

# Schrödinger Web Service

The Schrodinger API from the user's perspective:

From the underlying physics to realistic models with practical examples



# Scientific Background



" WHEN ALL ELSE FAILS, LOOK  
AT THE SCHRODINGER  
EQUATION." -- RUSSELL T. PACK,  
APRIL 1978



- Numerous nano-world phenomena are inherently quantum
- Their description and quantitative treatment requires usage of the apparatus of quantum mechanics.
- The Schrödinger equation (a “quantum analog” to the famous Newton’s equation in classical physics).

- For a stationary state of the system the Schrödinger equation has the form



$$\hat{H}\psi = E\psi$$

The Hamiltonian consists of the kinetic energy operator ( $\hat{K}(q)$ ) and the potential energy operator ( $\hat{V}(q)$ ):

$$\hat{H}(q) = \hat{K}(q) + \hat{V}(q)$$


- WHY DVR?????

- UPPSALLA, late 2009: “We’ve got to be more modern, and avoid the variational approach, which is so exploited!”
- 2010-2011: “It has been used in most of the published high-quality papers (and the guys from the University of Stockholm have used it extensively)”
- Just kidding, of course, BUT: There has to be some real reason for the advantageous usage of DVR (as compared to some other approaches)!

The solution may be sought within a finite basis set of  $n$  functions ( $\varphi_i(q)$ ), as in the variational approach:

$$\langle q|\psi\rangle = \sum_{i=1}^n c_i \cdot \langle q|\varphi_i\rangle$$


- Assuming an orthonormal set of basis functions

$$\langle \varphi_i|\varphi_j\rangle = \int \varphi_i^*(q) \cdot \varphi_j(q) dq = \delta_{ij}$$


- The expansion coefficients  $c_i$  and the set of eigenenergies can be found by solving the matrix eigenvalue problem

$$\mathbf{H}\mathbf{c} = E\mathbf{c}$$

$\mathbf{c}$  is the column  $n$ -vector  $[c_1, c_2, \dots, c_n]^T$ , while  $\mathbf{H}$  is  $n \times n$  square matrix containing the matrix elements of the Hamiltonian  $H_{ij}$ , given by



$$H_{ij} = \langle \varphi_i|\hat{H}|\varphi_j\rangle = \int \varphi_i^*(q)\hat{H}\varphi_j(q) dq$$

# The finite basis representation (FBR)

Such matrix-representation is often referred to as variational basis representation (VBR).



As a consequence of the orthonormality of the basis set functions, it can be straightforwardly shown that the expansion coefficients are given by:

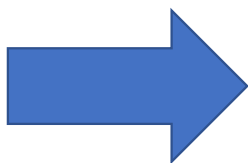


$$c_k = \langle \varphi_k | \psi \rangle = \int \langle \varphi_k | q \rangle \langle q | \psi \rangle dq$$

# The finite basis representation (FBR)

- Considering a Hamiltonian of the form:

$$\hat{H}(q) = \hat{H}_0(q) + \hat{V}'(q)$$



- $\hat{H}_0(q)$ : the harmonic oscillator “zeroth order” Hamiltonian
- $\hat{V}'(q)$ : the “complicated” potential energy part

The most complicated part of the calculation involves computation of the matrix elements:

$$V'_{ij} = \langle \psi_i | \hat{V}' | \psi_j \rangle = \int \psi_i^*(q) \hat{V}' \psi_j(q) dq$$

Any basis set that consists of orthogonal polynomials can be approximated by the so-called Gaussian quadratures technique. Approximating, however, the matrix elements by any quadrature technique, leads to the consequence that the results need not be the upper limits of the exact (true) eigenvalues. Such representation of the potential energy operator is called finite basis representation (FBR), to distinguish from variational basis representation (VBR)



The quadrature approximation is a straightforward method to compute the potential energy matrix elements



