Quantum Grid Dynamics: a method for solving the molecular Schrödinger Equation in Cartesian coordinates via angular momentum projection operators

Stavros C. Farantos

Institute of Electronic Structure and Lasers, Foundation for Research and Technology-Hellas, and
Department of Chemistry, University of Crete, Iraklion 711 10, Crete, Greece

EGEE09, Barcelona, September 22nd, 2009

THE PROBLEM

- Analytical derivation of the Hamiltonian in internal curvilinear coordinates and Euler angles is a cumpersome task for a N-atom molecule
- The appearance of cross derivatives in the kinetic term of the Hamiltonian implies a computational effort that scales as N^2

THE PROBLEM

- Analytical derivation of the Hamiltonian in internal curvilinear coordinates and Euler angles is a cumpersome task for a N-atom molecule
- The appearance of cross derivatives in the kinetic term of the Hamiltonian implies a computational effort that scales as N^2

Collaborators

- **Jaime Suarez, IESL/FORTH**
- **Stamatis Stamatiadis, Dept. Materials Science, UoC**
- **Lucas Lathouwers, Antwerp, Belgium**

Funding: EU Tok Programme: GRID-COMPCHEM

Bramley & Handy, JCP 98 (1989) 1378:Efficient calculation of rovibrational eigenstates of sequentially bonded four-atom molecules

from Table III) are shown in Table XII for $J=0$, while the $J=1$ calculations, required for ν_4 and ν_5, used basis XVI which is derived from XV by scaling NCBTR by $2J+1$; harmonic-oscillator basis functions Φ^S were used throughout in all three stretches. Convergence is somewhat more rapid and stretch–angular coupling less strong than for HOOH, although the lower symmetry of HCNO and the apparent need for large matrices early in the contraction scheme added considerably to the computational cost; the latter meant that the cost was, unusually, dominated by the calculation of angular matrix elements rather than by final matrix diagonalization. As with HOOH, it is necessary to ensure that all states of interest hold their true position in the ordering of eigenvalues before convergence can be reliably assessed: this has almost certainly been achieved with the XVII basis. Again, it turns out that high-quality calculations involve a formidable computational cost even for the lowest levels: the final matrices for the XVII basis are 5400×5400. However, the way ahead for deeper understanding of the nuclear potential function of HCNO almost certainly lies in more calculations of the kind presented here.

Note added in proof. In the preparation of the manuscript, the authors overlooked an example of an internal (Jacobi) coordinate $J=0$ four-atom variational calculation (on HOOH). This, Ref. 95, is brought to the reader's attention.

ACKNOWLEDGMENTS

We must acknowledge our debt to Dr. Stuart Carter for providing, along with much helpful advice, his tetra-atomic program as the starting point for the computational work described here; and, with Dr. Andrew Willetts, for making available details of the original calculations on HCCH and HOOH. We thank Nadja Pinnavaia for assistance with the HCNO calculations. We would also like to thank Dr. William H. Green and Professor Ian M. Mills for many useful discussions.

APPENDIX: REARRANGED $\hat{T}_{VR}$ FOR A–B–C–D

The four-atom rovibrational kinetic-energy operator $\hat{T}_{VR}$ in sequential bonding coordinates with a symmetrically embedded nuclear-fixed frame was first given in Ref. 14, where the coordinates are defined. Here the operator has been rearranged into a computationally more useful form by factorization so that each factor depending on one of r_1, r_2, r_3, (θ_1,θ_2), ϕ, $\hat{J}_x$, $\hat{J}_y$, or $\hat{J}_z$ is either Hermitian or anti-Hermitian, and so that factors depending on (r_1,r_2) and (θ_1,θ_2) are of either Σ_g^+ or Σ_u^+ symmetry in $\mathbf{D}_{\infty h}(\mathrm{M})$. Terms are labeled by superscripted numbers in square brackets.

As in Ref. 14, the volume element for integration is $\sin\theta_1 \sin\theta_2 \sin\beta\, dr_1\, dr_2\, dr_3\, d\theta_1\, d\theta_2\, d\phi\, d\alpha\, d\beta\, d\gamma$. Nuclear masses are M_1, M_2, M_3, M_4. The reduced masses μ_1, μ_2, μ_3 are then defined as

$$\frac{1}{\mu_1}=\frac{1}{M_1}+\frac{1}{M_2},\quad \frac{1}{\mu_2}=\frac{1}{M_3}+\frac{1}{M_4},\quad \frac{1}{\mu_3}=\frac{1}{M_2}+\frac{1}{M_3}.$$

$\hbar$ is taken to be 1.

$$\hat{T}_{VR}=-\frac{1}{2}\times\left[\frac{1}{2}\left(\frac{1}{\mu_1 r_1^2}+\frac{1}{\mu_2 r_2^2}\right)\left[\left\{\left(\cot\theta_1\frac{\partial}{\partial\theta_1}+\cot\theta_2\frac{\partial}{\partial\theta_2}\right)+\left(\frac{\partial^2}{\partial\theta_1^2}+\frac{\partial^2}{\partial\theta_2^2}\right)\right\}^{[1]}+\{(\csc^2\theta_1+\csc^2\theta_2)\}\left(\frac{\partial^2}{\partial\phi^2}^{[2]}-\frac{\hat{J}_z^2}{4}^{[3]}\right)\right.\right.$$

$$+\{-(\csc^2\theta_1-\csc^2\theta_2)\}\frac{\partial}{\partial\phi}i\hat{J}_z^{[4]}\Bigg]+\frac{1}{2}\left(\frac{1}{\mu_1 r_1^2}-\frac{1}{\mu_2 r_2^2}\right)\left[\left\{\left(\cot\theta_1\frac{\partial}{\partial\theta_1}-\cot\theta_2\frac{\partial}{\partial\theta_2}\right)+\left(\frac{\partial^2}{\partial\theta_1^2}-\frac{\partial^2}{\partial\theta_2^2}\right)\right\}^{[5]}\right.$$

