecules employing internal coordinates, [30,38,52] singular terms in the Hamiltonian [30,70–72] have to be confronted. A common singular term, also present in most of the above-mentioned examples, is the term r^{-2} with $r \in [0, \infty)$. Partly motivated by failures of certain DVR schemes to treat singularities, several useful alternative strategies have been advanced for treating singularities in grid-based applications; [38,72–76] however, these approaches are not discussed here. It is more relevant for the present discussion to note that when applying the diagonal DVR approximation for the calculation of matrix elements of r^{-2}, numerical computations show in some cases accurate results with fast convergence [21,52].

5.1 The case of a complete basis set

Assuming a complete set of basis functions, it is straightforward to prove the validity of applying the quadrature approximation for singular operators of the form r^{-n} with $n \in 1, 2, \ldots$, and $r \in [a, b]$. What needs to be shown is that the matrices of the singular operators are diagonal in the DVR representation, which can be thought of as a unitary transformation method [2,3]. This can be proven by showing that the matrices of the singular operators are the powers of the inverse of the coordinate operator matrix, since a matrix and its inverse, and the powers of its inverse, share the same set of eigenvectors.

For $n = 1$ this can be shown as follows. Let $Q_{ij} = \langle i|x|j \rangle$ and $R_{ij} = \langle i|x^{-1}|j \rangle$, where $|i\rangle$ is the ith basis function, x is the coordinate operator, and $\langle g|h \rangle$ is the usual inner product between the elements g and h defined in the Hilbert space of the given quantum mechanical system. Assuming an orthonormal basis and using the identity relation $\sum_{k=1}^{\infty} |k\rangle\langle k| = \hat{I}$,

$$(\mathbf{QR})_{ij} = \sum_{k=1}^{\infty} Q_{ik} R_{kj} = \sum_{k=1}^{\infty} \langle i|x|k\rangle\langle k|x^{-1}|j \rangle = \langle i|xx^{-1}|j \rangle = \langle i|j \rangle = \delta_{ij} = \mathbf{I}_{ij}. \tag{23}$$

Thus, $\mathbf{R}$ is the inverse of $\mathbf{Q}$, they have the same eigenvectors, and $\mathbf{R}$ is diagonal in the DVR.

For $n > 1$ the following can be said. Let $\mathbf{R}_{ij}^{(n)} = \langle i|x^{-n}|j\rangle$. Assuming an orthonormal basis,

$$\mathbf{(R)}_{ij}^{(n)} = \langle i|x^{-n}|j\rangle = \sum_{k_1,k_2,k_3,\dots,k_n=1}^{\infty} (\mathbf{R})_{ik_1}(\mathbf{R})_{k_1k_2}(\mathbf{R})_{k_2k_3}\dots(\mathbf{R})_{k_nj} = (\mathbf{R}^n)_{ij} \quad (24)$$

holds and the matrices of the singular operators with $n > 1$ are the powers of $\mathbf{R}$. Thus, they also have the same eigenvectors as the coordinate matrix $\mathbf{Q}$ and they are diagonal in the DVR.

5.2 The case of incomplete basis sets

When using an incomplete basis set, the considerations of Sect. 5.1 are not feasible, because $\sum_{k=1}^{N} |k\rangle\langle k| \neq \hat{I}$. However, following the idea of Dickinson and Certain [3] as reviewed, for example, by Light and Carrington, [15] one can provide an approximation to the error arising from the use of diagonal DVR matrices.

Let us take the set of $\{P_l(x)\}_{l=0}^{N-1}$ functions, defined in the $[a, b]$ interval of the coordinate, which are normed and orthogonal with respect to the real weight function $w(x)$. Let us also assume for the set of functions to have a corresponding quadrature with quadrature points $\{\lambda_i\}_{i=1}^{N}$ and real quadrature weights $\{w_i\}_{i=1}^{N}$, which are exact in representing the orthogonality of the above functions, i.e.,

$$\int_a^b w(x) P_k^*(x) P_l(x) dx = \sum_{i=1}^{N} w_i P_k^*(\lambda_i) P_l(\lambda_i) = \delta_{kl}. \quad (25)$$

A straightforward example for $\{P_l(x)\}_{l=0}^{N-1}$ is a set of the first N of some classical orthogonal polynomials [80] defined in the interval $[a, b]$, and $\{\lambda_i\}_{i=1}^{N}$ and $\{w_i\}_{i=1}^{N}$ arise from the corresponding Gaussian quadrature rules. In this case the integrals calculated with the quadrature are exact for integrands of $w(x)$ weight function times a polynomial of order up to $2N - 1$. A very useful and practical way for obtaining a set of quadrature points for a given orthonormal basis is to diagonalize the coordinate matrix.

