Solving the time-independent Schrödinger equation for a hindered methyl rotor potential with *QRotor.py*

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Time-independent Schrödinger equation for a hindered methyl rotor potential

The 1-dimensional time-independent Schrödinger equation is

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

The hamiltonian for a hindered methyl rotor can be expressed as a function of the angle φ. It can be written as a sum of the kinetic rotational energy and the potential energy,

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

with

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

The potential can be adjusted to the following form, where the coefficients are obtained via electronic calculation methods [1],

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

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. This way, the first derivative can be approximated as

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

And the second derivative as

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

This second derivative can be expressed in matrix form as

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

The multiplication of this operator and the wavefunction vector yields the second derivative at every grid point.

Finally, imposing periodic boundary conditions, the first and last grid points must be connected with an off-diagonal term,

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

To build the potential energy operator, the energy at each grid point is set to equal the potential energy. This results in a diagonal matix, 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 this system can be obtained as the eigenvalues of the newly-constructed hamiltonian matrix. QRotor solves this eigenvalue problem with the SciPy package.

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.