Solving the energies for a hindered methyl rotor potential with the *QRotor* Python package

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Theoretical background

Hamiltonian for a hindered methyl rotor potential

A hindered methyl rotor potential can be expressed as a function of the angle, φ. Thus its energies are given by the 1-dimensional time-independent Schrödinger equation,

$$H\Psi(\varphi) = E\Psi(\varphi)$$

The hamiltonian depends of the kinetic rotational energy and the potential energy,

$$H = -B\frac{d^2}{d\varphi^2} + V(\varphi) \tag{1}$$

The kinetic rotational energy depends on the inertia $I = mr^2$ of each hydrogen, as

$$B = \frac{1}{2I} = \frac{1}{2\sum_i m_i r_i^2} \tag{2}$$

In QRotor the potential can be introduced as a custom array. It can also be adjusted to a function such as follows, where the coefficients were previously obtained via electronic calculation methods [1],

$$V(\varphi) = c_0 + c_1 \sin(3\varphi) + c_2 \cos(3\varphi) + c_3 \sin(6\varphi) + c_4 \cos(6\varphi)$$

Solving the time-independent Schrödinger equation with the Finite Difference Method

The time-independent Schrödinger equation is a second-order differential equation. It can be solved numerically by discretizing it with the finite difference method [2]. This way, with a fine enough grid, the first derivative can be approximated as the slope,

$$\frac{d\Psi}{d\varphi} = \frac{\Psi(\varphi + \Delta\varphi) - \Psi(\varphi)}{\Delta\varphi}$$

Following the same procedure, the second derivative is

$$\frac{d^2\Psi}{d\varphi^2} = \nabla^2\Psi = \frac{\frac{\Psi(\varphi+\Delta\varphi)-\Psi(\varphi)}{\Delta\varphi} - \frac{\Psi(\varphi)-\Psi(\varphi-\Delta\varphi)}{\Delta\varphi}}{\Delta\varphi} = \frac{\Psi(\varphi + \Delta\varphi) - 2\Psi(\varphi) + \Psi(\varphi - \Delta\varphi)}{\Delta\varphi^2}$$

This second derivative can be expressed in matrix form as

$$\nabla^2 = \frac{1}{\Delta\varphi^2}\begin{bmatrix} -2 & 1 & 0 & \cdots & 0 & 0 \\ 1 & -2 & 1 & & 0 & 0 \\ 0 & 1 & \ddots & & & \vdots \\ \vdots & & & \ddots & 1 & 0 \\ 0 & 0 & & 1 & -2 & 1 \\ 0 & 0 & \cdots & 0 & 1 & -2 \end{bmatrix}$$

The multiplication of this operator and the wavefunction vector yields the second derivative at every grid point. To impose periodic boundary conditions, the first and last grid points are connected with an off-diagonal term,

$$\nabla^2 = \frac{1}{\Delta\varphi^2}\begin{bmatrix} -2 & 1 & 0 & \cdots & 0 & \mathbf{1} \\ 1 & -2 & 1 & & 0 & 0 \\ 0 & 1 & \ddots & & & \vdots \\ \vdots & & & \ddots & 1 & 0 \\ 0 & 0 & & 1 & -2 & 1 \\ \mathbf{1} & 0 & \cdots & 0 & 1 & -2 \end{bmatrix}$$

Finally, to build the potential energy operator, the energy at each grid point is set to equal the potential energy. This results in a diagonal matrix, with the potential energy at each point along the diagonal,

$$V(\varphi) = \begin{bmatrix} V(\varphi_1) & 0 & \cdots & 0 \\ 0 & V(\varphi_2) & & \vdots \\ \vdots & & \ddots & \vdots \\ 0 & \cdots & \cdots & V(\varphi_N) \end{bmatrix}$$