Define an  $n$ -point quadrature such consisting of the abscissa set of values  $\{x_1, x_2, \dots, x_n\}$  and the corresponding weights  $\{w_1, w_2, \dots, w_n\}$ . Such  $n$ -point quadrature leads to:

$$V_{ij} \approx V_{ij}^{FBR} = \sum_{k=1}^n w_k \psi_i^*(x_k) V(x_k) \psi_j(x_k)$$

# The finite basis representation (FBR)

**Defining**  $A_{ki} \equiv w_k^{1/2} \psi_i(x_k)$   $V_{kl}^{diag} = \delta_{kl} V(x_k)$



$$V_{ij}^{FBR} = \sum_{k=1}^n A_{ki}^* V_{kk}^{diag} A_{kj}$$

$$V^{FBR} = A^\dagger V^{diag} A$$

**The method of Harris, Engerholm and Gwinn for computation of potential energy matrix elements is actually equivalent to using the Gaussian quadrature approach in a basis set of orthogonal polynomials. In the FBR, the potential energy matrix is written as a unitary transformation of a diagonal matrix**

# The discrete variable representation (DVR) technique

- Apply unitary transformation such that the potential energy matrix is diagonal

$$\phi_k(x) = \sum_{i=1}^n A_{ki} \psi_i(x) \quad \phi_k(x_l) = \sum_{i=1}^n A_{ki} \psi_i(x_l) = \sum_{i=1}^n A_{ki} A_{li} w_l^{-\frac{1}{2}} = \delta_{kl} w_l^{-\frac{1}{2}}$$

- Evaluate the DVR functions at the quadrature points



**Any operator which is multiplicative in coordinate representation is diagonal in this basis**

$$\langle \phi_i | V | \phi_j \rangle = \sum_{k=1}^n w_k \phi_i(x_k) V(x_k) \phi_j(x_k) = \sum_{k=1}^n \delta_{ik} V(x_k) \delta_{jk} = V(x_k) \delta_{ij}$$

- The kinetic energy matrix is not diagonal in DVR (the kinetic energy operator is not multiplicative in coordinate representation)



**In the case of one-dimensional problems, the advantage of DVR over FBR is questionable**



**However, in multidimensional problems, the advantage of DVR becomes immediately evident**

# Schrödinger API



- **RESTful web service for solving multidimensional time-independent Schrödinger equation using Hermite DVR approach**
  - solution of **one-dimensional, two-dimensional** and **three-dimensional** time-independent Schrödinger equation based on the Gauss-Hermite Discrete Variable Representation (DVR) approach

The solution of **1D** Schrödinger equation is illustrated in the case of following model potentials:

- [Morse potential](#)
- [Simple Harmonic Oscillator \(SHO\) potential](#)
- [Sombrero potential \(Mexican hat\)](#)
- [Woods-Saxon potential](#)

Solutions of **2D** and **3D** Schrödinger equations are illustrated for the following two model potentials:

- [2D Morse potential](#)
- [2D SHO potential](#)
- [3D Morse potential](#)

# 1D Morse potential

One-dimensional Morse potential  $V(x)$ :

$$V(x) = D * (1 - \exp(-a * (x - x_0)))^2 - D$$

```
Request URL
https://schrodinger.chem-api.finki.ukim.mk/1dHermiteMorse?npts=5&D=3&a=0.5&x0=0&prec=8

Server response

Code      Details
200
Response body
[-2.41671645 -1.39124794 -0.28535681 1.09633735 7.42311473]
```

## Parameters:

npts - number of points (default value 10)

D - dissociation depth (default value 3.0)

a - inverse "width" of the potential (default value 0.5)

x0 - equilibrium bond distance (default value 0.0)

prec - precision (default value 6)



# 1D Sombbrero potential

One-dimensional version of the sombrero potential ( $a < 0$  and  $b > 0$ ):

$$V(x) = a * x^2 + b * x^4$$

```
Request URL
https://schrodinger.chem-api.finki.ukim.mk/1dHermiteSombbrero?npts=5&a=-5&b=1&prec=8

Server response

Code      Details
200
Response body
[-3.31729755 -3.29056942 -1.70943058 -1.67240256 2.48970011]
```

