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On direct product based discrete variable representations for angular coordinates and the treatment of singular terms in the kinetic energy operator

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Dedicated to Horst Köppel on the occasion of his 60th birthday.

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ABSTRACT

The use of curvilinear coordinates results in kinetic energy operators with singular terms. These singularities can be in the dynamically relevant region. The present work specifically considers $1/\sin^2\theta$ singularities and wavefunctions showing significant amplitude close to $\theta = 0$. It investigates the use of direct product-type discrete variable representations (DVRs) to describe such situations in quantum dynamics calculations and discusses the regularization of such repulsive singularities. A new scheme, the cot-DVR, is developed which can be used to construct well converging direct product DVRs for Hamiltonians showing a $1/\sin^2\theta$ singularity. The cot-DVR is based on the diagonalization of the $\cot\theta$-matrix and adds two additional basis function, $\sin(\theta)$ and $\sin(2\theta)$, to the standard basis of Legendre polynomials. It is particularly well suited for multi-configurational time-dependent Hartree calculations which employ one-dimensional (bottom layer) single-particle functions.

1. Introduction

Quantum dynamics calculations frequently employ curvilinear coordinates to describe molecular systems. These coordinate systems are typically composed of radial or distance coordinates and angular coordinates of polar and torsional character. Torsional coordinates typically give rise to terms like $1/\sin^2\theta \frac{\partial^2}{\partial\phi^2}$ in the kinetic energy operator where ϕ should denote a torsional angle and θ a corresponding polar angle. These terms show singularities when θ equals 0 or π related to the undefinedness of ϕ at these points.

Discrete variable representations (DVRs) [1–3] or fast Fourier transform (FFT) schemes [4] provide efficient schemes employed in quantum dynamics calculations to represent wavefunctions and to evaluate the action of the Hamiltonian on these wavefunctions. Multi-dimensional wavefunctions are most easily represented employing direct products of one-dimensional DVRs or FFT representations. The singular terms described above, however, depend on at least the two coordinates θ and ϕ. Their efficient treatment is a problem when using direct product representations. This problem has immediately been recognized in the late 1980 and early 1990s when DVR and FFT based quantum dynamics calculations started to become widely popular. Different schemes addressing this problem have been suggested [5–12]. These studies considered the scattering of molecules from surfaces [5–7,10] or the coupling of rotational and vibrational motion [8,9,11] where one of the Euler angles instead of an internal ϕ coordinate is coupled to the polar angle θ. Vibronic coupling in linear triatomic molecule results is another example where the polar angle θ and transition between Σ and Π electronic states are coupled in a similar way. Here a scheme was proposed by Köppel and coworkers [13,14].

Following these early works, subsequently most quantum dynamics studies relied on the use of non-direct product representations to avoid problems with the singularities discussed above. The close coupling wave packet approach [5,6,15,16] has been widely employed to study reactive processes. As a prototypical example, the benchmark calculations which presented the first accurate results for the state-selected reaction probabilities of a diatom–diatom reaction, $H_2 + OH \rightarrow H + H_2O$, could be named [17,18]. Following the work of Leforestier [9], Corey and Lemoine [10] and Bramley et al. [19], schemes combining a non-direct product finite basis representation (FBR) with a direct product DVR quadrature to evaluate the potential matrix elements are typically used to accurately calculate the vibrational states of molecules consisting of four, five, or even six atoms. An impressive example of the efficiency which can be achieved by this strategy is provided by the recent calculations of the low-lying vibrational states of CH_5^+ by Wang and Carrington [20].

Considering the development towards increasingly large polyatomic systems, a disadvantage of these strategies becomes apparent. When using a body-fixed coordinate system, polar angles θ_i and torsional angles ϕ_i typically do not appear in pairs. Since the Euler angles used to describe the overall rotation include one polar

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angle and two torsional ones, the number of polar angles present in the internal coordinate system frequently exceeds the number of torsional angles by one. Therefore the centrifugal singularities in the kinetic energy operator couple many polar and torsional angles. Using a diatom–diatom Jacobi coordinate system, for example, two polar coordinates θ_1 and θ_2 and only one torsional coordinate ϕ is present. Consequently singularities as $1/\sin^2\theta_1 \frac{\partial^2}{\partial\phi^2}$ and $1/\sin^2\theta_2 \frac{\partial^2}{\partial\phi^2}$ appear simultaneously (a detailed discussion based on the full kinetic energy operator is given in the Appendix). Thus, a three-dimensional non-direct product FBR including the coordinates θ_1, θ_2, and ϕ is required to avoid the explicit appearance of singular terms. When considering a six atom system as CH_5^+, four polar angle and three torsional angles appear in the Radau-based description employed by Wang and Carrington [20]. Now a seven-dimensional non-direct product FBR is required to avoid the explicit appearance of singularities. Thus, increasingly high-dimensional non-direct product FBRs are required to describe systems of increasing size.