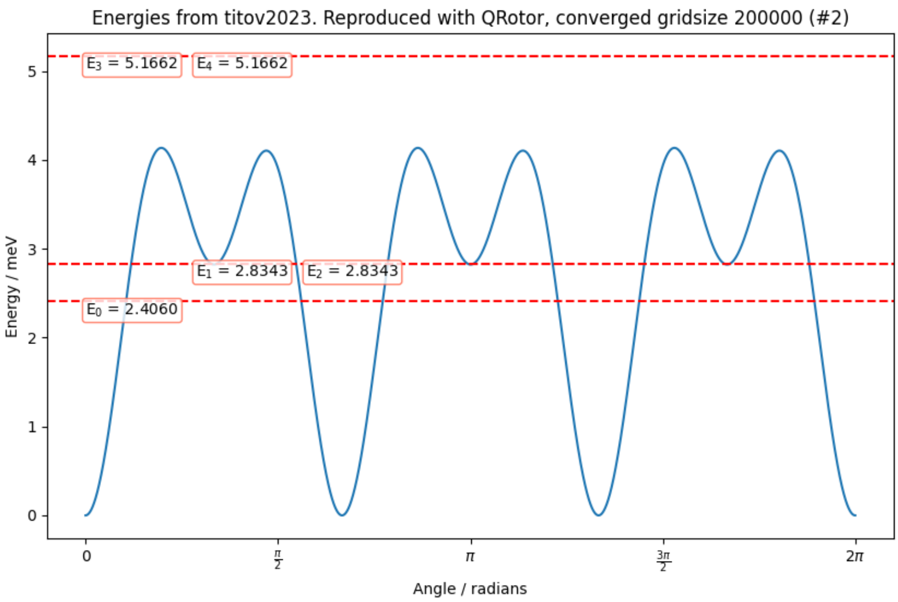
This way, the energy eigenvalues of the hindered methyl rotor can be obtained as the eigenvalues of the newly-constructed hamiltonian matrix from equation (1). QRotor solves this eigenvalue problem with the shift-inverted mode of the ARPACK package, provided through SciPy [3].

