

General Fit-Basis Functions and Specialized Coordinates in an Adaptive Density-Guided Approach to Potential Energy Surfaces

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Motivation

- Solving the **vibrational Schrödinger equation** (VSE) to obtain anharmonic vibrational wave functions requires that a potential energy surface (PES) for the molecular system under investigation can be supplied.
- The construction of accurate PESs is often a bottle-neck in treating medium to large sized molecules due to the massive amount of single point calculations (SPCs) needed in a full quantum chemical treatment.
- Consequently, a reduction in the number of SPCs for PES construction is the aim of this project.

Potential energy surfaces

- The M -dimensional PES, where $M = 3N - 6(5)$, is often approximated for medium to large molecules by means of the **n -mode expansion** in order to solve the VSE

$$V^{(1)}(\mathbf{Q}), V^{(2)}(\mathbf{Q}), V^{(3)}(\mathbf{Q}), \dots, V^{(M)}(\mathbf{Q}).$$

- The PES of the truncated n -mode expansion is recast on an analytical **sum-over-product** (SOP) form by fitting a direct product of one-mode operators to the grid of single points

$$V(\mathbf{Q}) = \sum_{t=1}^T c_t \prod_{m=1}^M \hat{h}_t^m,$$

- The placement of single points in the grid that comprises the PES is carried out with the **iterative black-box adaptive density-guided approach** (ADGA) [1], which relies on intermediate vibrational self-consistent field (VSCF) calculations to construct the **average vibrational density** at a given iteration

$$\rho_{\text{iter}}^{\text{ave}}(Q_m) = \frac{1}{N_{\text{modal}}} \sum_{s^m=1}^{N_{\text{modal}}} |\phi_{s^m}^m(Q_m)|^2.$$

- Significant changes, as define by the three ADGA convergence criteria, in the **energy-like quantity**

$$\int_i \rho_{\text{iter}}^{\text{ave}}(Q_m) V_{\text{iter}}^{\text{mn}}(Q_m) dQ_m,$$

determine if new single points should be included in the grid.

Rectilinear coordinates

- Employing **rectilinear normal coordinates** (NCs) ensures that the kinetic energy operator (KEO) maintains the simple form

$$\hat{T}_{\text{nuc}}(\mathbf{Q}) = -\frac{\hbar^2}{2} \sum_{m=1}^M \frac{\partial^2}{\partial Q_m^2}.$$

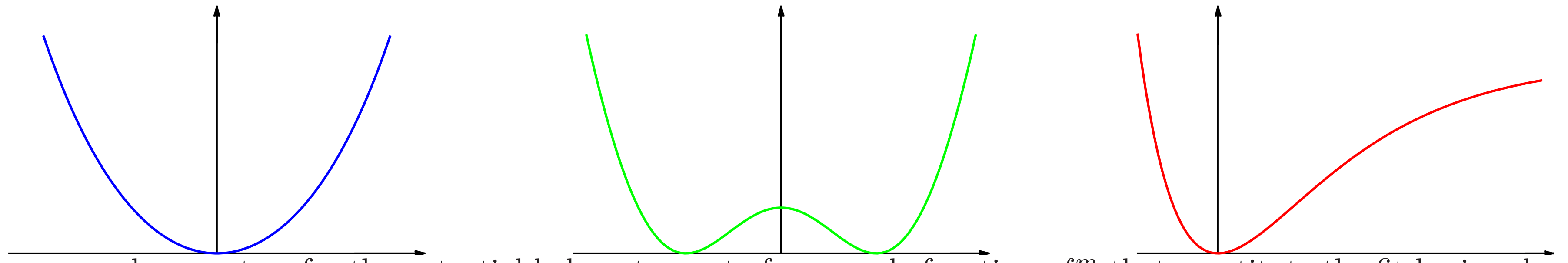
- Sets of rectilinear orthogonal coordinates can be obtained from another set by orthogonal transformation if the sets occupy the same space $\mathbf{Q}^{\text{new}} = \mathbf{U}^T \mathbf{Q}$ with the aid of an orthogonal transformation matrix $\mathbf{U}^T \mathbf{U} = \mathbf{U} \mathbf{U}^T = \mathbf{I}$.
- Hybrid optimized and localized coordinates** (HOLCs) are a set of coordinates with more localized character than NCs and are defined as the set of coordinates that minimizes the hybrid optimization criterion

$$M_{\text{hyb}}(\mathbf{Q}) = w_E E_{\text{VSCF}}(\mathbf{Q}) + w_P P(\mathbf{Q}).$$