## Parameters:

npts - number of points (default value 10)

D - dissociation depth (default value 3.0)

a - inverse "width" of the potential (default value 0.5)

x0 - equilibrium bond distance (default value 0.0)

prec - precision (default value 6)

# 1D Woods-Saxon potential

## Woods-Saxon potential

$$V(r) = - V_0 / (1. + \exp((r - R) / z)) \text{ where } R = r_0 * A^{(1/3)}$$

```
Request URL
https://schrodinger.chem-api.finki.ukim.mk/1dHermitWoodSax?npts=5&V0=50&z=0.5&r0=1.2&A=16&prec=8

Server response
Code      Details
200
Response body
[-49.73342002 -49.02383 -47.92816698 -46.25839997 -42.70563227]
```

### Parameters:

- npts - number of points (default value 5)
- V0 - potential depth (default value 50.0)
- z - surface thickness (default value 0.5)
- r0 - rms nuclear radius (default value 1.2)
- A - mass number (default value 16)
- prec - precision (default value 8)

# 2D Morse potential

```
Request URL
https://schrodinger.chem-api.finki.ukim.mk/2dHermiteMorse?npts=5&D1=3&a1=0.5&D2=3&a2=0.5&x0=0&y0=0&prec=8

Server response
Code      Details
200      Response body
[-4.83343289 -3.80796439 -3.80796439 -2.78249589 -2.70207325]
```

## Parameters:

npts - number of points (default value 5)

D1 - dissociation depth for x (default value 3.0)

a1 - inverse "width" of the potential for x (default value 0.5)

x0 - equilibrium bond distance for x (default value 0.0)