To move forward, let our incomplete basis set of N functions be defined as $\{\phi_l(x) = \sqrt{w(x)} P_l(x)\}_{l=0}^{N-1}$. Then, the exact matrix elements (VBR representation) of the $f(x)$ operator are

$$\mathbf{F}_{kl}^{\text{VBR}} = \int_a^b \phi_k^*(x) f(x) \phi_l(x) dx. \quad (26)$$

The approximate matrix elements (FBR representation) calculated within the quadrature approximation are

$$\mathbf{F}_{kl}^{\text{FBR}} = \sum_{i=1}^{N} \frac{w_i}{w(\lambda_i)} \phi_k^*(\lambda_i) f(\lambda_i) \phi_l(\lambda_i), \tag{27}$$

while the matrix elements in the diagonal DVR approximation are

$$\mathbf{F}_{ij}^{\text{DVR}} = f(\lambda_i) \delta_{ij}. \tag{28}$$

Let us define next the matrix $\mathbf{T}_{sl} = [w_s/w(\lambda_s)]^{1/2} \phi_l(\lambda_s) \in C^{N \times N}$, which is unitary if Eq. (25) holds,

$$(\mathbf{TT}^\dagger)_{ij} = \sum_{s=1}^{N} \mathbf{T}_{is} \mathbf{T}_{js}^* = \int_a^b w(x) P_j^*(x) P_i(x) dx = \delta_{ij}. \tag{29}$$

With the help of the $\mathbf{T}$ matrix and a little algebra, one can derive the following relation,

$$\begin{aligned}
\mathbf{F}_{ij}^{\text{DVR}} &= \sum_{s=1}^{N} f(\lambda_s) \delta_{is} \delta_{js} = \sum_{s=1}^{N} f(\lambda_s) \left(\mathbf{TT}^\dagger\right)_{is} \left(\mathbf{T}^\dagger \mathbf{T}\right)_{js} \\
&= \sum_{s,k,l=1}^{N} f(\lambda_s) \mathbf{T}_{ik} (\mathbf{T}^\dagger)_{ks} (\mathbf{T}^\dagger)_{jl} \mathbf{T}_{ls} \\
&= \sum_{s,k,l=1}^{N} f(\lambda_s) \mathbf{T}_{ik} \mathbf{T}_{sk}^* \mathbf{T}_{jl}^* \mathbf{T}_{sl} = \sum_{k,l=1}^{N} \mathbf{T}_{jl}^* \mathbf{T}_{ik} \sum_{s=1}^{N} f(\lambda_s) \mathbf{T}_{sk}^* \mathbf{T}_{sl} \\
&= \sum_{k,l=1}^{N} \mathbf{T}_{jl}^* \mathbf{T}_{ik} \sum_{s=1}^{N} \frac{w_s}{w(\lambda_s)} \phi_k^*(\lambda_s) f(\lambda_s) \phi(\lambda_s) \\
&= \sum_{k,l=1}^{N} \mathbf{T}_{jl}^* \mathbf{T}_{ik} \mathbf{F}_{kl}^{\text{FBR}} = \left(\mathbf{TF}^{\text{FBR}} \mathbf{T}^\dagger\right)_{ij}. \tag{30}
\end{aligned}$$

Thus, the diagonal DVR is a unitary transform of the FBR, the eigenvalues are the same in the two representations. This means that during the computation of the eigenvalues the error of the diagonal approximation using N basis functions is equivalent to the error arising from calculating the matrix element integrals with an N-point quadrature.

5.3 Sample computations

In nuclear motion Hamiltonians singularities arise when building an internal coordinate system on a manifold. If the Jacobian of the transformation vanishes, certain members of the coordinate system seize to exist. If the wave function does not vanish at a singular geometry than the wave function is in the wrong space. However, as shown below, this may not cause unsurmountable difficulties for the actual nuclear motion computations.