$$+\{(\csc^2\theta_1-\csc^2\theta_2)\}\left(\frac{\partial^2}{\partial\phi^2}^{[6]}-\frac{\hat{J}_z^2}{4}^{[7]}\right)+\{-(\csc^2\theta_1+\csc^2\theta_2)\}\frac{\partial}{\partial\phi}i\hat{J}_z^{[8]}\Bigg]+\frac{1}{2}\frac{1}{r_3}\left(\frac{1}{M_2 r_1}+\frac{1}{M_3 r_2}\right)$$

$$\times\left[\left\{2(\cos\theta_1+\cos\theta_2)+4\left(\sin\theta_1\frac{\partial}{\partial\theta_1}+\sin\theta_2\frac{\partial}{\partial\theta_2}\right)-2\left(\csc\theta_1\frac{\partial}{\partial\theta_1}+\csc\theta_2\frac{\partial}{\partial\theta_2}\right)\right.\right.$$

$$-2\left(\cos\theta_1\frac{\partial^2}{\partial\theta_1^2}+\cos\theta_2\frac{\partial^2}{\partial\theta_2^2}\right)\Bigg\}^{[9]}+\Bigg\{-(\sin\theta_1\cot\theta_2+\sin\theta_2\cot\theta_1)+\left(\cos\theta_1\frac{\partial}{\partial\theta_1}\cot\theta_2+\cos\theta_2\frac{\partial}{\partial\theta_2}\cot\theta_1\right)$$

$$+\left(\csc\theta_1\frac{\partial}{\partial\theta_2}+\csc\theta_2\frac{\partial}{\partial\theta_1}\right)+2(\cos\theta_1+\cos\theta_2)\frac{\partial^2}{\partial\theta_1\partial\theta_2}\;2\left(\sin\theta_1\frac{\partial}{\partial\theta_2}+\sin\theta_2\frac{\partial}{\partial\theta_1}\right)\Bigg\}\cos\phi^{[10]}$$

$$+\Bigg\{2(\sin\theta_1\cot\theta_2+\sin\theta_2\cot\theta_1)-2\left(\cos\theta_1\frac{\partial}{\partial\theta_1}\cot\theta_2+\cos\theta_2\frac{\partial}{\partial\theta_2}\cot\theta_1\right)-2\left(\csc\theta_1\frac{\partial}{\partial\theta_2}+\csc\theta_2\frac{\partial}{\partial\theta_1}\right)$$

$$-2(\csc\theta_1\cot\theta_2+\csc\theta_2\cot\theta_1)\Bigg\}\left(\sin\phi\frac{\partial}{\partial\phi}+\frac{1}{2}\cos\phi\right)^{[11]}+\{-2(\csc\theta_1\cot\theta_2+\csc\theta_2\cot\theta_1)\}$$

$$\times\Bigg[\bigg(\cos\phi\,\frac{\partial^2}{\partial\phi^2}-\sin\phi\,\frac{\partial}{\partial\phi}-\frac{1}{2}\cos\phi\bigg)^{[12]}+\frac{1}{4}\cos\phi\;\hat{J}_z^2{}^{[13]}\Bigg]+\{2(\cot\theta_1\csc\theta_1+\cot\theta_2\csc\theta_2)\}$$

$$\times\bigg(-\frac{\partial^2}{\partial\phi^2}{}^{[14]}+\frac{1}{4}\hat{J}_z^2{}^{[15]}\bigg)+\bigg\{2\bigg(\cos\theta_1\frac{\partial}{\partial\theta_1}+\cos\theta_2\frac{\partial}{\partial\theta_2}\bigg)+(\csc\theta_1+\csc\theta_2)$$

$$-2(\sin\theta_1+\sin\theta_2)\bigg\}\sin(\phi/2)i\hat{J}_x{}^{[16]}$$

$$+\{2(\csc\theta_1+\csc\theta_2)\}\Bigg[\bigg(\cos(\phi/2)\frac{\partial}{\partial\phi}-\frac{1}{4}\sin(\phi/2)\bigg)i\hat{J}_x{}^{[17]}-\frac{1}{4}\sin(\phi/2)[\hat{J}_y,\hat{J}_z]_+{}^{[18]}\Bigg]$$

$$+\bigg\{2\bigg(\cos\theta_1\frac{\partial}{\partial\theta_1}-\cos\theta_2\frac{\partial}{\partial\theta_2}\bigg)+(\csc\theta_1-\csc\theta_2)-2(\sin\theta_1-\sin\theta_2)\bigg\}\cos(\phi/2)i\hat{J}_y{}^{[19]}+\{-2(\csc\theta_1-\csc\theta_2)\}$$

$$\times\Bigg[\bigg(\sin(\phi/2)\frac{\partial}{\partial\phi}+\frac{1}{4}\cos(\phi/2)\bigg)i\hat{J}_y{}^{[20]}-\frac{1}{4}\cos(\phi/2)[\hat{J}_x,\hat{J}_z]_+{}^{[21]}\Bigg]+\bigg\{(\sin\theta_1\cot\theta_2-\sin\theta_2\cot\theta_1)$$

$$-\bigg(\cos\theta_1\frac{\partial}{\partial\theta_1}\cot\theta_2-\cos\theta_2\frac{\partial}{\partial\theta_2}\cot\theta_1\bigg)+\bigg(\csc\theta_1\frac{\partial}{\partial\theta_2}-\csc\theta_2\frac{\partial}{\partial\theta_1}\bigg)\bigg\}\sin\phi\;\;i\hat{J}_z{}^{[22]}$$

$$+\{2(\cot\theta_1\csc\theta_1-\cot\theta_2\csc\theta_2)\}\frac{\partial}{\partial\phi}i\hat{J}_z{}^{[23]}\Bigg]+\frac{1}{2}\frac{1}{r_3}\bigg(\frac{1}{M_2r_1}-\frac{1}{M_3r_2}\bigg)\Bigg[\bigg\{2(\cos\theta_1-\cos\theta_2)$$