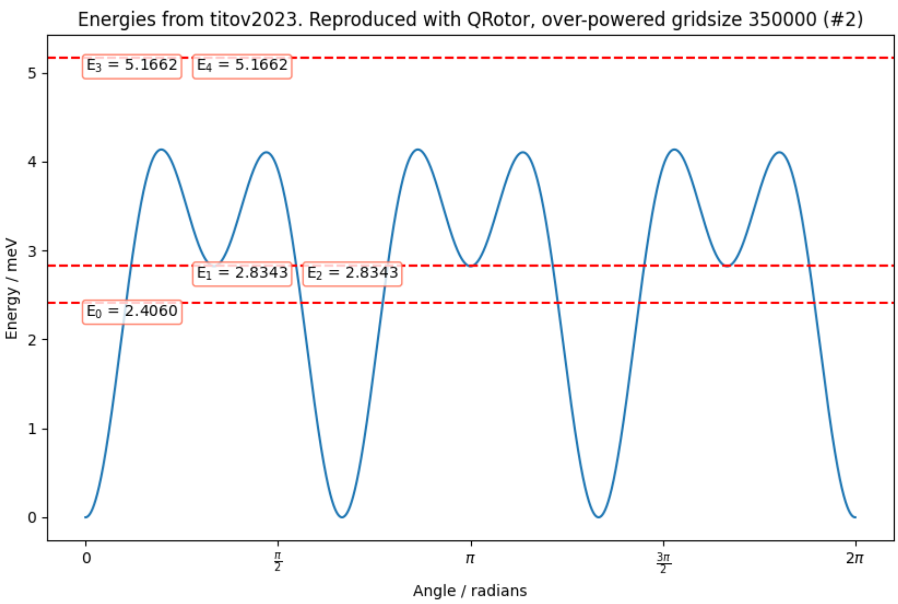
Energy convergence

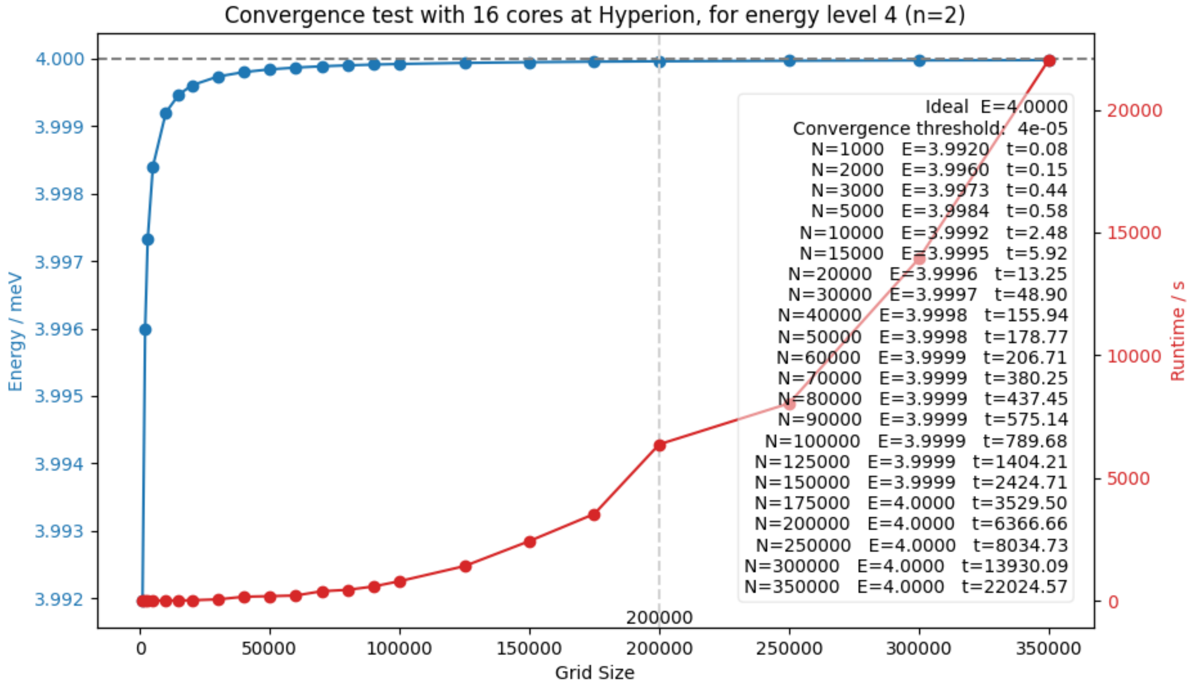
The convergence of the eigenvalues with the grid size was initially studied for a zero potential. These results were later confirmed for a known potential. The calculations were performed on DIPC's Hyperion cluster [4], with 16 cores and a varying RAM size up to 1Tb for the largest grid sizes.

A reasonable convergence of 3 decimals was observed for the energies with quantum numbers n=1 and n=2 with grids of 5,000 and 20,000 respectively. For a convergence of 4 decimals, for n=1 and n=2 the grids grow up to 50,000 and 200,000 respectively. The results from the convergence study are summarized in the following table. A comparison for a known potential [1] between a converged and an oversized grid is presented. Notice that the energy levels are labeled without degeneration for computational purposes.

Quantum n. (n)	Energy level	Decimal precision	Threshold	Gridsize	Runtime
0	0	-	-	-	-
1	1, 2	3	0.0004	5,000	0.6s
1	1, 2	4	0.00004	50,000	3min
2	3, 4	3	0.0004	20,000	13s
2	3, 4	4	0.00004	200,000	1h 45min
3	5, 6	3	0.0004	50,000	3min
4	7, 8	3	0.0004	90,000	9min 30s
5	9	3	0.0004	150,000	40min



