Using *ScalIT* for Performing Accurate Rovibrational Spectroscopy Calculations for Triatomic Molecules:
A practical guide.

Corey Petty and Bill Poirier

Department of Chemistry and Biochemistry, and Department of Physics,
Texas Tech University, Box 41061, Lubbock, Texas 79409-1061

In this document we focus on the operation of *ScalIT* from the *non*-expert user's perspective, rather than on the underlying numerical methods *per se.* The latter are already well described in the extant literature,[1–20] to which the interested reader is referred—especially the overview presented in Paper I (Ref. 1).

In the context of bound rovibrational spectroscopy calculations for triatomic molecules, a typical *ScalIT* calculation will proceed in three (or four) separate stages:

1. Compute 1D PSO effective potentials and basis sets for radial coordinates, r and R.

2. Construct 4D (Coriolis-coupled) rovibrational Hamiltonian matrix for given J and ϵ.

3. Solve the Hamiltonian matrix eigenproblem to compute rovibrational energy levels and (optionally) wavefunctions.

4. (optional) Create plotting data for specified rovibrational wavefunctions.

Each stage has a different high-level *ScalIT* module (or set of modules) associated with it, as well as its own short input file (typically 6–10 lines each).

Stage 1 above is problem- (i.e. PES-) specific. For each of a very large number of uniformly-spaced points for a given radial coordinate (e.g. r), the PES is *globally* minimized with respect to all other coordinates, to determine the value of the radial PSO effective potential at that point [e.g. $V_r(r)$].[8–10] Although using *local* minima can, under some circumstances, provide a more efficient PSO DVR (and is computationally far less expensive), the global minimum is always reliable, and is therefore safest for use as the default choice for *ScalIT*.[11] In any case, thousands of sampling points are used to avoid spline-ringing problems,[9] and also to ensure that the subsequent PSO variational basis representation (VBR) calculation (an intermediate step towards generating the PSO DVR) is *extremely* well converged (i.e., to several digits of precision beyond that of the final calculation, so as to rule out Stage 1 as a significant source of numerical error). Because the number of sampling points (technically sinc-DVR points[21]) is so large, the minimization stage of the calculation is somewhat slow (e.g. requires several hours on a single core), but need only be performed a single time for any given PES. (Parallelization would be trivial, but is not yet implemented in the current version of *ScalIT*.) Once the radial PSO effective potentials are determined, they are used to compute the 1D radial PSO VBR functions via diagonalization of the corresponding 1D effective radial sinc-DVR Hamiltonian matrices; the data is then stored as intermediate output for the later stages. This part of the calculation also only needs to be performed a single time, provided the number of radial PSO VBR functions computed (specified by the user in the input file) is larger than or equal to the largest radial PSO DVR basis size used in the later Stages 2 and 3. Other user-specified inputs include the masses, the potential energy surface (PES), and the radial sinc-DVR coordinate ranges and grid spacings.

Stage 2 employs one of three standard *ScalIT* modules—depending on whether the triatomic molecule of interest is of the AB_2 form (i.e. two identical nuclei) or not, and if so, whether the even- or odd-permutation symmetry block is desired. In the input file, the user specifies the total angular momentum value, J, the inversion parity, ϵ, the PSO DVR basis size for both radial coordinates, r and R, and the maximum j value to use in the basis expansion, $j_{\max}$. Radial PSO DVRs of the specified sizes are constructed using the PSO VBR data previously computed in Stage 1. The bend-angle basis functions are automatically combined with the appropriate body-fixed rotational states ($M = 0$, but parity-adapted $0 \leq K \leq J$), with optional application of energy truncation to the combined bend-rotation states (K truncation could also be applied). The various components of the full-dimensional, but sparse, rovibrational Hamiltonian matrix are then stored in separate data files (one for the radial PSO DVR grid point and matrix data, the other for the angular contributions). Stage 2 must be repeated for each separate convergence calculation—i.e., for each distinct set of basis parameters used. However, it is quite fast for triatomic systems, typically requiring only seconds to minutes of CPU time.

Stage 3, the "meat" of the **ScalIT** package, employs but a single standard module—designed to accommodate calculations of arbitrary symmetry and dimensionality (i.e., tetraatomic and pentaatomic calculations use this same module). The coordinates may also be combined into "layers," if desired. The first phase of Stage 3 is the OSB preconditioner construction phase,[2–6,15–17] for which the default choice is to treat the radial coordinates as separate inner coordinate layers, and the combined bend-rotation states as a single outermost layer. For standard OSB preconditioning, no user parameters are required, although more sophisticated preconditioning schemes do require this (e.g., specification of the Wyatt window center and width, for OSBW preconditioning). In the second phase of stage 3, the PIST method[12–14] is used to compute a predetermined number of rovibrational eigenstate energies (and wavefunctions if desired) in the vicinity of a specified central energy, E, to within a predetermined (iterative) error (generally chosen to be far smaller than the basis set convergence error). Note that wavefunction calculations do *not* require a second PIST calculation. Also, the Lanczos component of PIST requires only very few iterations, M (typically ~ 2 times the desired number of states) thus rendering explicit reorthogonalization feasible. As for the QMR component of PIST, it is hoped that preconditioning has reduced the number of QMR iterations per Lanczos iteration, L, to a manageably small value. As input for stage 3, users specify the number of (possibly combined) coordinates, the energy window over which rovibrational states are to be computed, and various other parameters as described above. An output file is generated that lists the computed rovibrational eigenvalues. Also, various optional data files may be written—as may be used, e.g., for wavefunction plotting purposes in Stage 4.

The optional Stage 4 is executed if wavefunction plots are desired. All of the requisite data may be found in the optional output files of Stage 3. However, this data is not presented in a form that would be useful for plotting via standard packages such as *Mathematica*. It is the purpose of Stage 4 to extract and output such information, for selected wavefunctions. Specifically, this module will output explicit values for the eigenstate wavefunction density, as a function of the four coordinates, R, r, θ, and K. An optional summation over all K values can also be computed, as well as a transformation from Jacobi to hyperspherical coordinate systems.

The four stages described above are logical, and easy to use in practice. To date, even undergraduate and high school students (with some guidance) have been able to converge triatomic rovibrational state calculations using **ScalIT** as described above.

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