$$+4\bigg(\sin\theta_1\frac{\partial}{\partial\theta_1}-\sin\theta_2\frac{\partial}{\partial\theta_2}\bigg)-2\bigg(\csc\theta_1\frac{\partial}{\partial\theta_1}-\csc\theta_2\frac{\partial}{\partial\theta_2}\bigg)-2\bigg(\cos\theta_1\frac{\partial^2}{\partial\theta_1^2}-\cos\theta_2\frac{\partial^2}{\partial\theta_2^2}\bigg)\bigg\}^{[24]}$$

$$+\bigg\{-(\sin\theta_1\cot\theta_2-\sin\theta_2\cot\theta_1)+\bigg(\cos\theta_1\frac{\partial}{\partial\theta_1}\cot\theta_2-\cos\theta_2\frac{\partial}{\partial\theta_2}\cot\theta_1\bigg)+\bigg(\csc\theta_1\frac{\partial}{\partial\theta_2}-\csc\theta_2\frac{\partial}{\partial\theta_1}\bigg)$$

$$+2(\cos\theta_1-\cos\theta_2)\frac{\partial^2}{\partial\theta_1\partial\theta_2}-2\bigg(\sin\theta_1\frac{\partial}{\partial\theta_2}-\sin\theta_2\frac{\partial}{\partial\theta_1}\bigg)\bigg\}\cos\phi^{[25]}+\bigg\{2(\sin\theta_1\cot\theta_2-\sin\theta_2\cot\theta_1)$$

$$-2\bigg(\cos\theta_1\frac{\partial}{\partial\theta_1}\cot\theta_2-\cos\theta_2\frac{\partial}{\partial\theta_2}\cot\theta_1\bigg)-2\bigg(\csc\theta_1\frac{\partial}{\partial\theta_2}-\csc\theta_2\frac{\partial}{\partial\theta_1}\bigg)-2(\csc\theta_1\cot\theta_2-\csc\theta_2\cot\theta_1)\bigg\}$$

$$\times\bigg(\sin\phi\frac{\partial}{\partial\phi}+\frac{1}{2}\cos\phi\bigg)^{[26]}+\{-2(\csc\theta_1\cot\theta_2-\csc\theta_2\cot\theta_1)\}\Bigg[\bigg(\cos\phi\frac{\partial^2}{\partial\phi^2}-\sin\phi\frac{\partial}{\partial\phi}-\frac{1}{2}\cos\phi\bigg)^{[27]}$$

$$+\frac{1}{4}\cos\phi\;\hat{J}_z^2{}^{[28]}\Bigg]+\{2(\cot\theta_1\csc\theta_1-\cot\theta_2\csc\theta_2)\}\bigg(-\frac{\partial^2}{\partial\phi^2}{}^{[29]}+\frac{1}{4}\hat{J}_z^2{}^{[30]}\bigg)+\bigg\{2\bigg(\cos\theta_1\frac{\partial}{\partial\theta_1}-\cos\theta_2\frac{\partial}{\partial\theta_2}\bigg)$$

$$+(\csc\theta_1-\csc\theta_2)-2(\sin\theta_1-\sin\theta_2)\bigg\}\sin(\phi/2)i\hat{J}_x{}^{[31]}+\{2(\csc\theta_1-\csc\theta_2)\}$$

$$\times\Bigg[\bigg(\cos(\phi/2)\frac{\partial}{\partial\phi}-\frac{1}{4}\sin(\phi/2)\bigg)i\hat{J}_x{}^{[32]}-\frac{1}{4}\sin(\phi/2)[\hat{J}_y,\hat{J}_z]_+{}^{[33]}\Bigg]+\bigg\{2\bigg(\cos\theta_1\frac{\partial}{\partial\theta_1}+\cos\theta_2\frac{\partial}{\partial\theta_2}\bigg)$$

$$+(\csc\theta_1+\csc\theta_2)-2(\sin\theta_1+\sin\theta_2)\bigg\}\cos(\phi/2)i\hat{J}_y{}^{[34]}+\{-2(\csc\theta_1+\csc\theta_2)\}$$

$$\times\Bigg[\bigg(\sin(\phi/2)\frac{\partial}{\partial\phi}+\frac{1}{4}\cos(\phi/2)\bigg)i\hat{J}_y{}^{[35]}-\frac{1}{4}\cos(\phi/2)[\hat{J}_x,\hat{J}_z]_+{}^{[36]}\Bigg]+\bigg\{(\sin\theta_1\cot\theta_2+\sin\theta_2\cot\theta_1)$$

$$-\bigg(\cos\theta_1\frac{\partial}{\partial\theta_1}\cot\theta_2+\cos\theta_2\frac{\partial}{\partial\theta_2}\cot\theta_1\bigg)+\bigg(\csc\theta_1\frac{\partial}{\partial\theta_2}+\csc\theta_2\frac{\partial}{\partial\theta_1}\bigg)\bigg\}\sin\phi\;\;i\hat{J}_z{}^{[37]}$$

$$+\{2(\cot\theta_1\csc\theta_1+\cot\theta_2\csc\theta_2)\}\frac{\partial}{\partial\phi}i\hat{J}_z{}^{[38]}\Bigg]+\frac{1}{\mu_3r_3^2}\Bigg[\bigg\{\bigg(\cot\theta_1\frac{\partial}{\partial\theta_1}+\cot\theta_2\frac{\partial}{\partial\theta_2}\bigg)+\bigg(\frac{\partial^2}{\partial\theta_1^2}+\frac{\partial^2}{\partial\theta_2^2}\bigg)\bigg\}^{[39]}$$

