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Alexandra Viel, Claude Leforestier

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LSDSMS (UMR 5636) - CC 014,
Université des Sciences et Techniques du Languedoc,
34095 MONTPELLIER Cedex 05, France.
e-mail: lefores@lsd.univ-montp2.fr

Adiabatic contraction of molecular bases

Alexandra Viel and Claude Leforestier

Study of the (ro)vibrational levels of tetraatomic molecules constitutes a drastic change as compared to triatomic calculations. The reason is that the number of internal degrees of freedom doubles from 3 to 4 atoms, and as a consequence, the basis set size is roughly squared. Furthermore, quite often, the energy domain of interest lies in the middle of the spectrum. Amongst examples, one can cite

- the isomerization of acetylene to vinylidene [1];
- the Stimulated Emission Pumping spectrum of the fluoryl formide HFCO above the dissociation threshold [2];
- the far-infrared spectrum of the water dimer $(\text{H}_2\text{O})_2$ [3], which corresponds to six degrees of freedom within the rigid rotor approximation for each monomer.

This huge increase in basis set size precludes building the Hamiltonian matrix in most cases due to core memory limitations.

In recent years, an alternative approach called the *direct* method has emerged as a powerful tool. It consists of directly acting the Hamiltonian operator \mathbf{H} on a wavefunction, without the help of the associated matrix. First implementations were made by Feit and Fleck [4] and Kosloff and Kosloff [5] through the Fast Fourier Transform method. It relies on using two different representations of the wavefunction, and has been shown able to achieve very high accuracy [6]. Because only a few vectors have to be kept in core memory, ultra-large basis sets can be considered in a direct method.

The direct approach became very popular due to the emergence of the Discrete Variable Representation method of Light and coworkers [7]. In this method, one emphasizes the grid representation in which the potential is diagonal. The direct approach has been used in conjunction with iterative schemes such as the Lanczos algorithm [8], the Chebychev time propagator [9] or the GMRes linear solver [10], to cite a few applications. The direct DVR method can result in a broad spectrum of the Hamiltonian operator when use is made of curvilinear coordinates. This is due to the presence of almost singular terms in the kinetic energy operator, such as $(1/\sin^2 \theta)\partial^2/\partial\phi^2$. A

DVR representation of the θ variable will badly behave close to $\theta = 0$ or $\theta = \pi$, as the correct asymptotic form of the solution is not enforced [11].

To cope with this problem, the direct method can also be used with a spectral representation as the primary one, such as spherical harmonics [12] or Wigner rotation functions [13]. In this case, acting the Hamiltonian operator requires transforming between two or more representations by means of pseudo-spectral schemes [14].

Whatever is the primary representation (grid or spectral) in use, calculations can be made more efficient by preconditioning the basis set. This technique allows one to reduce the basis set size significantly in the case of a straight diagonalization approach, or to resort eventually to some perturbation scheme. For iterative approaches, preconditioning becomes essential as the convergence of such schemes strongly depends on the total width of the spectrum associated with H . We present below an adiabatic pseudo-spectral method which is currently applied to the calculation of the vibrational levels of the HFCO molecule. But first, we recall the Successive Adiabatic Reduction method of Bacic and Light which is used as the reference approach.

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- The Successive Adiabatic Reduction method
 - The Adiabatic Pseudo-Spectral method

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The Successive Adiabatic Reduction method

Specially well adapted to large-amplitude motions, or equivalently to high energy motions, is the Successive Adiabatic Reduction (SAR) method of Bacic and Light [15, 16]. For a two-variable system (x,y) , described by the Hamiltonian operator $\mathbf{H} = \mathbf{T}_x + \mathbf{T}_y + V(\mathbf{x}, \mathbf{y})$, it consists in first computing the adiabatic solutions at fixed y ,

$$\{\mathbf{T}_x + V(\mathbf{x}, y_q)\} \varphi_n(\mathbf{x}; y_q) = \epsilon_n(y_q) \varphi_n(\mathbf{x}; y_q). \quad (1)$$

The two-dimensional eigenstates are finally expressed in terms of these adiabatic states,

$$|\Psi_N\rangle = \sum_{n,q} C_{nq,N} |\varphi_n(y_q)\rangle |y_q\rangle, \quad (2)$$

where $|\varphi_n(y_q)\rangle$ is the ket corresponding to $\varphi_n(\mathbf{x}; y_q)$ and $\{|y_q\rangle\}_{q=1}^Q$ is a DVR for the y coordinate. In the $\{|\varphi_n(y_q)\rangle |y_q\rangle\}$ basis set, \mathbf{H} has the matrix elements

$$\langle y_{q'} | \langle \varphi_{n'}(y_{q'}) | \mathbf{H} | \varphi_n(y_q) \rangle | y_q \rangle = \langle \varphi_{n'}(y_{q'}) | \varphi_n(y_q) \rangle \langle y_{q'} | \mathbf{T}_y | y_q \rangle + \epsilon_n(y_q) \delta_{nn'} \delta_{qq'}. \quad (3)$$

The above formulation can be extended to molecular systems depending on several variables $\mathbf{x}, y, \dots, t, z$ by successive adiabatic reduction along the \mathbf{x}, y, \dots, t variables. This method has been shown to lead to extremely compact bases, and mainly applied to triatomic systems.

Although straightforward in principle, the application of this method to tetraatomic systems leads rapidly to memory capacity problem. The reason can be seen in Eq. (3) which displays the overlap matrix $\langle \varphi_{n'}(y_{q'}) | \varphi_n(y_q) \rangle$. If N_{ad} is the total number of adiabatic states retained at the end of the preconditioning step, the size of this matrix will scale as N_{ad}^2

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The Adiabatic Pseudo-Spectral method

To circumvent this problem, the Adiabatic Pseudo-Spectral method has been proposed by Friesner and coworkers [17]. The main difference as compared to the SAR method is to avoid dealing with the overlap matrix by means of a pseudo-spectral approach recalled now.

