Pushing the limit for the grid-based treatment of Schroedinger's equation: a sparse Numerov approach for one, two and three dimensional quantum problems

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Supplementary Material

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Improved Numerov approach in three Dimensions

In the three-dimensional case the Schrödinger equation is given by

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = f(x,y,z)\psi(x,y,z). \tag{S1}$$

It has to be solved on an $N \times M \times L$ grid. Analogous to two dimensions the gridsize h in all directions has to be the same. The notation is shortened analogously to the two-dimensional case:

$$\psi(x_i, y_j, z_k) = \psi_{i,j,k} \text{ and } \psi(x_i \pm a \cdot h, y_j \pm b \cdot h, z_k \pm c \cdot h) = \psi_{i\pm a, j\pm b, k\pm c}.$$

The stencil to approximate the Hamiltonian becomes also threedimensional. Therefore the notation introduced in section 2.1.2 in the manuscript has to be extended. This is done by adding slices to the notation given in equation (14) in the manuscript:

$$\begin{pmatrix} \psi_{i+1,j-1,k} & \psi_{i+1,j,k} & \psi_{i+1,j+1,k} \\ \psi_{i,j-1,k} & \psi_{i,j,k} & \psi_{i,j+1,k} \\ \psi_{i-1,j-1,k} & \psi_{i-1,j,k} & \psi_{i-1,j+1,k} \end{pmatrix}_k, \tag{S2}$$

where k denotes the index for the z-direction. The derivation starts with a sum of different Taylor series:

$$\begin{aligned} &\psi_{i+1,j+1,k+1} + \psi_{i+1,j+1,k-1} + \psi_{i+1,j-1,k+1} + \psi_{i+1,j-1,k-1} + \psi_{i-1,j+1,k+1} + \psi_{i-1,j+1,k-1} + \psi_{i-1,j-1,k+1} \\ &\quad + \psi_{i-1,j-1,k-1} - 8\psi_{i,j,k} = 4h^2 f_{i,j,k}\psi_{i,j,k} \\ &\quad + \sum_{l=2}^{n} 8\frac{h^{2l}}{(2l)!}\left(\sum_{m=0}^{l}\sum_{n=0}^{l-m} \frac{(2l)!}{(2l-2m-2n)!(2m)!(2n)!}\frac{\partial^{(2l)}\psi}{\partial x^{2l-2m-2n}\partial y^{2m}\partial z^{2n}}\right) + \mathcal{O}(h^{2n+2}). \end{aligned} \tag{S3}$$

For the standard Numerov method the series is truncated at $n = 2$ analogously to the one- and two-dimensional case. There appear only mixed derivatives with two variables. How this derivatives are approximated was described in section 2.1.2 in the manuscript. Analogously to the two-dimensional case a short calculation leads to equation

$$\frac{1}{h^2}\left[\begin{pmatrix} 3 & -4 & 3 \\ -4 & 16 & -4 \\ 3 & -4 & 3 \end{pmatrix}_{k-1}, \begin{pmatrix} -4 & 16 & -4 \\ 16 & -72 & 16 \\ -4 & 16 & -4 \end{pmatrix}_{k}, \begin{pmatrix} 3 & -4 & 3 \\ -4 & 16 & -4 \\ 3 & -4 & 3 \end{pmatrix}_{k+1}\right] = \\ = \left[\begin{pmatrix} 0 & 0 & 0 \\ 0 & f_{i,j} & 0 \\ 0 & 0 & 0 \end{pmatrix}_{k-1}, \begin{pmatrix} 0 & f_{i+1,j} & 0 \\ f_{i,j-1} & 6f_{i,j} & f_{i,j+1} \\ 0 & f_{i-1,j} & 0 \end{pmatrix}_{k}, \begin{pmatrix} 0 & 0 & 0 \\ 0 & f_{i,j} & 0 \\ 0 & 0 & 0 \end{pmatrix}_{k+1}\right]. \tag{S4}$$

As one can easiliy see also in the three-dimensional case the standard approach leads to two matrices $\mathbb{A}$ and $\mathbb{B}$. Same as in the two-dimensional case the problem can still be written as a matrix eigenvalue equation: The three-dimensional grid gets also arranged in a vector. Given is a $N \times M \times L$ grid, the indices (i, j, k) yield a scalar vector index being $i \cdot ML + j \cdot L + k$.