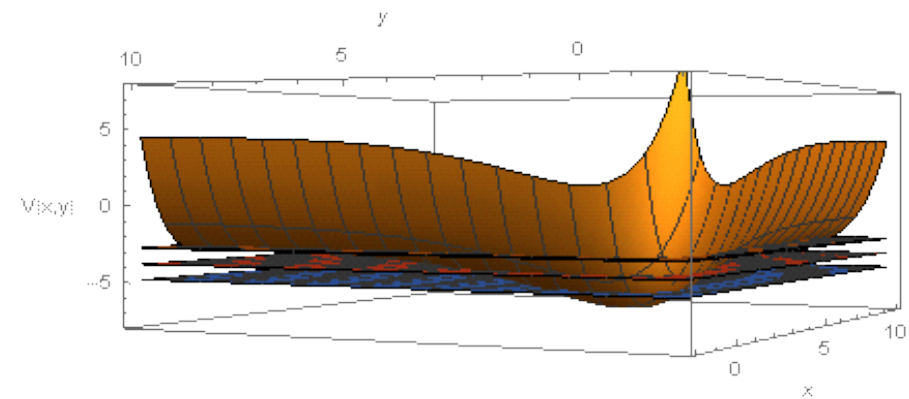
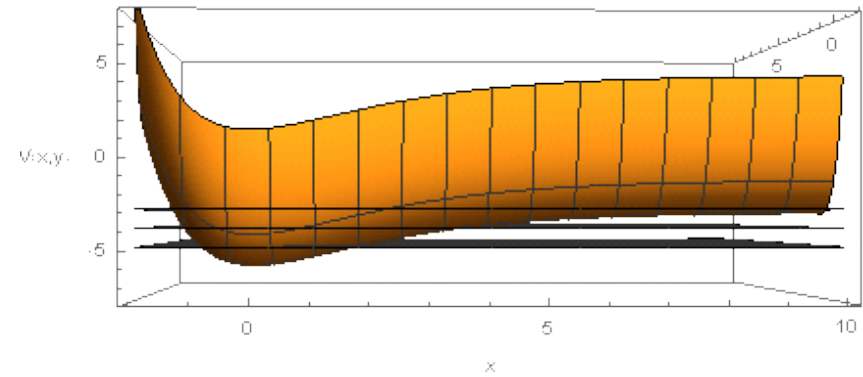
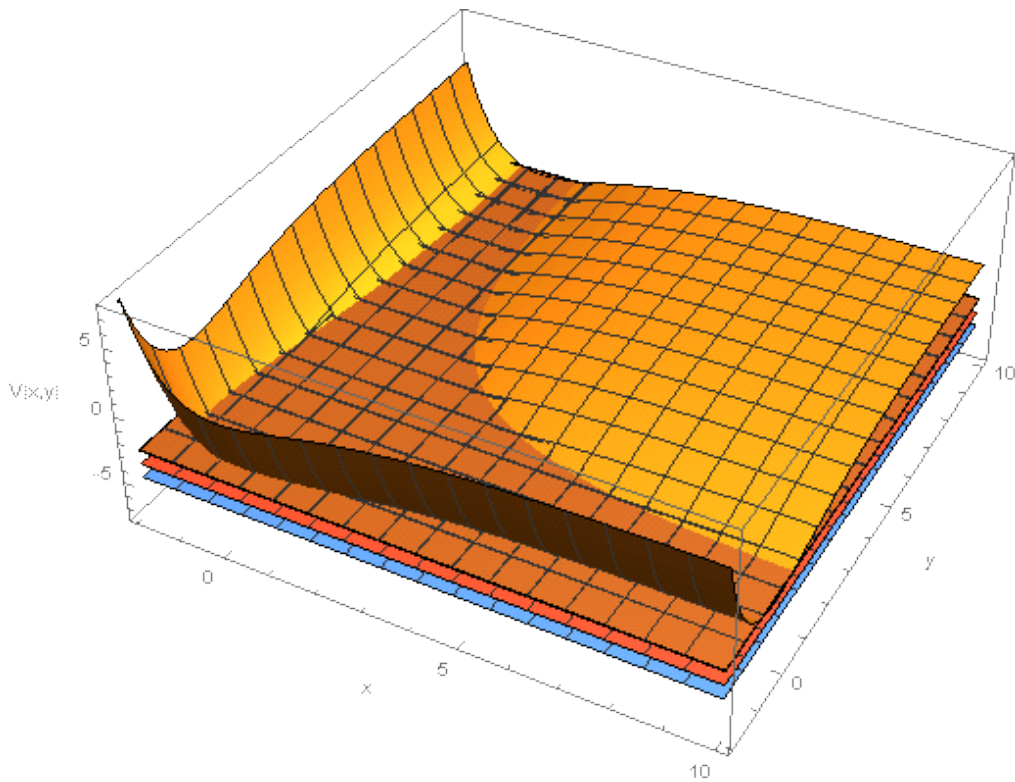
D2 - dissociation depth for y (default value 3.0)

a2 - inverse "width" of the potential for y (default value 0.5)

y0 - equilibrium bond distance for y (default value 0.0)

prec - precision (default value 6)

# 2D Morse potential



# 3D Morse potential

```
Request URL
https://schrodinger.chem-api.finki.ukim.mk/3dHermiteMorse?npts=5&D1=3&a1=0.5&D2=3&a2=0.5&D3=3&a3=0.5&x0=0&y0=0&z0=0&prec=8

Server response

Code      Details
-----
200      Response body
[-7.25014934 -6.22468084 -6.22468084 -6.22468084 -5.19921233]
```

## Parameters:

npts - number of points (default value 5)

D1 - dissociation depth for x (default value 3.0), D2 - dissociation depth for y (default value 3.0), D3 - dissociation depth for z (default value 3.0)

a1 - inverse "width" of the potential for x (default value 0.5), a2 - inverse "width" of the potential for y (default value 0.5), a3 - inverse "width" of the potential for z (default value 0.5)

x0 - equilibrium bond distance for x (default value 0.0), y0 - equilibrium bond distance for y (default value 0.0), z0 - equilibrium bond distance for z (default value 0.0)

prec - precision (default value 6)