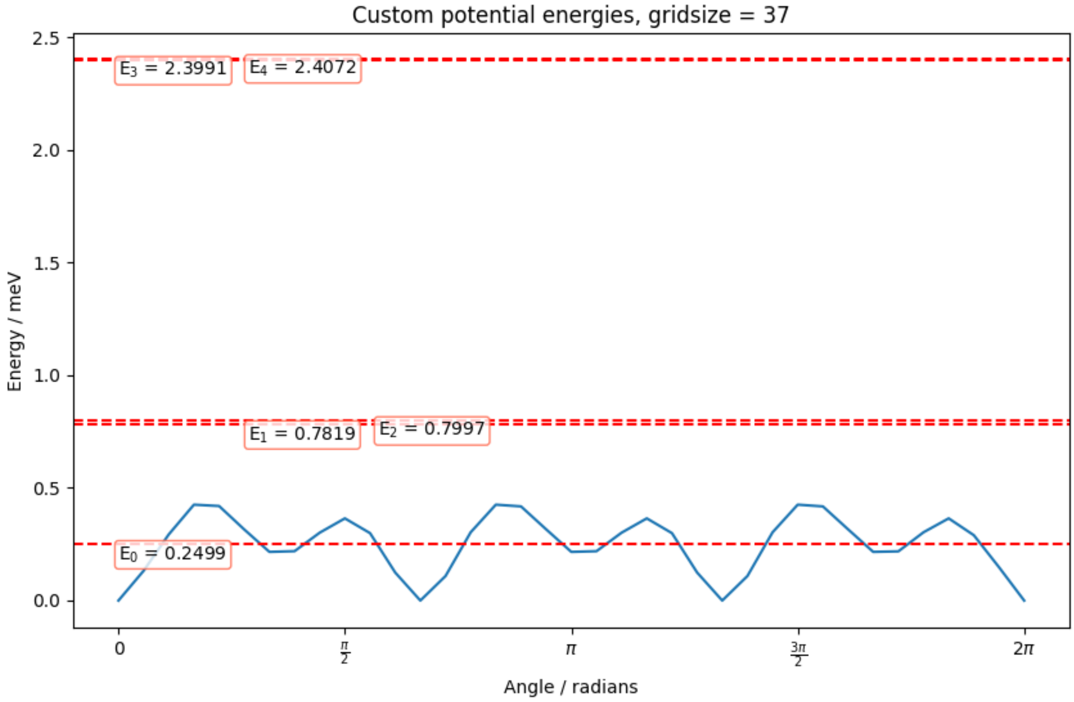




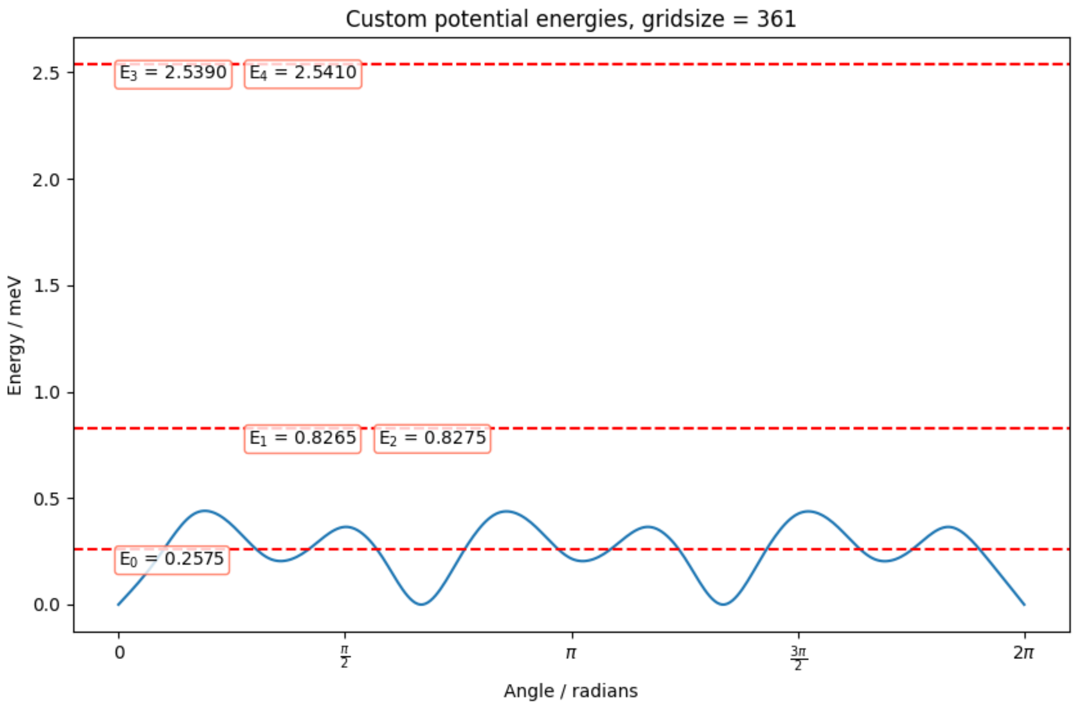
Interpolation of custom potentials

QRotor reads input potentials as `*.dat` files, with angle and energy information. This potential data can be previously calculated with electronic structure methods. The potential can then be interpolated to a bigger grid size with `qr.solve.interpolate_potential` to converge the energies. This method takes advantage of SciPy's Cubic Splines, where the interpolated