The resulting matrices are block-matrices. They contain bigger blocks with the dimension $ML \times ML$, which contain blocks of the size $L \times L$. This $ML \times ML$ submatrices have the same structure as the two-dimensional ones, with varying coefficients due to the additional dimension.

In this article an exemplary approach with accuracy $\mathcal{O}(h^6)$ is derived. Truncating the series in equation (S3) at $n = 3$ and a short calculation leads to equation

$$\begin{aligned} 4f_{i,j,k}\psi_{i,j,k} = & \frac{\psi_{i+1,j+1,k+1} + \psi_{i+1,j+1,k-1} + \psi_{i+1,j-1,k+1} + \psi_{i+1,j-1,k-1}}{h^2} + \\ & + \frac{\psi_{i-1,j+1,k+1} + \psi_{i-1,j+1,k-1} + \psi_{i-1,j-1,k+1} + \psi_{i-1,j-1,k-1} - 8\psi_{i,j,k}}{h^2} - \\ & - \frac{8h^2}{4!}\left(\frac{\partial^4\psi}{\partial x^4} + \frac{\partial^4\psi}{\partial y^4} + \frac{\partial^4\psi}{\partial z^4} + 6\frac{\partial^4\psi}{\partial x^2\partial y^2} + 6\frac{\partial^4\psi}{\partial x^2\partial z^2} + 6\frac{\partial^4\psi}{\partial y^2\partial z^2}\right) - \\ & - \frac{8h^4}{6!}\left(\frac{\partial^6\psi}{\partial x^6} + \frac{\partial^6\psi}{\partial y^6} + \frac{\partial^6\psi}{\partial z^6} + 15\frac{\partial^6\psi}{\partial x^4\partial y^2} + 15\frac{\partial^6\psi}{\partial x^4\partial z^2} + 15\frac{\partial^6\psi}{\partial y^4\partial z^2} + 15\frac{\partial^6\psi}{\partial x^2\partial y^4} + 15\frac{\partial^6\psi}{\partial x^2\partial z^4} + 15\frac{\partial^6\psi}{\partial y^2\partial z^4} + 90\frac{\partial^6\psi}{\partial x^2\partial y^2\partial z^2} \right. \\ & + \mathcal{O}(h^6). \end{aligned} \tag{S5}$$

All the appearing mixed derivatives have to be approximated. Because of the three-dimensional form of the stencil this has to be done coefficientwise. The approximated derivatives requiring the inclusion of the largest number of gridpoints are, as in the two-dimensional case, the fourth and the sixth derivative. This leads to a stencils size of $7 \times 7 \times 7$, although not every entry has to be non-zero. Consider this stencil as a cube $C_{i,j,k}$, with $i, j, k = 1, \ldots, 7$. The i denotes the x-direction, j the y-direction and k the z-direction. Given are the stencils for the approximation of the derivative in every direction, named

S^x, S^y and S^z. Then the entries of the cube have the form

$$C_{i,j,k} = S_i^x \cdot S_j^y \cdot S_k^z.$$

If there is no derivative in a certain direction to be approximated it reduces to