# Service DEMO



Jupyter notebook link:

<https://notebooks.finki.ukim.mk/user/user1/notebooks/SchrodingerAPI.ipynb>

**User:** user1

**Password:** User1DEMO

# Practical Example



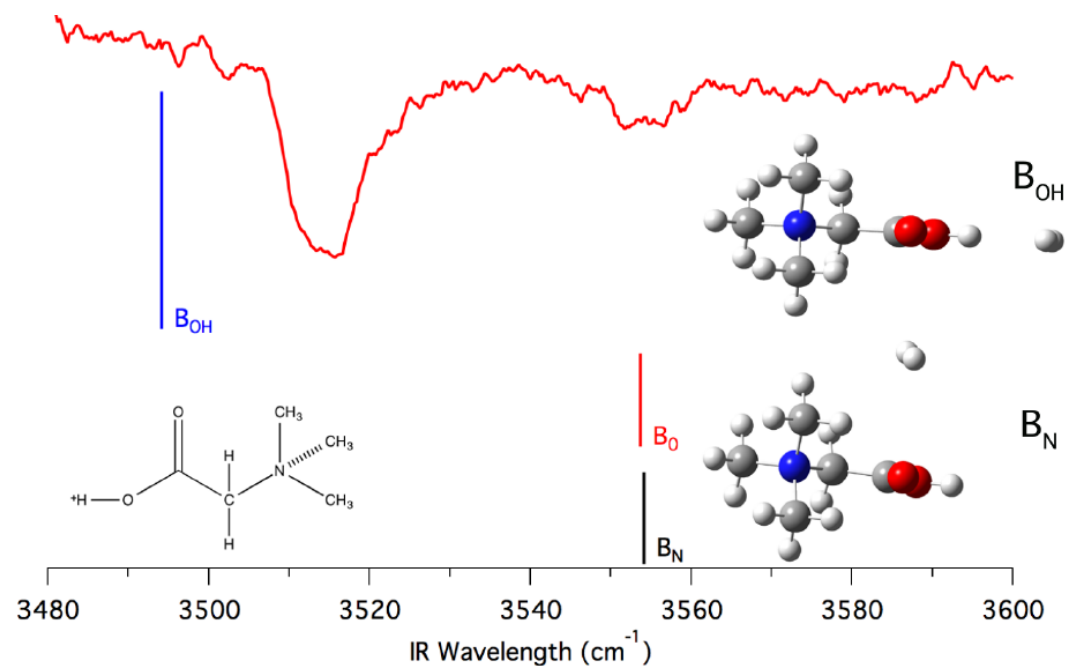
## Molecular hydrogen messengers can lead to structural infidelity: A cautionary tale of protonated glycine

Antoine Masson,<sup>1,a)</sup> Evan R. Williams,<sup>2,b)</sup> and Thomas R. Rizzo<sup>1,b)</sup>

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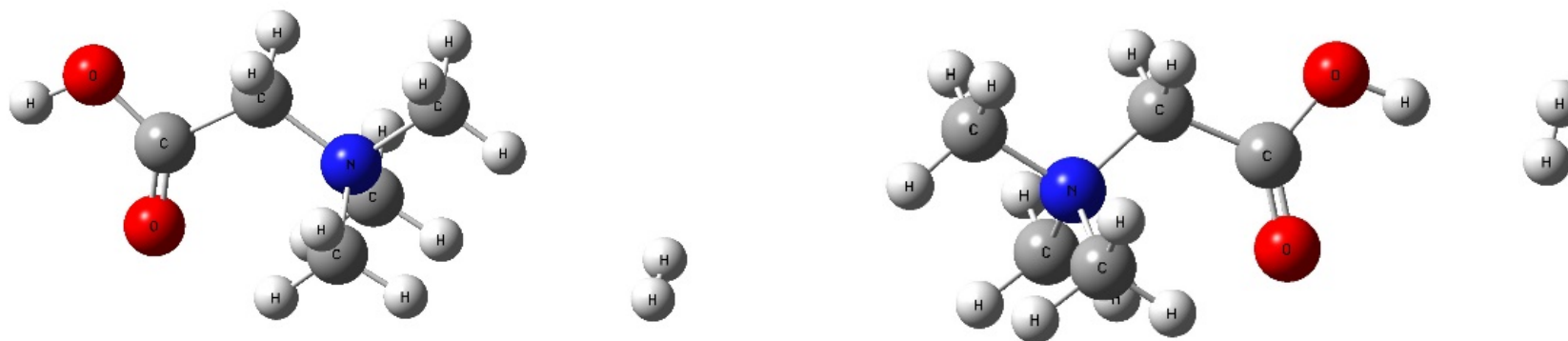
(Received 7 July 2015; accepted 25 August 2015; published online 14 September 2015)