- The **delocalization penalty** $P(\mathbf{Q}) = -\xi_{\text{at}}(\mathbf{Q})$ is constituted by the atomic localization criterion [3].
- The HOLCs are able to **reduce mode-mode correlation** and thereby **increase the rate of convergence** towards the full vibrational configuration interaction (FVCI) limit for vibrational structure calculations [2].

General fit-basis functions

- The overall shape of one-mode (non-coupled) potentials can be very different, which means that if an analytical expression for the PES is sought by means of fitting routines, then the fit-basis functions should be able to accommodate these general shapes. The general one-mode potential shapes of interest for this project was those being **symmetrical** or **unsymmetrical** around one minimum and the **symmetrical double-well**.



- The one-mode operators for the potential belong to a set of one-mode functions f_k^m that constitute the fit-basis, where N_{func} is the total number of fit functions that can be used by the fitting routine for each individual mode in the non-coupled part of the potential

$$\hat{h}_t^m \in \{f_1^m(Q_m), f_2^m(Q_m), \dots, f_{N_{\text{func}}}^m(Q_m)\}.$$

- A standard set of fit-basis functions is the set of **polynomial type fit-basis functions**. Two additional sets of fit-basis functions have been tested, namely **Morse and double-well type fit-basis functions** defined by

$$f_{k,\text{Poly}}^m(Q_m) = Q_m^k$$

$$f_{k,\text{Morse}}^m(Q_m) = \exp(-k\alpha Q_m) - 1$$

$$f_{k,\text{Double-well}}^m(Q_m) = \begin{cases} \exp(-k\alpha Q_m^2) - 1, & \text{if } k \text{ odd} \\ Q_m^k, & \text{if } k \text{ even.} \end{cases}$$

- The non-linear fitting parameter α is determined by the Fletcher-Reeves-Polak-Ribière non-linear **conjugate gradient** (CG) method. Derivatives are supplied by automatic differentiation with the LIBTAYLOR library of Ekström. The non-linear optimization of Morse and double-well fit-basis functions have, respectively, been performed with the optimization functions

$$F_{\text{optfunc}}^{m,\text{OM}}(Q_m) = D_e (\exp(-\alpha Q_m) - 1)^2$$

$$F_{\text{optfunc}}^{m,\text{ODW}}(Q_m) = \frac{1}{2} \cdot \omega^2 \cdot Q_m^2 + A \cdot \exp(-\alpha \cdot Q_m^2).$$

- This procedure results in **optimized Morse** (OM) and **optimized double-well** (ODW) type fit-basis functions.

Results for general fit-basis functions

- Calculations were performed in order to ascertain the performance of the specialized fit-basis functions on the basis of analytical and numerical potentials.

- Analytical potentials were investigated for the Morse oscillator potential, the ammonia inversion mode potential as parametrized by Lin *et al.* and the Partridge-Schwenke water potential.

- Numerical potentials were calculated for the three molecules H₂, HF and N₂ at the CCSD(T*)-F12b/cc-pCVQZ-F12 level of theory. Fundamental and overtone excitations were calculated for both types of potentials.