$$C_{i,j,4} = S_i^x \cdot S_j^y \text{ or } C_{i,4,4} = S_i^x.$$

All other entries are supposed to be zero. All derivatives have to be approximated separately and summed up afterwards. Symmetry of the Taylor-series can be used to reduce the effort.
The fourth derivatives need an approximation with accuray $\mathcal{O}(h^4)$, the sixth derivatives an accuracy of $\mathcal{O}(h^2)$. The term $\frac{\partial^6 \psi}{\partial x^2 \partial y^2 \partial z^2}$ is the only one where more than a slice of the cube C is filled, namely $C_{i,j,k}$ with $i, j, k = 3, 4, 5$. In all other cases the filled entries of the cube can be represented as a slice: $C_{i,j,4}$, $C_{i,4,k}$ or $C_{4,j,k}$, with $i, j, k = 1, \ldots, 7$. One can see that in higher dimensions there are always zero entries if the stencil is represented by a matrix or a cube, if the minimum stencil size to achieve the required accuracy is used. Also higher stencils can be used to approximate the derivatives. However, while this leads to a higher number of non-zero entries in the resulting stencil, the accuracy remains limited by the 7-point approximation of the fourth and sixth derivative. The three-dimensional stencil with the accuracy of $\mathcal{O}(h^6)$ is presented below. As one can see many entries of the $(7 \times 7 \times 7)$ stencil are equal zero. In higher dimensions more entries are filled because of the higher amount of mixed derivatives in all three dimensions.

$$\begin{pmatrix}
0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\
0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\
0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\
0.00000000 & 0.00000000 & 0.00000000 & 0.04444444 & 0.00000000 & 0.00000000 & 0.00000000 \\
0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\
0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\
0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000
\end{pmatrix}_{k-3} \tag{S6}$$

$$\begin{pmatrix} 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & -0.01388889 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.05555556 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & -0.01388889 & 0.05555556 & -0.76666667 & 0.05555556 & -0.01388889 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.05555556 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & -0.01388889 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \end{pmatrix}_{k-2} \tag{S7}$$

$$\begin{pmatrix} 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.05555556 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & -0.22222222 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.05555556 & -0.22222222 & 6.66666667 & -0.22222222 & 0.05555556 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & -0.22222222 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.05555556 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \end{pmatrix}_{k-1} \tag{S8}$$

$$\begin{pmatrix} 0.00000000 & 0.00000000 & 0.00000000 & 0.04444444 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & -0.01388889 & 0.05555556 & -0.76666667 & 0.05555556 & -0.01388889 & 0.00000000 \\ 0.00000000 & 0.05555556 & -0.22222222 & 6.66666667 & -0.22222222 & 0.05555556 & 0.00000000 \\ 0.04444444 & -0.76666667 & 6.66666667 & -34.16666667 & 6.66666667 & -0.76666667 & 0.04444444 \\ 0.00000000 & 0.05555556 & -0.22222222 & 6.66666667 & -0.22222222 & 0.05555556 & 0.00000000 \\ 0.00000000 & -0.01388889 & 0.05555556 & -0.76666667 & 0.05555556 & -0.01388889 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.04444444 & 0.00000000 & 0.00000000 & 0.00000000 \end{pmatrix}_{k} \tag{S9}$$

$$\begin{pmatrix} 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.05555556 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & -0.22222222 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.05555556 & -0.22222222 & 6.66666667 & -0.22222222 & 0.05555556 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & -0.22222222 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.05555556 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \end{pmatrix}_{k+1} \tag{S10}$$

$$\begin{pmatrix} 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & -0.01388889 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.05555556 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & -0.01388889 & 0.05555556 & -0.76666667 & 0.05555556 & -0.01388889 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.05555556 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & -0.01388889 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \end{pmatrix}_{k+2} \tag{S11}$$

$$\begin{pmatrix} 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.04444444 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \\ 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 & 0.00000000 \end{pmatrix}_{k+3} \tag{S12}$$