As perhaps first discussed in Ref. [30], if the wave function becomes vanishingly small nearby a singular geometry it is possible to deal with singular terms with suitable schemes of numerical integration or by choice of a suitable DVR, whereby points in the vicinity of the singularity are avoided during computation of the singular matrix elements. If, however, the wave function does not vanish at the singular geometry, the situation becomes somewhat more complex, as is the case for the H_3^+ molecular ion when the vibrations are treated in the Jacobi coordinate system.

Sample computations concerning the common singular term r^{-2} with $r \in [0, \infty)$ often arising in practical applications in one and three dimensions have been performed. Eigenenergies for the spherical oscillator model problem (1-D) and for the vibrational energies of the H_3^+ molecule (3-D) show that when basis functions with proper boundary conditions, i.e., satisfying the boundary conditions implied by the physical system, are used, the diagonal DVR approximation is adequate to get converged eigenstates. The 1-D case is treated in detail in Ref. [52] so it is not elaborated further in here.

Some relevant numerical results for the vibrational energies of the H_3^+ molecular ion are presented in Fig. 1 and Table 1, obtained using the Hamiltonian given in Eq. (1)
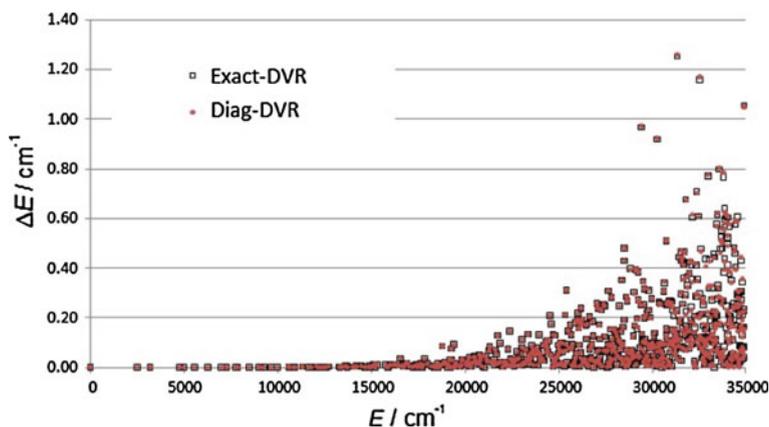

Fig. 1 Pictorial representation of the convergence of the even-parity vibrational states of the H_3^+ molecule. The computations were performed with (Diag-DVR) or without (Exact-DVR) using the diagonal DVR approximation for the r^{-2} singular terms in the Jacobi coordinate system and employed 105 and 100 PO Bessel-DVR functions for the two distance-type and 35 Legendre basis functions for the angle-type coordinates. Absolute deviations from the fully converged eigenenergies obtained with 120, 120, and 51 basis functions applying the Exact-DVR technique are shown

Table 1 Average relative errors, in %, of the eigenvalues and matrix elements of the singular operator r^{-2} with $r \in (0, \infty)$ in an FBR, obtained with Gaussian approximation, taken with respect to the appropriate VBR values

Eigenvalues	Matrix elements									
0.6	26	39	50	59	67	74	80	86	92	97
0.7	39	41	50	59	67	74	80	86	92	97
0.9	50	50	52	59	67	74	80	86	92	97
1.1	59	59	59	60	67	74	80	86	92	97
1.4	67	67	67	67	68	74	80	86	92	97
1.8	74	74	74	74	74	75	80	86	92	97
2.4	80	80	80	80	80	80	81	86	92	97
3.5	86	86	86	86	86	86	86	87	92	97
6.1	92	92	92	92	92	92	92	92	93	97
25.1	97	97	97	97	97	97	97	97	97	98