Molecule	$N_{\text{overtones}}^{\text{calc}}$	N_{func}	Type	N_{SPC}	$\text{MAD}_{\text{fundamental}}$	$\text{MAD}_{\text{overtones}}$
H ₂ ⁺ (Morse oscillator)	4	4	OM	5	$1.5268 \cdot 10^{-8}$	$1.3429 \cdot 10^{-8}$
		12	Polynomial	18	$6.5319 \cdot 10^{-9}$	$1.6662 \cdot 10^{-5}$
NH ₃ (Inversion mode)	8	4	ODW	22	$5.7282 \cdot 10^{-3}$	$2.7541 \cdot 10^{-5}$
		12	Polynomial	22	$5.8235 \cdot 10^{-3}$	$2.6659 \cdot 10^{-5}$
H ₂	4	12	OM	14	$2.8438 \cdot 10^{-4}$	$2.4430 \cdot 10^{-4}$
		12	Polynomial	42	$3.2556 \cdot 10^{-4}$	$1.7414 \cdot 10^{-4}$
HF	4	12	OM	17	$1.5873 \cdot 10^{-3}$	$1.4072 \cdot 10^{-3}$
		12	Polynomial	20	$1.5873 \cdot 10^{-3}$	$1.4071 \cdot 10^{-3}$
N ₂	4	8	OM	8	$5.5180 \cdot 10^{-3}$	$6.0336 \cdot 10^{-3}$
		12	Polynomial	15	$5.5181 \cdot 10^{-3}$	$6.0334 \cdot 10^{-3}$

- The specialized fit-basis functions facilitate a cheaper construction of the PES by reducing the number of required SPCs without compromising accuracy in the vibrational excitation energies. Furthermore it is possible to reduce the number of terms for the PES on a SOP form, which decrease the cost of performing subsequent vibrational structure calculations.

Molecule	$N_{\text{overtones}}^{\text{calc}}$	N_{func}	Type	N_{SPC}	$\text{MAD}_{\text{fundamental}}^*$	$\text{MAD}_{\text{overtones}}^*$
H ₂ O (NC rep.)	1	12	OM	787	$1.9504 \cdot 10^{-4}$	$1.8057 \cdot 10^{-4}$
		12	Polynomial	870	$2.1513 \cdot 10^{-4}$	$2.1278 \cdot 10^{-4}$
H ₂ O (HOLC rep.)	1	12	OM	427	$1.8136 \cdot 10^{-4}$	$1.8177 \cdot 10^{-4}$
		12	Polynomial	665	$1.8727 \cdot 10^{-4}$	$1.5574 \cdot 10^{-4}$

- The localized character of the HOLCs increase the efficiency of the ADGA by reducing mode-mode correlation, while providing better conditions for employing OM type fit-basis functions than the NCs.

$$\text{MAD}_{\text{fundamental}} = \frac{1}{M} \sum_{m=1}^M \frac{|\nu_m^{\text{calc}} - \nu_m^{\text{ref}}|}{\nu_m^{\text{ref}}}, \quad \text{MAD}_{\text{overtones}} = \frac{1}{M} \sum_{m=1}^M \frac{1}{N_{\text{overtones}}^{\text{calc}}} \sum_{\gamma=1}^{N_{\text{overtones}}^{\text{calc}}} \frac{|\gamma \nu_m^{\text{calc}} - \gamma \nu_m^{\text{ref}}|}{\gamma \nu_m^{\text{ref}}}.$$

Extension towards curvilinear coordinates

- The localized stretching vibrations of the HOLCs are similar to those naturally obtained with **curvilinear coordinates** of which the polyspherical coordinates are a special class [4].
- This indicates that the application of curvilinear coordinates can provide better conditions for using the ADGA and general fit-basis framework compared to rectilinear coordinates.
- A set of curvilinear coordinates features both distances and angles in contrast to a set of rectilinear coordinates which

only includes distances. This means that additional flexibility in the choice of fit-basis functions are required and especially periodic one-mode functions are of interest.

- A clear disadvantage in the use of curvilinear coordinates is that the KEO becomes quite complicated to evaluate [5]

$$\hat{T}_{\text{nuc}}(\tilde{\mathbf{Q}}) = -\frac{\hbar^2}{2} \sum_{i,j=1}^{3N} J^{-1}(\tilde{\mathbf{Q}}) \frac{\partial}{\partial \tilde{Q}_i} J(\tilde{\mathbf{Q}}) G^{ij}(\tilde{\mathbf{Q}}) \frac{\partial}{\partial \tilde{Q}_j}.$$

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