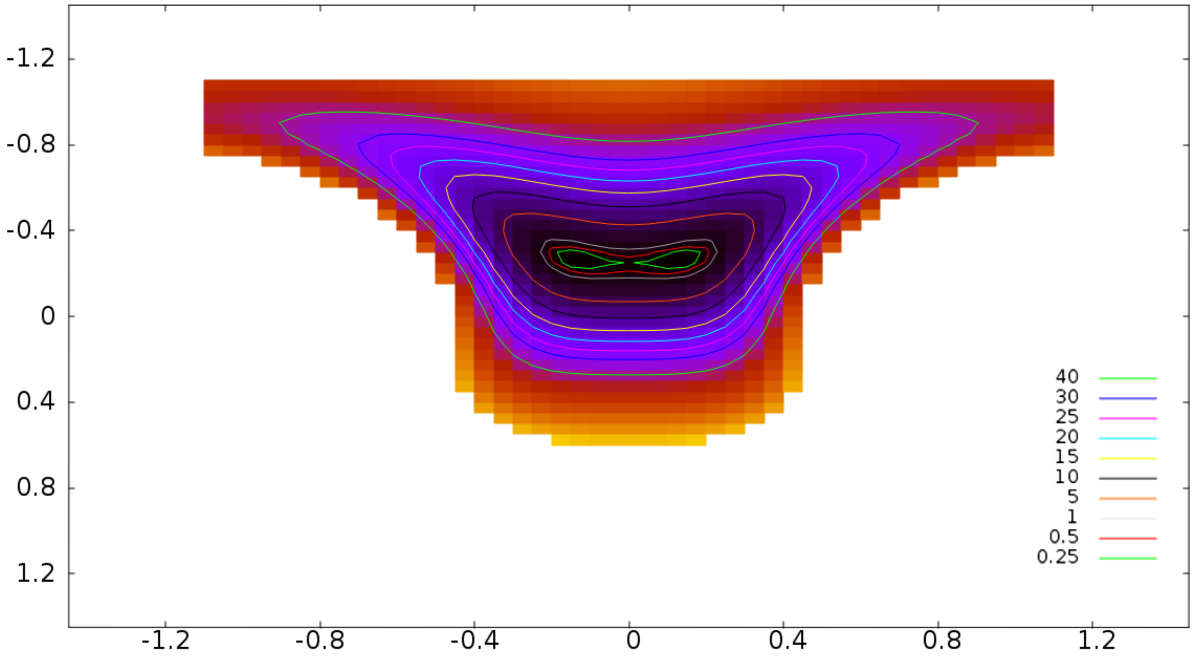

Figure S1: Potential scan of the malonaldehyde in the symmetric configuration. The potential is plotted up to 100 kcal/mol. The double-well barrier is lowered to a value of appoximately 0.3 kcal/mol