# Practical example

- Understanding the H<sub>2</sub> – tagging of biomolecules by theoretical anharmonic vibrational spectroscopy with standard and long-range corrected exchange-correlation functionals



$$\dot{\vec{r}}(\text{O}) = \frac{m_{\text{H}}}{m} \cdot \dot{\vec{r}}$$

$$\dot{\vec{r}}(\text{H}) = \frac{m_{\text{O}}}{m} \cdot \dot{\vec{r}}$$

$$\vec{r} = \vec{r}(\text{H}) - \vec{r}(\text{O})$$

$$V = f(r_{\text{OH}})$$

$$V(r_{\text{OH}}) = D \cdot \{1 - \exp[-a \cdot (r_{\text{OH}} - r_{\text{OH},0})]\}^2 - D$$

# Practical example

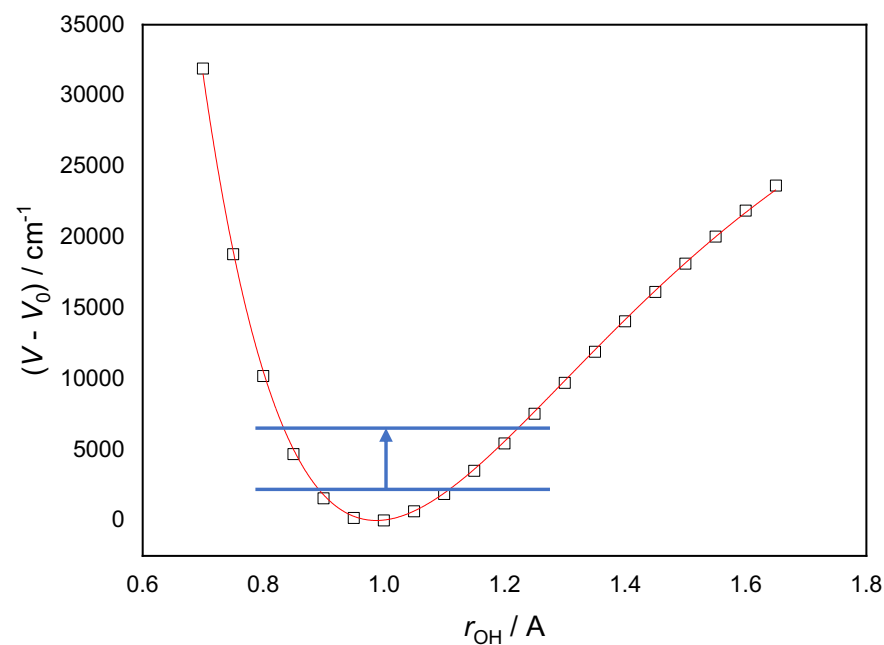
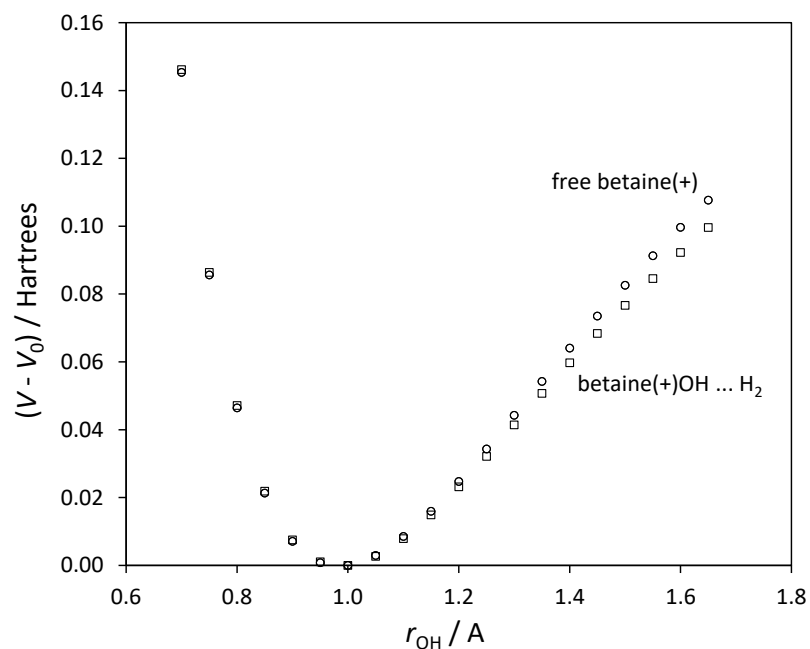
- A diatomic intramolecular oscillator may be conveniently described by a Morse potential with the following parameters:
  - $D = 0.176$  (a.u.)
  - $a = 1.02$  (a.u.)<sup>-1</sup>
  - $x_0 = 1.4$  (a.u.)
- Find the ground state energy level of this oscillator, as well as the first two excited levels

```
import requests
response = \
requests.get('https://schrodinger.chem-api.finki.ukim.mk/ldHermiteMorse?npts=20&D=0.176&a=1.02&x0=1.4&prec=32')
if response.status_code == 200:
    print(response.content.decode('utf-8'))
else:
    print("None")
```

```
[3.8921199517049934e-02 3.9038990155621445e-01 9.7429027058233031e-01 1.7762049809339091e+00 2.7957732113286857e+00
4.0424446176786830e+00 5.5349419642707067e+00 7.3058068540176428e+00 9.4075531043067695e+00 1.1922958051944608e+01 1.
5257271309631083e+01 1.9669185870427675e+01 3.9962671614302174e+01 1.0407010971408560e+02 2.9596256113277428e+02 8.85