$$+\bigg\{-2\frac{\partial^2}{\partial\theta_1\partial\theta_2}-\bigg(\cot\theta_1\frac{\partial}{\partial\theta_2}+\cot\theta_2\frac{\partial}{\partial\theta_1}\bigg)\bigg\}\cos\phi^{[40]}+\bigg\{2\bigg(\cot\theta_1\frac{\partial}{\partial\theta_2}+\cot\theta_2\frac{\partial}{\partial\theta_1}\bigg)+2\cot\theta_1\cot\theta_2\bigg\}$$

$$
\begin{aligned}
&\times\left(\sin\phi\,\frac{\partial}{\partial\phi}+\frac{1}{2}\cos\phi\right)^{[41]}+\{1\}\left(-2\,\frac{\partial^2}{\partial\phi^2}{}^{[42]}-\hat{J}_x^2{}^{[43]}-\hat{J}_y^2{}^{[44]}+\frac{1}{2}\hat{J}_z^2{}^{[45]}\right)\\
&+\{2\cot\theta_1\cot\theta_2\}\Bigg[\left(\cos\phi\,\frac{\partial^2}{\partial\phi^2}-\sin\phi\,\frac{\partial}{\partial\phi}-\frac{1}{2}\cos\phi\right)^{[46]}+\frac{1}{4}\cos\phi\;\hat{J}_z^2{}^{[47]}\Bigg]\\
&+\{(\csc^2\theta_1+\csc^2\theta_2)\}\left(\frac{\partial^2}{\partial\phi^2}{}^{[48]}-\frac{1}{4}\hat{J}_z^2{}^{[49]}\right)+\Bigg\{-2\left(\frac{\partial}{\partial\theta_1}+\frac{\partial}{\partial\theta_2}\right)-(\cot\theta_1+\cot\theta_2)\Bigg\}\sin(\phi/2)\,i\hat{J}_x{}^{[50]}\\
&+\{-2(\cot\theta_1+\cot\theta_2)\}\Bigg[\left(\cos(\phi/2)\,\frac{\partial}{\partial\phi}-\frac{1}{4}\sin(\phi/2)\right)i\hat{J}_x{}^{[51]}-\frac{1}{4}\sin(\phi/2)\,[\hat{J}_y,\hat{J}_z]_+{}^{[52]}\Bigg]\\
&+\Bigg\{-2\left(\frac{\partial}{\partial\theta_1}-\frac{\partial}{\partial\theta_2}\right)-(\cot\theta_1-\cot\theta_2)\Bigg\}\cos(\phi/2)\,i\hat{J}_y{}^{[53]}\\
&+\{2(\cot\theta_1-\cot\theta_2)\}\Bigg[\left(\sin(\phi/2)\,\frac{\partial}{\partial\phi}+\frac{1}{4}\cos(\phi/2)\right)i\hat{J}_y{}^{[54]}-\frac{1}{4}\cos(\phi/2)\,[\hat{J}_x,\hat{J}_z]_+{}^{[55]}\Bigg]\\
&+\Bigg\{-\left(\cot\theta_1\,\frac{\partial}{\partial\theta_2}-\cot\theta_2\,\frac{\partial}{\partial\theta_1}\right)\Bigg\}\sin\phi\;\;i\hat{J}_z{}^{[56]}+\{-(\csc^2\theta_1-\csc^2\theta_2)\}\,\frac{\partial}{\partial\phi}\,i\hat{J}_z{}^{[57]}\Bigg]\\
&+\frac{1}{2}\frac{1}{r_3}\left(\frac{1}{M_2}\frac{\partial}{\partial r_1}+\frac{1}{M_3}\frac{\partial}{\partial r_2}\right)\Bigg[\Bigg\{-2(\cos\theta_1+\cos\theta_2)-2\left(\sin\theta_1\,\frac{\partial}{\partial\theta_1}+\sin\theta_2\,\frac{\partial}{\partial\theta_2}\right)\Bigg\}^{[58]}\\
&+\Bigg\{2\left(\sin\theta_1\,\frac{\partial}{\partial\theta_2}+\sin\theta_2\,\frac{\partial}{\partial\theta_1}\right)+(\sin\theta_1\cot\theta_2+\sin\theta_2\cot\theta_1)\Bigg\}\cos\phi\,{}^{[59]}\\
&+\{-2(\sin\theta_1\cot\theta_2+\sin\theta_2\cot\theta_1)\}\left(\sin\phi\,\frac{\partial}{\partial\phi}+\frac{1}{2}\cos\phi\right)^{[60]}+\{2(\sin\theta_1+\sin\theta_2)\}\sin\,(\phi/2)\,i\hat{J}_x{}^{[61]}\\
&+\{2(\sin\theta_1-\sin\theta_2)\}\cos\,(\phi/2)\,i\hat{J}_y{}^{[62]}+\{-(\sin\theta_1\cot\theta_2-\sin\theta_2\cot\theta_1)\}\sin\phi\;\;i\hat{J}_z{}^{[63]}\Bigg]\\
&+\frac{1}{2}\frac{1}{r_3}\left(\frac{1}{M_2}\frac{\partial}{\partial r_1}-\frac{1}{M_3}\frac{\partial}{\partial r_2}\right)\Bigg[\Bigg\{-2(\cos\theta_1-\cos\theta_2)-2\left(\sin\theta_1\,\frac{\partial}{\partial\theta_1}-\sin\theta_2\,\frac{\partial}{\partial\theta_2}\right)\Bigg\}^{[64]}\\
&+\Bigg\{2\left(\sin\theta_1\,\frac{\partial}{\partial\theta_2}-\sin\theta_2\,\frac{\partial}{\partial\theta_1}\right)+(\sin\theta_1\cot\theta_2-\sin\theta_2\cot\theta_1)\Bigg\}\cos\phi\,{}^{[65]}\\
&+\{-2(\sin\theta_1\cot\theta_2-\sin\theta_2\cot\theta_1)\}\left(\sin\phi\,\frac{\partial}{\partial\phi}+\frac{1}{2}\cos\phi\right)^{[66]}+\{2(\sin\theta_1-\sin\theta_2)\}\sin(\phi/2)\,i\hat{J}_x{}^{[67]}\\
&+\{2(\sin\theta_1+\sin\theta_2)\}\cos(\phi/2)\,i\hat{J}_y{}^{[68]}+\{-(\sin\theta_1\cot\theta_2+\sin\theta_2\cot\theta_1)\}\sin\phi\;\;i\hat{J}_z{}^{[69]}\Bigg]\\
&+\frac{1}{2}\left(\frac{1}{M_2r_1}+\frac{1}{M_3r_2}\right)\frac{\partial}{\partial r_3}\Bigg\{-2(\cos\theta_1+\cos\theta_2)-2\left(\sin\theta_1\,\frac{\partial}{\partial\theta_1}+\sin\theta_2\,\frac{\partial}{\partial\theta_2}\right)\Bigg\}^{[70]}\\
&+\frac{1}{2}\left(\frac{1}{M_2r_1}-\frac{1}{M_3r_2}\right)\frac{\partial}{\partial r_3}\Bigg\{-2(\cos\theta_1-\cos\theta_2)-2\left(\sin\theta_1\,\frac{\partial}{\partial\theta_1}-\sin\theta_2\,\frac{\partial}{\partial\theta_2}\right)\Bigg\}^{[71]}\\
&+\left(\frac{1}{\mu_1}\frac{\partial^2}{\partial r_1^2}+\frac{1}{\mu_2}\frac{\partial^2}{\partial r_2^2}\right)\{1\}^{[72]}+\frac{1}{2}\left(\frac{1}{M_2}\frac{\partial^2}{\partial r_1\partial r_3}+\frac{1}{M_3}\frac{\partial^2}{\partial r_2\partial r_3}\right)\{2(\cos\theta_1+\cos\theta_2)\}^{[73]}\\
&+\frac{1}{2}\left(\frac{1}{M_2}\frac{\partial^2}{\partial r_1\partial r_3}-\frac{1}{M_3}\frac{\partial^2}{\partial r_2\partial r_3}\right)\{2(\cos\theta_1-\cos\theta_2)\}^{[74]}+\frac{1}{\mu_3}\frac{\partial^2}{\partial r_3^2}\{1\}^{[75]}\Bigg].
\end{aligned}
$$

