An improved implementation of MARVEL

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MARVEL[1], standing for *M*easured *A*ctive *R*otational-*V*ibrational *E*nergy *L*evels, is a program system, written in C++, which can be applied for determining experimental energy levels and their uncertainties from a database of experimentally measured and assigned transitions. The set of MARVEL energy levels is called active because if new experimental transitions become available the MARVEL process can be carried out over and over again and a new set of rotational-vibrational energy levels with improved estimates for positions and uncertainties can be obtained. The energy levels are considered measured as they are obtained from experiment.

Although the MARVEL code was successfully applied to handle and validate the measured transitions of several isotopologues of the water molecule ($H_2{}^{17}O$ [2,3], $H_2{}^{18}O$[2,3], $HD^{16}O$[3], $HD^{17}O$[3], and $HD^{18}O$[3]) it was not fast enough to use for our main target molecule, $H_2{}^{16}O$. Therefore, we carefully checked the applied algorithms and found considerably faster ways to execute the inversion. The MARVEL algorithm is based on the following two critical steps, where we could improve the code[4]:

1) The exact value of an energy level within a spectroscopic network (SN) can be determined if there exists a path from this level to the root of the graph. Therefore, we need a code which can a) determine the number of components of the experimental SN, and b) decide whether a given energy level has a connection to the chosen root or not. The depth-first search (DFS) algorithm appears to be the best choice for finding components and its members.
2) The value of the energy levels can be obtained by solving an overdetermined system of linear equations. There are two ways how we can determine the energies and its uncertainties: a) if the exact values of the uncertainties (which are the diagonal elements of the inverse matrix) are needed, we have to use a direct solver. The best possible choice is the sparse-adaptive LDL^T decomposition, a special type of Cholesky linear solver. b) during the validation the approximate value of the uncertainties is sufficient, so we can use an iterative solver, for example the preconditioned conjugate gradient method. In this case we use an efficient expression to approximate the uncertainties.

Using the improved version of MARVEL we could build up and validate one of the largest spectroscopic databases, the $H_2{}^{16}O$ database [5]. We also applied successfully the MARVEL code for the H_3^+, H_2D^+, and D_2H^+ molecules [6,7].

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