curve is made of points with matching first and second derivatives [5].

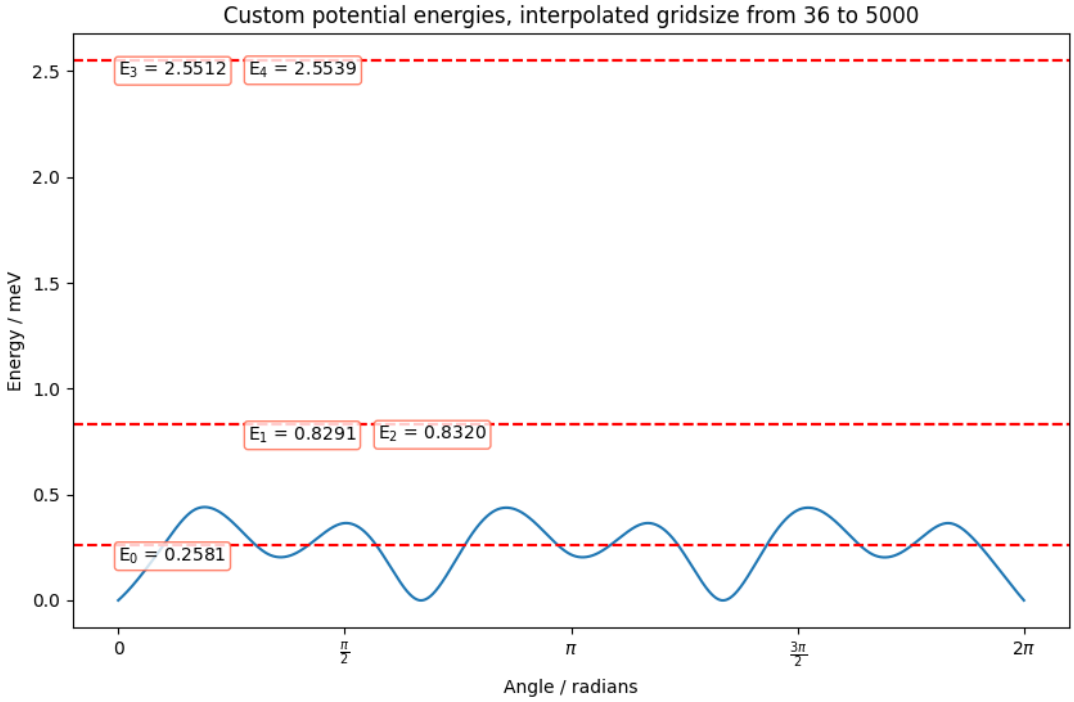
To validate the interpolation method, a test potential with 360 points was capped to 36 points. An interpolation to its previous size proved to match the original potential. Further interpolation to a grid of size 5000 showed the expected convergence between the original and the capped potential up to the 3rd decimal place. The results are shown in the following figures.