Kinetic operator in Cartesian coordinates

$$T_{VR} = -\sum_{i=1}^{3N-3} \frac{\hbar^2}{2\mu_i} \frac{\partial^2}{\partial x_i^2} \quad (1)$$

The Time Dependent Schrödinger Equation (TDSE)

$$H\Psi(x,t) = \left[-\frac{\hbar^2}{2}\nabla^2 + V(x)\right]\Psi(x,t) = \mathrm{i}\hbar\frac{\partial\Psi(x,t)}{\partial t}, \qquad (2)$$

For time-independent potentials

$$\Psi(x,t) = U(t,H)\Psi_0(x) = \exp(-iHt/\hbar)\Psi_0(x), \qquad (3)$$

The 4 Steps to solve TDSE

- **STEP 1**: Discretise the wavefunction $\boldsymbol{\Psi}$ on a grid of points in the Cartesian coordinate space and approximate the wavefunction over these grid points with Lagrange interpolation polynomials
- **STEP 2**: Project the initial wavefunction, $\boldsymbol{\Psi_0}$, on a specific irreducible representation subspace of the total angular momentum, $\boldsymbol{J}$ (of dimension $\boldsymbol{2J+1}$)
- **STEP 3**: Evaluate the action of the Hamiltonian operator $\boldsymbol{H}$ on the projected wavefunction $\boldsymbol{\Psi_J}$
- **STEP 4**: Propagate $\boldsymbol{\Psi_J}$ in time

The 4 Steps to solve TDSE

- **STEP 1**: Discretise the wavefunction $\boldsymbol{\Psi}$ on a grid of points in the Cartesian coordinate space and approximate the wavefunction over these grid points with Lagrange interpolation polynomials
- **STEP 2**: Project the initial wavefunction, $\boldsymbol{\Psi_0}$, on a specific irreducible representation subspace of the total angular momentum, $\boldsymbol{J}$ (of dimension $\boldsymbol{2J+1}$)
- **STEP 3**: Evaluate the action of the Hamiltonian operator $\boldsymbol{H}$ on the projected wavefunction $\boldsymbol{\Psi_J}$
- **STEP 4**: Propagate $\boldsymbol{\Psi_J}$ in time

The 4 Steps to solve TDSE

- **STEP 1**: Discretise the wavefunction $\boldsymbol{\Psi}$ on a grid of points in the Cartesian coordinate space and approximate the wavefunction over these grid points with Lagrange interpolation polynomials
- **STEP 2**: Project the initial wavefunction, $\boldsymbol{\Psi_0}$, on a specific irreducible representation subspace of the total angular momentum, $\boldsymbol{J}$ (of dimension $\boldsymbol{2J+1}$)
- **STEP 3**: Evaluate the action of the Hamiltonian operator $\boldsymbol{H}$ on the projected wavefunction $\boldsymbol{\Psi_J}$
- **STEP 4**: Propagate $\boldsymbol{\Psi_J}$ in time

The 4 Steps to solve TDSE

- **STEP 1**: Discretise the wavefunction $\boldsymbol{\Psi}$ on a grid of points in the Cartesian coordinate space and approximate the wavefunction over these grid points with Lagrange interpolation polynomials
- **STEP 2**: Project the initial wavefunction, $\boldsymbol{\Psi_0}$, on a specific irreducible representation subspace of the total angular momentum, $\boldsymbol{J}$ (of dimension $\boldsymbol{2J+1}$)
- **STEP 3**: Evaluate the action of the Hamiltonian operator $\boldsymbol{H}$ on the projected wavefunction $\boldsymbol{\Psi_J}$
- **STEP 4**: Propagate $\boldsymbol{\Psi_J}$ in time

