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ABSTRACTS 1.2

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Using preconditioned inexact spectral transform methods to calculate vibrational energy levels and metastables state lifetimes

We demonstrate that with a good preconditioner an inexact spectral transform method is an efficient tool for calculating energy levels of small molecules. To calculate energy levels close to E and their corresponding wavefunctions we apply the Lanczos algorithm to $(E\mathbf{I}-\mathbf{H})^{-1}$, where $\mathbf{H}$ is the matrix representation of the Hamiltonian. Rather than evaluating matrix-vector products with $(E\mathbf{I}-\mathbf{H})^{-1}$ accurately (which is costly), computing exact eigenvalues of $(E\mathbf{I}-\mathbf{H})^{-1}$ and extracting exact eigenvalues of $\mathbf{H}$ from those of $(E\mathbf{I}-\mathbf{H})^{-1}$, we evaluate matrix-vector products with $(E\mathbf{I}-\mathbf{H})^{-1}$ approximately and diagonalise $\mathbf{H}$ in a basis of the approximate Lanczos vectors of $(E\mathbf{I}-\mathbf{H})^{-1}$. Approximate matrix-vector products with $(E\mathbf{I}-\mathbf{H})^{-1}$ are computed by solving systems of linear equations $(E\mathbf{I}-\mathbf{H})\mathbf{w}=\mathbf{v}$ using QMR and stopping QMR when the residual is smaller than a pre-defined error. We discuss an extremely efficient preconditioner consisting of two components: (1) transformation to an optimal separable basis, in terms of which the total perturbation is minimized; (2) removal of all perturbation coupling near the energies of interest. The new preconditioner works extremely well; for high-lying vibrational states of H_2O, it reduces the required number of matrix–vector products by orders of magnitude.

To calculate lifetimes of metastable states one must compute eigenvalues of a complex symmetric matrix obtained from the Hamiltonian matrix by adding and imaginary symmetric matrix that represents an absorbing potential. We have used preconditioning and an inexact spectral transform to compute metastable state lifetimes for HCO.