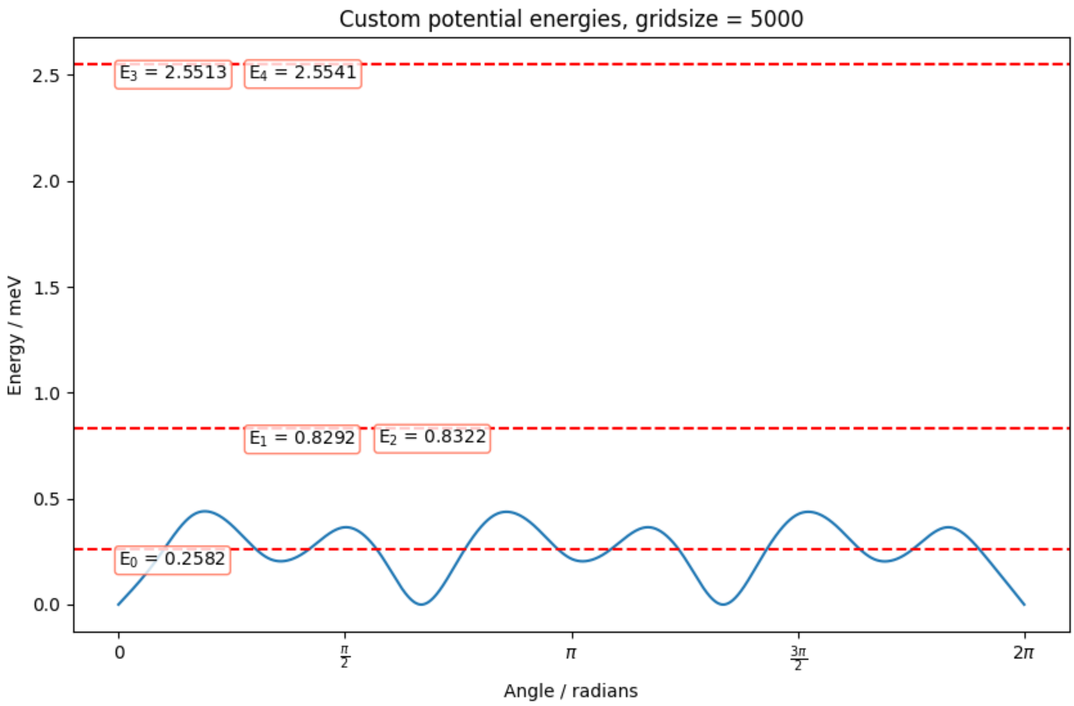


Custom potential energies, gridsize = 37
E3 = 2.3991
E4 = 2.4072
E1 = 0.7819
E2 = 0.7997
E0 = 0.2499
Energy / meV
Angle / radians