STEP 1: Lagrange interpolation polynomials and their derivatives

B. Fornberg, *A Practical Guide to Pseudospectral Methods*, Cambridge University Press, 1998

R. Guantes, S. C. Farantos, *High order finite difference algorithms for solving the Schrödinger equation in molecular dynamics*, J. Chem. Phys. 111 (1999) 10827

$$n_s = 2s + 1 \text{ (stencil)}$$
$$n_s \longrightarrow n_g, \text{ (DVR limit)}$$

$$\left.\frac{\mathrm{d}^m u(x)}{\mathrm{d}x^m}\right|_{x=x_k} \approx \sum_{j=1}^{n_s} b^m_{n_s j} u(x_j), \qquad (4)$$

STEP 2: Angular Momentum Projection Operators (AMPO)

J.Broeckhove, L. Lathouwers, in: C. Cerjan (Ed.), Numerical Grid Methods and their Applications to Schrödinger Equation, Kluwer Academic Publishers, 1993, pp. 49–56

$$(P^J)^2 = P^J, \tag{5}$$

$$(P^J)^\dagger = P^J, \tag{6}$$

$$[H, P^J] = 0. \tag{7}$$

STEP 2: Angular Momentum Projection Operators (AMPO)

$$P^J_{MK} = \frac{2J+1}{8\pi^2}\int d\Omega D^{*J}_{MK}(\Omega)R(\Omega), \tag{8}$$

$$D^J_{MK}(\Omega) = \mathrm{e}^{-iM\phi} d^J_{MK}(\theta)\mathrm{e}^{-iK\gamma} \tag{9}$$

$$P^J = \sum_K P^J_{KK}, \quad \sum_J P^J = 1 \tag{10}$$

AMPO (P^J) and Autocorrelation Functions (C_J)

$$\begin{aligned} C_J(t) &= <\Psi(0)|P^J \exp(-iHt/\hbar) P^J|\Psi(0)> \qquad (11) \\ &= <\Psi(0)|\exp(-iHt/\hbar)|P^J\Psi(0)> . \qquad (12) \end{aligned}$$

$$\Psi_J(x) = P^J\Psi_0(x) = \frac{2J+1}{8\pi^2}\int d\Omega \sum_K D^{*J}_{KK}(\Omega)\, R(\Omega)\Psi_0(x). \qquad (13)$$

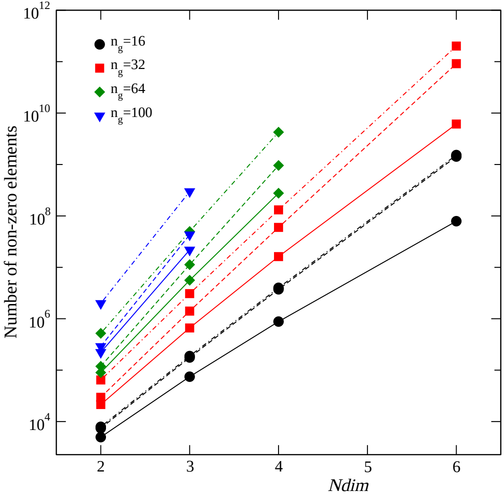
STEP 3: Matrix-Vector Multiplication

- In a discretised scheme and a FD approximation of the Hamiltonian, this operation turns into a sparse matrix-vector multiplication.
- The sparsity of the Hamiltonian depends on the length of the stencil ($n_s = 2s + 1$) employed in the calculation of the Laplacian, which is a matrix with $(3N - 3)(n_s - 1) + 1$ non-zero matrix elements per row.

STEP 3: Matrix-Vector Multiplication

- In a discretised scheme and a FD approximation of the Hamiltonian, this operation turns into a sparse matrix-vector multiplication.
- The sparsity of the Hamiltonian depends on the length of the stencil ($n_s = 2s + 1$) employed in the calculation of the Laplacian, which is a matrix with $(3N - 3)(n_s - 1) + 1$ non-zero matrix elements per row.

Nonzero Matrix Elements in Multidimensional Harmonic Oscillators



STEP 4: Time Propagation

Finite Difference of Second Order

$$\Psi(t+\Delta) = \Psi(t-\Delta) - \frac{2i\Delta}{\hbar} H \Psi(t), \tag{14}$$

Chebyshev Expansion of the Time Propagator

$$\Psi(t+\Delta) \approx \sum_{k=0}^{M} a_k T_k \left(\frac{-i\tilde{H}\Delta}{\hbar} \right) \Psi(t). \tag{15}$$

STEP 4: Autocorrelation Functions

$$C(t) = <\Psi(x,0)|\Psi(x,t)> = \int \Psi^*(x,0)\Psi(x,t)\mathrm{d}x, \quad (16)$$

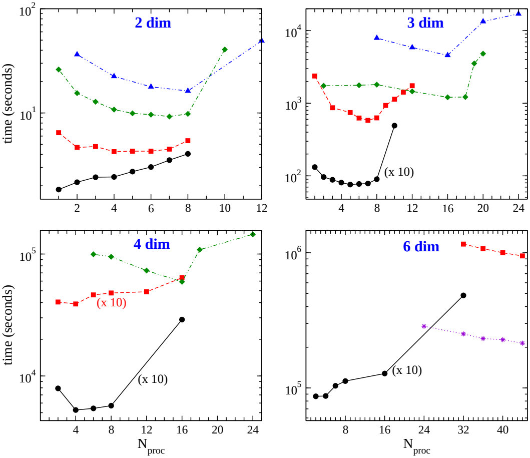
and its Fourier transform

$$I(E) = \left| \int \exp(iEt/h) C(t) \mathrm{d}t \right|^2. \quad (17)$$

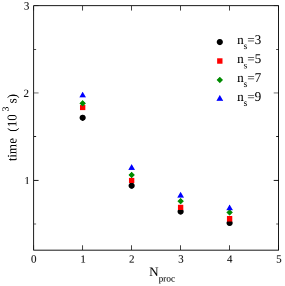
Multidimensional Harmonic Oscillators (H.O.)

$$V = \frac{1}{2} \sum_{i}^{N_{dim}} k(i) \left(x(i) - x_0(i) \right)^2 , \tag{18}$$

Execution times for different H.O. grid points. Stencil 15 and integration time 1000 a.u.