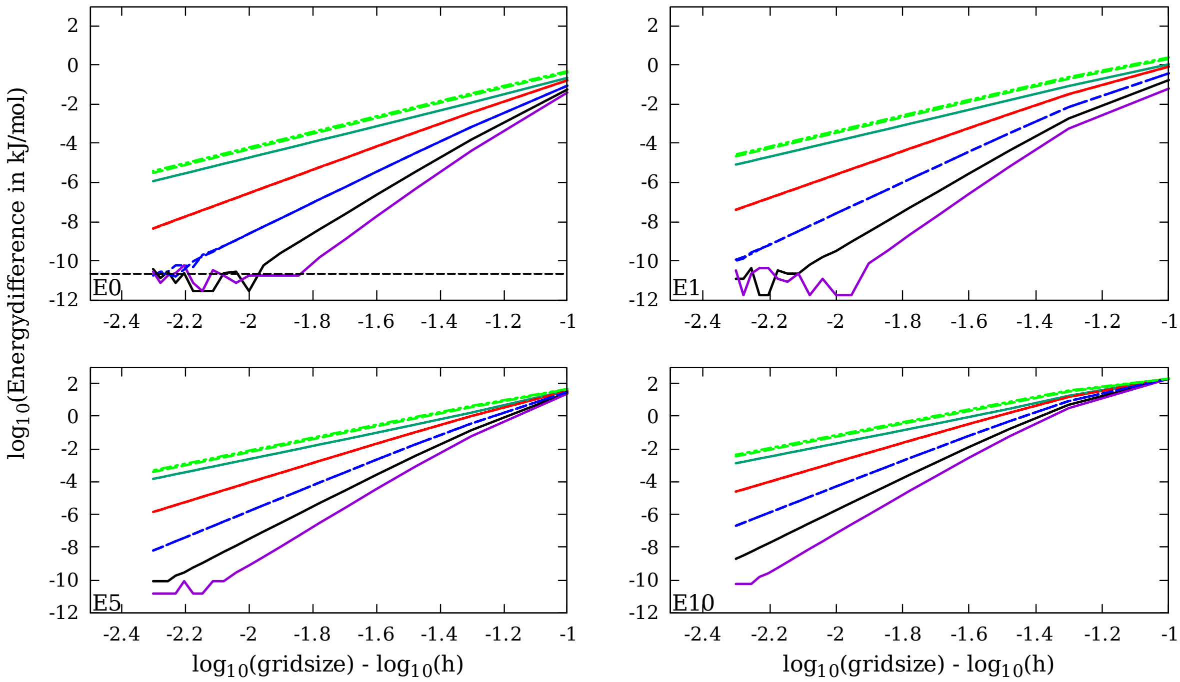

Figure S2: Ground state, first, fifth and tenth exited state of the harmonic oscillator in one dimension. Standard Numerov $\mathcal{O}(h^4)$ - 3-point(dark green), $\mathcal{O}(h^4)$ - 5-point (dashed green), $\mathcal{O}(h^6)$ (dashed red), $\mathcal{O}(h^8)$(dashed blue).
Improved Numerov: $\mathcal{O}(h^4)$ (green), $\mathcal{O}(h^6)$ (red), $\mathcal{O}(h^8)$ (blue), $\mathcal{O}(h^{10})$ (black), $\mathcal{O}(h^{12})$(violet).
The dashed lines are nearly congruent to the continuous lines and are therefore barely visible.