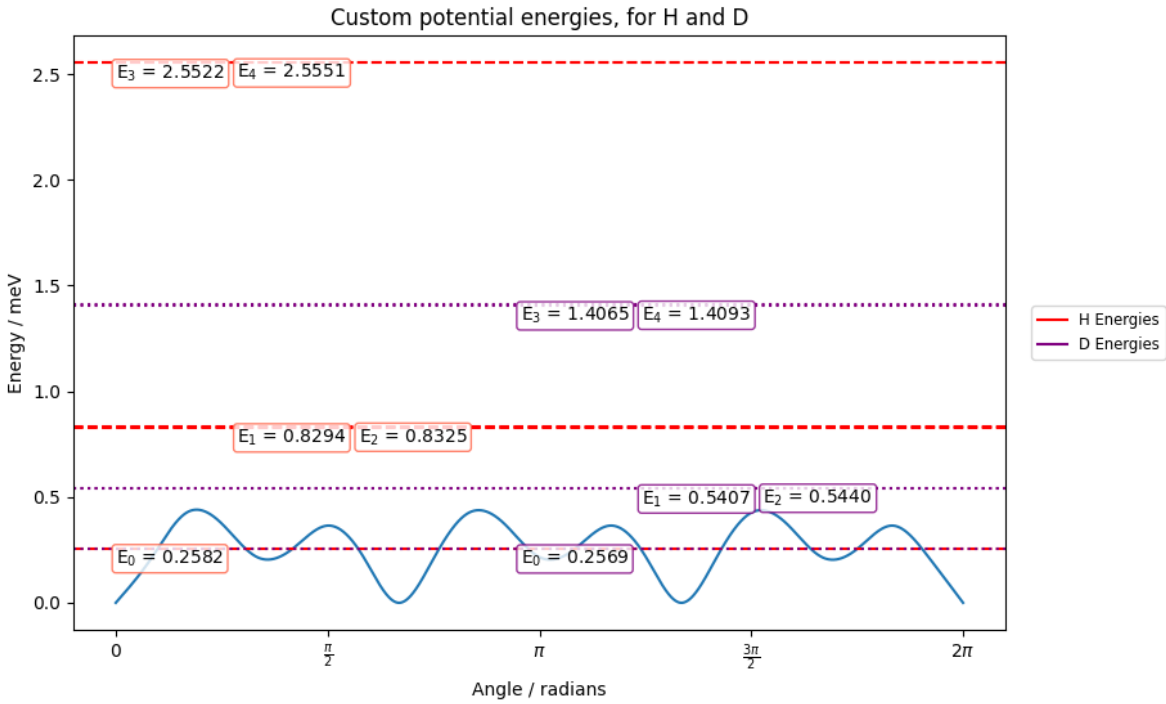
Custom potential energies, gridsize = 361
E3 = 2.5390
E4 = 2.5410
E1 = 0.8265
E2 = 0.8275
E0 = 0.2575
Energy / meV
Angle / radians


Custom potential energies, interpolated gridsize from 36 to 5000
E3 = 2.5512
E4 = 2.5539
E1 = 0.8291
E2 = 0.8320
E0 = 0.2581
Energy / meV
Angle / radians
0
π/2
π
3π/2
2π
0.0
0.5
1.0
1.5
2.0
2.5


Custom potential energies, gridsize = 5000
E3 = 2.5513
E4 = 2.5541
E1 = 0.8292
E2 = 0.8322
E0 = 0.2582
Energy / meV
Angle / radians
0
π/2
π
3π/2
2π
0.0
0.5
1.0
1.5
2.0
2.5

Isotopic effects

It is expected from eq. (2) to observe a lower rotational energy as a result of an increase in the atomic masses. The isotopic effects on the energies of the hindered methyl rotor were studied by replacing the hydrogen mass with that of deuterium. A given potential was interpolated to a grid of size 200000 to ensure an optimal convergence. As expected, the results show a shift to lower energies for the deuterated counterpart.



References

[1] K. Titov, M. R. Ryder, A. Lamaire, Z. Zeng, A. K. Chaudhari, J. Taylor, E. M. Mahdi, S. M. J. Rogge, S. Mukhopadhyay, S. Rudić, V. Van Speybroeck, F. Fernandez-Alonso, and J.-C. Tan, “Quantum tunneling rotor as a sensitive atomistic probe of guests in a metal-organic framework,” vol. 7, no. 7, p. 073402.

[2] Q. Kong, T. Siauw, and A. Bayen, “Finite Difference Method,” in *Python Programming And Numerical Methods: A Guide For Engineers And Scientists*, 1st ed. Elsevier. [Online]. Available: https://pythonnumericalmethods.berkeley.edu/notebooks/chapter23.03-Finite-Difference-Method.html

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[4] Hyperion overview - DIPC Technical Documentation. [Online]. Available: https://scc.dipc.org/docs/systems/hyperion/overview/

[5] 1-D interpolation with Cubic Splines — SciPy v1.13.0 Manual. [Online]. Available: https://docs.scipy.org/doc/scipy/tutorial/interpolate/1D.html#cubic-splines