Execution times for a 3D H.O. and several stencils. Number of grid points 32 and total integration time 1000 a.u.



Bipolar expansion of a Gaussian function for diatomic molecules

K. Kaufmann and W. Baumeister J. Phys. B 22 (1989)1

$$e^{-\alpha(x-x_0)^2} = 4\pi e^{-\alpha(r_x^2+r_0^2)} \sum_{L=0}^{\infty} \sum_{M=-L}^{L} i_L(2\alpha r_x r_0) Y_{LM}(\phi_x, \theta_x) Y_{LM}^{*}(\phi_0, \theta_0),$$

$$P^J \, e^{-\alpha(x-x_0)^2} = 4\pi e^{-\alpha(r_x^2+r_0^2)} \frac{2J+1}{8\pi^2}$$

$$\int d\Omega \sum_K D_{KK}^{*J}(\Omega) \sum_{L,M} i_L(2\alpha r_x r_0) \left[R(\Omega)\, Y_{LM}(\phi_x, \theta_x)\right] Y_{LM}^{*}(\phi_0, \theta_0). \quad (19)$$

$$R(\Omega)\, Y_{LM}(\phi_x, \theta_x) = \sum_N D^L_{NM}\, Y_{LN}(\phi_x, \theta_x). \tag{20}$$

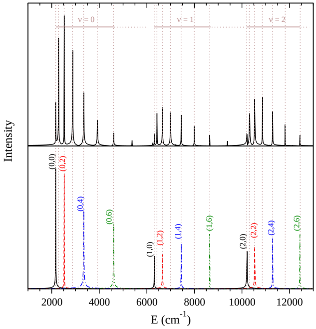
$$\int d\Omega\, D^{*J}_{KK}(\Omega) D^L_{NM}(\Omega) = \frac{8\pi^2}{2J+1} \delta_{JL}\delta_{KN}\delta_{KM}. \tag{21}$$

$$P^J\, e^{-\alpha(x-x_0)^2} = e^{-\alpha(r_x^2+r_0^2)}\, i_J(2\alpha r_x r_0) \sum_K Y_{JK}(\phi_x, \theta_x) Y^*_{JK}(\phi_0, \theta_0). \tag{22}$$

To test numerical integration over Euler angles

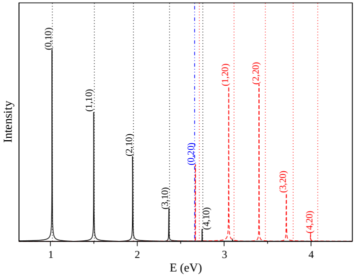
H_2 molecule

D. A. Morales, *Supersymmetric improvement of the Pekeris approximation for the rotating Morse potential*, Chem. Phys. Lett. 394 (2004) 68



H_2 molecule

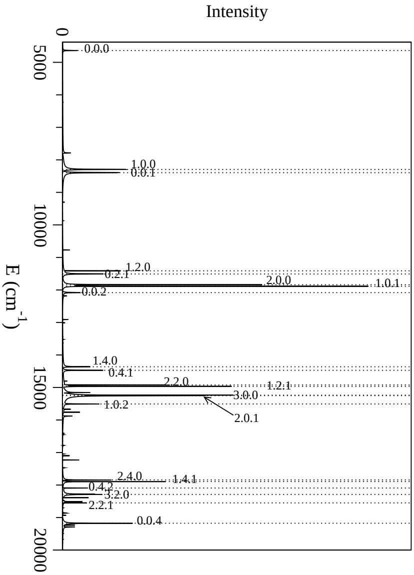
J. P. Killingbeck, A. Grosjean, G. Jolicard, *The Morse potential with angular momentum*, J. Chem. Phys. 116 (2002) 447



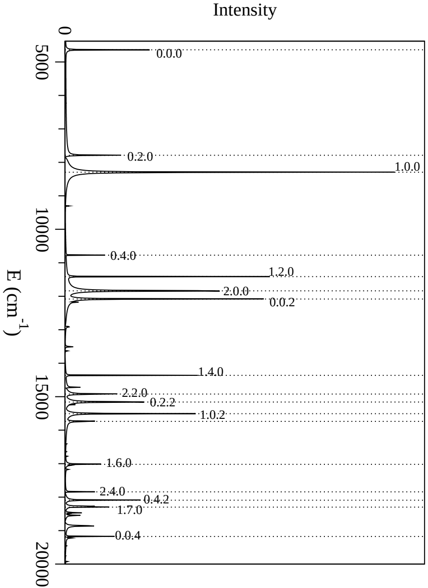
Triatomic molecule with 3D - Jacobi coordinates

$$
\begin{aligned}
H &= -\frac{\hbar^2}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2} \\
&\quad -\frac{\hbar^2}{2}\left(\frac{1}{\mu_R R^2} + \frac{1}{\mu_r r^2}\right)\left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta}\right) + V(R, r, \theta)
\end{aligned}
$$