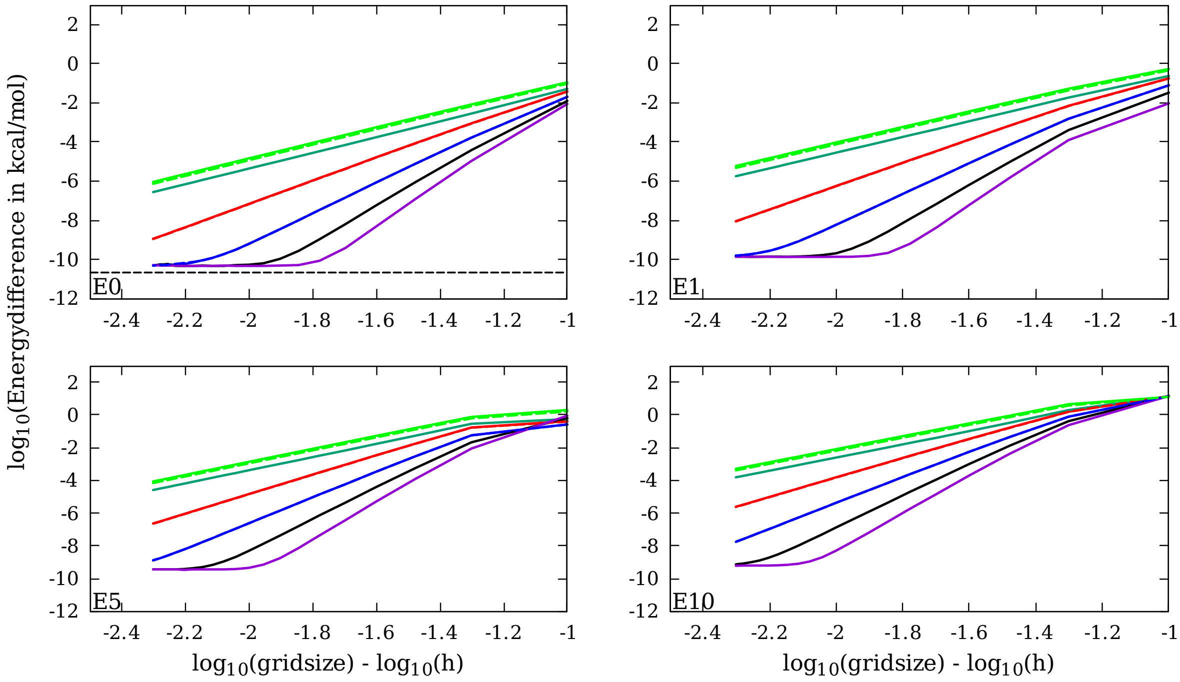

Figure S3: Ground state, first, fifth and tenth exited state of the morse potential. Standard Numerov $\mathcal{O}(h^4)$ - 3-point(dark green), $\mathcal{O}(h^4)$ - 5-point (dashed green), $\mathcal{O}(h^6)$ (dashed red), $\mathcal{O}(h^8)$(dashed blue). Improved Numerov: $\mathcal{O}(h^4)$ (green), $\mathcal{O}(h^6)$ (red), $\mathcal{O}(h^8)$ (blue), $\mathcal{O}(h^{10})$ (black), $\mathcal{O}(h^{12})$(violet). The dashed lines are nearly congruent to the continuous lines and are therefore barely visible..

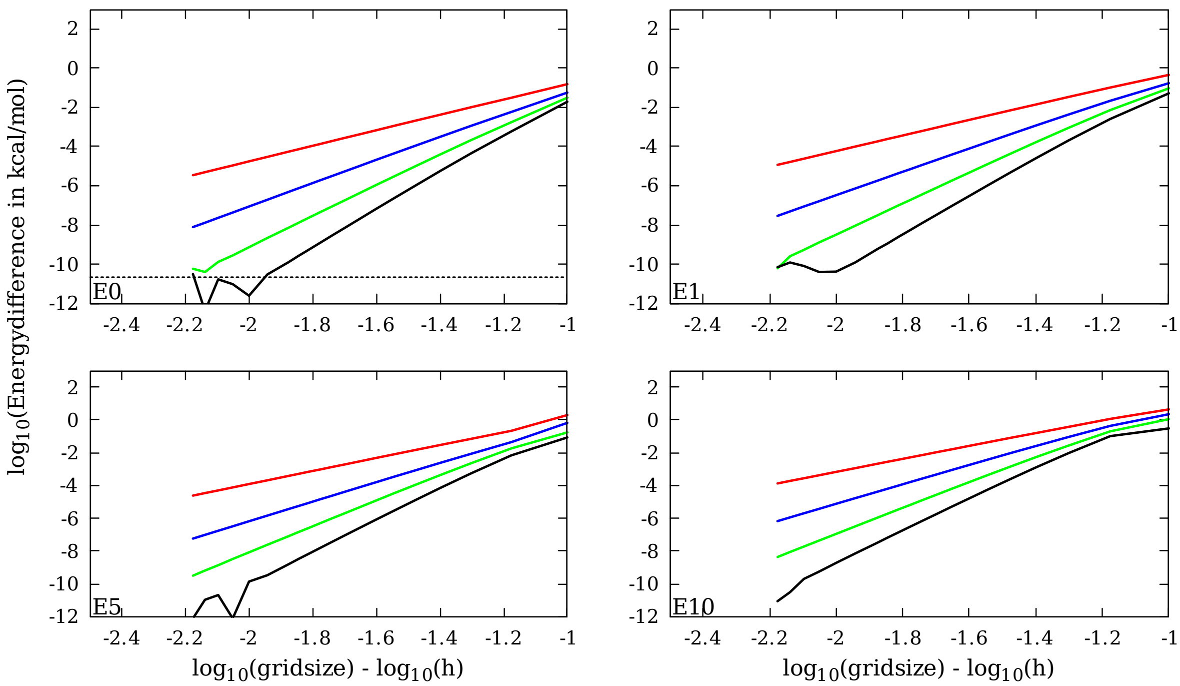

Figure S4: Ground state, first, fifth and tenth exited state of the harmonic oscillator in two dimensions. Improved Numerov: $\mathcal{O}(h^4)$ (red), $\mathcal{O}(h^6)$ (blue), $\mathcal{O}(h^8)$ (green), $\mathcal{O}(h^{10})$ (black).