On the road towards accurate quantum dynamics calculations of increasingly large systems, the multi-configurational time-dependent Hartree (MCTDH) approach [21,22] has been found to be particular successful. The time-dependent single-particle functions (SPFs) employed in the MCTDH approach usually are represented using DVR or FFT techniques. While in the original formulation of the MCTDH scheme only one-dimensional SPFs have been considered, multi-dimensional SPFs can be used in mode-combination MCTDH [23–25] and multi-layer MCTDH [26–28] schemes. However, the efficiency of the MCTDH approach is lost if the bottom-layer SPFs depend on too many physical coordinates. Thus, the use of high-dimensional FBRs is incompatible with an efficient MCTDH treatment.

Meyer and coworkers avoided the problem in some MCTDH calculations (see, e.g., Refs. [29,30]) by an incomplete separation of the overall rotation. Separating only two instead of three Euler angles from the internal coordinates (as typically done for linear molecules), only singularities of the type $1/\sin^2\theta_i \frac{\partial^2}{\partial\phi_i^2}$ appear and direct products of two-dimensional FBRs for each θ_i, ϕ_i pair can be used. While this strategy seems to work well for scattering problems where overall and internal rotation are significantly coupled, it is less attractive for systems where rotational and internal motion are almost separable.

The present work investigates possibilities to describe Hamiltonians showing $1/\sin^2\theta$ singularities without resorting to non-direct product FBRs at all. The ability of one-dimensional DVRs for polar coordinates to properly describe such Hamiltonians is studied. Since the present work aims on developing schemes to be used in MCTDH calculations, the efficiency of these DVRs in standard wave packet calculations is not in the focus of the present work. Since the efficiency of MCTDH calculations does not strongly depend on the size of the time-independent grids employed in the representation of the SPF, the numbers of DVR points employed is not as important as in standard wave packet calculations. Therefore a direct product DVR which can properly describe the singularities might be attractive for MCTDH calculations even if it requires a somewhat larger number of grid points than an optimal non-direct product FBR.

The present article is organized as follows: Section 2 discusses the regularization of singular terms in the Hamiltonian. It shows that due to the repulsive nature of these terms direct product DVRs can in principle provide a correct description. Section 3 shows numerical results for the Legendre DVR and highlights features which can complicate calculations. An improved DVR treatment is then developed in Sections 4 and 5. The article ends with a concluding discussion.

2. Regularization of repulsive singular terms

As a model for the singular kinetic energy terms studied in the present work, the kinetic energy operator

$$\widehat{T} = -\frac{1}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \qquad (1)$$

depending on the polar angles θ and ϕ is considered. This kinetic energy operator shows the typical singularity for θ equal to 0 or π resulting from the non-unique definition of the torsional angle ϕ at these values of θ. Similar singularities are present in N-body kinetic energy operators employing polar and torsional angles and a body-fixed coordinate system to separate the overall rotational motion. A more detailed discussion highlighting the general nature of the problem and specifying the notion of a repulsive singularity is given in the Appendix.

The present work will investigate the direct product representations of the wavefunction in the coordinates θ and ϕ,

$$\psi(\theta,\phi) = \sum_l \sum_m A_{lm} f_l(\theta) g_m(\phi) \qquad (2)$$

For the sake of clarity and simplicity, we will restrict the further discussion to ϕ-independent potentials $V = V(\theta)$ and consequently take the $g_m(\phi)$ to be $\frac{1}{\sqrt{2\pi}}e^{im\phi}$. Here the quantum number m can be any integer number. This choice does not restrict the generality of our below conclusions which could easily be extended to general potentials and other basis functions $g_m(\phi)$. It results in a simple one-dimensional Hamiltonian

$$\widehat{H}_m = -\frac{1}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{m^2}{2I\sin^2\theta} + V(\theta) \qquad (3)$$

only parametrically depending on the quantum number m.

Due to the direct product form (2), however, the same m-independent basis $f_l(\theta)$ has to be used to represent the θ-dependence of the wavefunction for any m. The torsional motion in ϕ thus gives rise to a singularity at θ equal to 0 or π if $m \neq 0$. This singularity is absent if $m = 0$. The same basis $f_l(\theta)$ therefore must be able to represent the wavefunction in the presence and absence of the $1/\sin^2\theta$ singularity. This does not constitute an essential problem since the singularity is repulsive, i.e., the singular term is always positive in the neighborhood of the singular point. Consequently the wavefunction will always vanish sufficiently rapidly in the neighborhood of the singular point and the singular term can be regularized.

To investigate the effect of the repulsive singularity in detail, a harmonic oscillator system with an equilibrium geometry directly on top of the singular point at $\theta = 0$ will be studied. Such a system gives an example where the wavefunction amplitude at the singular point is maximal and thus provides a demanding test for the (numerical) treatment of the singularity. The present work employs the potential

$$V(\theta) = \frac{1}{2}I\omega^2 \cdot \theta^2 \qquad (4)$$

For the numerical test presented below, parameter values for moment of inertia I and the frequency ω roughly corresponding to the bending of a hydrogen atom in the methane molecule will be chosen: $I = 8000$ a.u., $\omega = 1500\ \mathrm{cm}^{-1}$.

Before starting the numerical studies, basic analytic considerations regarding the regularization of the singularity provide a useful introduction. In the limit of small amplitude motion, $I\omega \to \infty$, the lowest eigenstate of $\widehat{H}_m$ for a given value of m shows the eigenenergies

$$E_m = \omega \cdot (|m| + 1) \qquad (5)$$