For a two-variable (x,y) system, one writes the eigenvectors $\Psi_N(\mathbf{x}, y)$ as

$$\Psi_N(\mathbf{x}, y) = \sum_{n_1} \chi_{n_1}(y) \varphi_{n_1}^{(1)}(\mathbf{x}; y), \quad (4)$$

as in the standard Born-Oppenheimer approach, where the $\{\varphi_{n_1}^{(1)}(\mathbf{x}; y)\}$ represent the adiabatic solutions at fixed y (Eq. (4)). For each value of the n_1 index, the motion along y is described in terms of the adiabatic basis set $\{\varphi_{n_1 n_2}^{(2)}(y)\}$, solutions of the equation

$$\{\mathbf{T}_y + \epsilon_{n_1}(y)\} \varphi_{n_1 n_2}^{(2)}(y) = \epsilon_{n_1 n_2} \varphi_{n_1 n_2}^{(2)}(y). \quad (5)$$

This new definition allows one to expand any wavefunction $\Psi(\mathbf{x}, y)$ in the form

$$\Psi(\mathbf{x}, y) = \sum_{n_1, n_2} \Psi_{n_1, n_2} \varphi_{n_1}^{(1)}(\mathbf{x}; y) \varphi_{n_1 n_2}^{(2)}(y). \quad (6)$$

This adiabatic basis set $\{\varphi_{n_1}^{(1)} \varphi_{n_1 n_2}^{(2)}\}$ is then used within the following direct scheme in order to compute the result of \mathbf{H} acting on the function $\Psi(\mathbf{x}, y)$,

$$\begin{aligned} \mathbf{H}\Psi(\mathbf{x}, y) &= \sum_{n_1, n_2} \Psi_{n_1, n_2} (\mathbf{T}_x + V) \varphi_{n_1}^{(1)} \varphi_{n_1 n_2}^{(2)} + \mathbf{T}_y \Psi(\mathbf{x}, y) \\ &= \sum_{n_1, n_2} \Psi_{n_1, n_2} \epsilon_{n_1}(y) \varphi_{n_1}^{(1)} \varphi_{n_1 n_2}^{(2)} + \mathbf{T}_y \Psi(\mathbf{x}, y). \end{aligned} \quad (7)$$

The $\mathbf{T}_y \Psi(\mathbf{x}, y)$ term, from which non-adiabatic corrections arise, is then evaluated by the following pseudo-spectral scheme:

i) One first expresses the function on the grid

$$\Psi_{ab} \equiv \Psi(x_a, y_b) = \sum_{n_1, n_2} \mathbf{R}_{a n_1}^{(b)} \mathbf{R}_{b n_2}^{(n_1)} \Psi_{n_1, n_2}, \quad (8)$$

where the $\mathbf{R}^{(b)}$ and $\mathbf{R}^{(n_1)}$ collocation matrices are defined from the adiabatic states,

$$\begin{cases} \mathbf{R}_{\alpha n_1}^{(b)} = \varphi_{n_1}^{(1)}(\mathbf{x}_\alpha; y_b) \\ \mathbf{R}_{b n_2}^{(n_1)} = \varphi_{n_1 n_2}^{(2)}(y_b) \end{cases}.$$

ii) The value of $\mathbf{T}_y \Psi(\mathbf{x}, y)$ at grid point (\mathbf{x}_α, y_b) then corresponds to

$$\mathbf{T}_y \Psi|_{\mathbf{x}_\alpha, y_b} \equiv \Psi_{\alpha b}^{(T)} = \sum_{b'} T_{bb'}^{(y)} \Psi_{\alpha b'}, \quad (9)$$

where $T_{bb'}^{(y)}$ corresponds to the matrix element $\langle y_b | \mathbf{T}_y | y_{b'} \rangle$.

iii) In order to switch back to the $\{\varphi_{n_1}^{(1)}, \varphi_{n_1 n_2}^{(2)}\}$ representation, one makes use of the inverse transformations

$$\Psi_{n_1 n_2}^{(T)} = \sum_{\alpha b} \mathbf{Q}_{n_1 \alpha}^{(b)} \mathbf{Q}_{n_2 b}^{(n_1)} \Psi_{\alpha b}^{(T)}, \quad (10)$$

where the $\mathbf{Q}^{(b)}$ and $\mathbf{Q}^{(n_1)}$ matrices are defined by least-squares fitting [18],

$$\begin{cases} \mathbf{Q}^{(b)} = [\mathbf{R}^{(b)+} \cdot \mathbf{R}^{(b)}]^{-1} \mathbf{R}^{(b)+} \\ \mathbf{Q}^{(n_1)} = [\mathbf{R}^{(n_1)+} \cdot \mathbf{R}^{(n_1)}]^{-1} \mathbf{R}^{(n_1)+} \end{cases}.$$

Such a definition is required because, at each diagonalization step during the preconditioning procedure, the number of adiabatic functions ($\varphi_{n_1}^{(1)}(\mathbf{x}; y)$ or $\varphi_{n_1 n_2}^{(2)}(y)$) is smaller than the number of grid points used (N_x or N_y).

This approach was first applied to the HCN molecule as a test case, considering all three variables [17]. It showed a threefold reduction in core memory requirement as compared to the SAR method. It is currently being applied to a six-dimensional study of the vibrational bound states of the HFCO molecule [19].

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