Matrix elements of the singular operator were computed using 100 basis functions based on spherical oscillator functions. The values presented in the table were obtained through averaging every 10 eigenvalues and the corresponding 10×10 matrix elements

of Ref. [52] and the corresponding volume element. The 3-D test computations [52] of the vibrational energy levels up to near dissociation were carried out using Jacobi coordinates and a direct product basis set, applying potential optimized (PO) [31,78,79] Bessel-DVR basis functions for the stretching-type coordinates and Legendre polynomials for the angle-type coordinate. This choice of the Hamiltonian, volume element, and basis functions, exhibiting the appropriate boundary conditions, ensures that (a) the eigenfunction (wave function times the stretching coordinates) vanishes at the singularity; and (b) the numerical procedure yields correct eigenvalues. Figure 1 shows the absolute error of non-converged even-parity vibrational energy levels, with respect to the converged results, obtained either via using the diagonal DVR approximation or via computing all the matrix elements of the r^{-2} radial singular terms analytically. As can be seen in Fig. 1, the error of the vibrational eigenenergies are nearly identical in the two cases, the diagonal DVR approximation can be applied for the evaluation of singular operator matrix elements. This general result can be of great help to reduce the cost of computations limited by computer power, such as (ro)vibrational calculations on larger molecules.

As detailed above, the error in the eigenvalues obtained with the diagonal DVR approximation are about the same as the error of eigenvalues obtained in the FBR using Gaussian quadrature for evaluating matrix elements. Table 1 presents the case of spherical-oscillator basis functions [52] (with the same boundary conditions as the PO Bessel-DVR functions). The spherical oscillator basis functions have boundary conditions such that the integrands in the integrals defining the matrix elements of the r^{-2} singular operator are not singular. However, when one uses Gaussian quadrature for computing the integrals it is necessary to defactor the weight function of the Gaussian quadrature, which causes the integrand to become singular. As expected, the matrix elements of the r^{-2} singular operator obtained in the FBR through Gaussian

quadrature have huge relative errors with respect to the VBR. Nevertheless, the eigenvalues show much less deviation from the VBR eigenvalues. This observation is related to the applicability of the diagonal DVR approximation for evaluating matrix elements of the r^{-2} singular term.

6 Summary

Henderson et al. (HTS) [38] found numerically a simple analytical relationship between certain exact Hamiltonian matrix elements and those obtained by a DVR and offered no explanation for it. The accuracy of the Lagrange-mesh method has been considered astonishing [21] yet unexplained by Baye et al. [21,29]. Szidarovszky et al. [52] found that even when singular integrals are computed inaccurately with a DVR the numerical difficulties may not compromise the quality and convergence of the related eigenvalues. In this paper a partial explanation is offered for the paradox of obtaining highly accurate eigenpairs from inaccurate Hamiltonian matrices.

The explanation offered exploits the following well known but perhaps not always appreciated facts about grid-based representation techniques. (1) The transformation of a matrix representation of an eigenvalue equation by an invertible transformation leaves the approximate eigenvalues unaffected. Such a transformation amounts to transforming from an initial truncated basis to another finite basis. (2) The initial representation can lead to accurate approximate eigenpairs if most of the matrix elements in the initial basis are accurate, or if there exists another truncated basis related to the initial one by an invertible transformation, in which most of the matrix elements are calculated accurately by the same method of integration as the one employed in calculating the matrix elements in the initial basis.

The observation of HTS has been explained analytically. Interestingly, a highly similar result can be given for the case of the Bessel-DVR functions.

An example studied numerically in Ref. [29] has been worked out in detail to make the general arguments of the explanation of the high accuracy of the Lagrange-mesh method transparent. In addition, the relations connecting orthonormal bases and the corresponding Lagrange bases have been generalized to relations connecting nonorthogonal, regularized bases and the corresponding nonorthogonal, regularized Lagrange bases.

It is straightforward to show the utility of the DVR approximation if a complete set of basis functions is used. For an incomplete basis set, the situation is more difficult. Since the diagonal DVR is a unitary transform of the FBR, the eigenvalues carry the error of computing the matrix elements with the quadrature approximation instead of using analytical formulae. Although this could imply the breakdown of the diagonal DVR approximation for singular operators, the numerical examples involving the singular term r^{-2} show it otherwise.

Finally, note an interesting and related property of the optimal generalized finite basis and discrete variable representations studied by Szalay [9,77]. By relating the optimal generalized FBR of a quantum mechanical Hamiltonian to a non-Hermitian effective Hamiltonian matrix, [77] it can be shown that eigenvalues corresponding to an optimal generalized FBR/DVR with potential optimized grids can have orders

of magnitude higher accuracy than those resulting from a fully variational computation employing the "same" truncated basis, while the matrix elements of the two representations are extremely different.

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