27537847856104e+02 2.7912331820222394e+03 9.4889099112009353e+03 3.6531903728941070e+04 1.8117696113249165e+05]
```

# Practical example

- Understanding the H<sub>2</sub> – tagging of biomolecules by theoretical anharmonic vibrational spectroscopy with standard and long-range corrected exchange-correlation functionals



# Practical example

- Understanding the H<sub>2</sub> – tagging of biomolecules by theoretical anharmonic vibrational spectroscopy with standard and long-range corrected exchange-correlation functionals

|   | Static approach |           |         | ADMP    | Exp. | HCTH<br>(static) |
|---|-----------------|-----------|---------|---------|------|------------------|
|   | B3LYP           | CAM-B3LYP | DFTB(A) | DFTB(A) |      |                  |
| Betaine(+)                                  | 3534.6          | 3575.6    | 3486.7  | 3473.8  | 3554 | 3509.1           |
| Betaine(+)OH...H <sub>2</sub>               | 3447.7          | 3483.0    | 3412.7  | 3405.2  | 3514 | 3466.0           |
| $\Delta v$                                  | -86.9           | -92.6     | -74.0   | -68.6   | -40  | -43.1            |
|   |                 |           |         |         |      |                  |
| Betaine(+)CH <sub>3</sub> ...H <sub>2</sub> | 3551.4          | 3593.1    | 3486.9  | 3475.9  | 3558 | 3525.8           |
| $\Delta v$                                  | 16.8            | 17.5      | 0.2     | 2.1     | 4    | 16.7             |

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