Water ***3D***: Partridge and Schwenke, JCP 106 (1997) 4618



Water ***3D***: Partridge and Schwenke, JCP 106 (1997) 4618

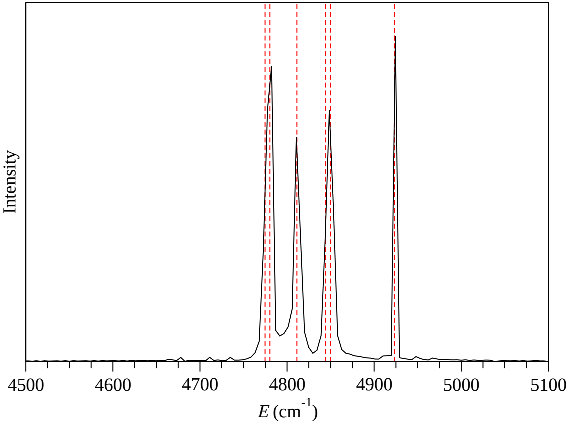


Filter Diagonalisation		Lanczos		Partridge and Schwenke			
E	$E - E_{ref}$	E	$E - E_{ref}$	E_{ref}	ν_1	ν_2	ν_3
4637.97	0.00	4637.97	0.00	4637.97	0	0	0
7789.61	0.01	7789.60	0.00	7789.60	0	2	0
8295.01	0.00	8295.03	0.02	8295.01	1	0	0
8393.95	0.02	8393.94	0.01	8393.93	0	0	1
10772.11	0.10	10772.11	0.10	10772.01	0	4	0
11413.11	0.04	11413.11	0.04	11413.07	1	2	0
11509.48	0.01	11509.48	0.01	11509.47	0	2	1
11839.51	0.01	11839.63	0.11	11839.52	2	0	0
11887.81	0.02	11887.92	0.09	11887.83	1	0	1
12083.12	0.03	12083.14	0.05	12083.09	0	0	2
14364.07	1.70	14364.07	1.70	14362.37	1	4	0
14471.62	0.02	14471.67	0.07	14471.60	0	4	1
14922.35	0.03	14922.48	0.16	14922.32	2	2	0
14966.63	0.01	14966.74	0.10	14966.64	1	2	1
15159.82	0.08	15159.82	0.08	15159.74	0	2	2
15237.65	0.00	15238.06	0.41	15237.65	3	0	0
15251.69	0.32	15251.69	0.32	15251.37	2	0	1
15507.09	0.23	15507.09	0.23	15506.86	1	0	2
17045.61	0.01	17045.61	0.01	17045.62	1	1	2
17844.65	1.54	17844.65	1.54	17843.11	2	4	0
17894.80	0.58	17894.81	0.59	17894.22	1	4	1
18092.49	0.81	18092.49	0.81	18091.68	0	4	2
18279.86	1.31	18279.87	1.31	18278.55	3	2	0
18290.84	0.41	18290.84	0.41	18290.43	2	2	1
18548.95	0.19	18548.95	0.19	18548.76	1	2	2
19176.11	0.72	19176.12	0.73	19175.39	0	0	4

6D Cartesian coordinates defined by Jacobi vectors

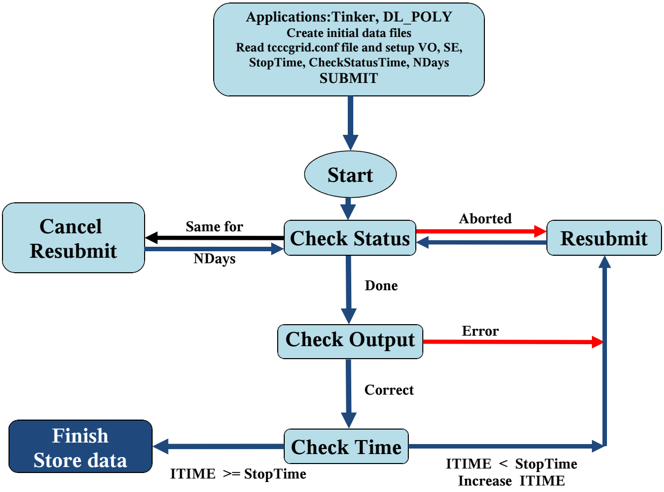
$$H\Psi(x,t) = -\sum_{i=1}^{6} \frac{\hbar^2}{2\mu_i} \frac{\partial^2}{\partial x_i^2} \Psi(x,t) + V\Psi(x,t) = \mathrm{i}\hbar \frac{\partial \Psi(x,t)}{\partial t}. \tag{23}$$

Water $\mathbf{6D}$, $\boldsymbol{v} = \mathbf{0}$ and $\boldsymbol{J} = \mathbf{3}$



$E_{Lanczos}$	E_{ref}	E_{dif}	J	K_a	K_c
136.38	136.76	0.37	3	0	0
142.02	142.28	0.26	3	1	3
172.94	173.36	0.42	3	1	2
206.04	206.30	0.26	3	2	2
211.95	212.15	0.20	3	2	1
284.89	285.21	0.32	3	3	1
285.08	285.41	0.33	3	3	0

A Scheme for long time propagation in the GRID



Conclusions

- GridTDSE a general purpose Fortran code for solving the Time (IN)Dependent Schrödinger Equation in Cartesian coordinates exists, but memory and CPUs are required.
- Calculations can be executed on the Grid by parametrising them with the total angular momentum and the number of vibrational eigenvalues to be filtered out.
- Computer Physics Communications, 180, 2025-2033, 2009.

Conclusions

- GridTDSE a general purpose Fortran code for solving the Time (IN)Dependent Schrödinger Equation in Cartesian coordinates exists, but memory and CPUs are required.
- Calculations can be executed on the Grid by parametrising them with the total angular momentum and the number of vibrational eigenvalues to be filtered out.
- Computer Physics Communications, 180, 2025-2033, 2009.

Conclusions

- GridTDSE a general purpose Fortran code for solving the Time (IN)Dependent Schrödinger Equation in Cartesian coordinates exists, but memory and CPUs are required.
- Calculations can be executed on the Grid by parametrising them with the total angular momentum and the number of vibrational eigenvalues to be filtered out.
- Computer Physics Communications, 180, 2025-2033, 2009.