Chemistry Faculty Research and Publications   Chemistry, Department of

10-2014

Interactive Tool for Visualization of Adiabatic Adjustment in APH Coordinates for Computational Studies of Vibrational Motion and Chemical Reactions

Alexander Teplukhin
Marquette University

Dmitri Babikov
Marquette University, dmitri.babikov@marquette.edu

Interactive Tool for Visualization of Adiabatic Adjustment in APH Coordinates for Computational Studies of Vibrational Motion and Chemical Reactions

Alexander Teplukhin
Chemistry Department, Wehr Chemistry Building, Marquette University, Milwaukee, WI
Dmitri Babikov
Chemistry Department, Wehr Chemistry Building, Marquette University, Milwaukee, WI

Abstract

The *adiabatically-adjusting principal-axes hyperspherical* (APH) coordinates reviewed in this letter are one of the best coordinate sets developed for computational treatment of spectroscopy and dynamics of triatomic molecules. Unfortunately, it is not so easy to understand and interpret them, compared to other simpler coordinates, like valence coordinates or Jacobi coordinates. To address this issue, we developed a desktop

application called APHDemo. This tool visualizes the process of adjustment of the APH coordinates to the shape of a triatomic molecule during molecular vibrations or chemical reaction, and helps to understand their physical meaning without going into complicated math.

Graphical abstract
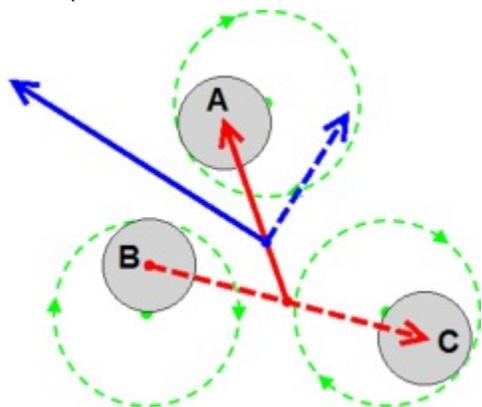
1. Introduction

Quantum molecular dynamics in triatomic systems takes special place in the fundamental chemical theory and in the chemistry education as well, because it allows introducing and studying spectroscopy (three normal vibration modes for low-amplitude motion in ABC) and chemical reactions (large-amplitude motion leading to A + BC → AB + C), all using the smallest possible number of atoms [1], [2]. Also, many important gas-phase molecules are triatomic, which makes this topic directly relevant to the real life problems in environmental chemistry [3], atmospheric chemistry [4], [5], [6], [7], [8] and astrochemistry [9], [10].

Any theoretical description of a molecule starts with the choice of suitable coordinates to represent the arrangement of atoms in ABC, which gives the molecular shape or geometry. Three coordinates are needed in order to describe a shape of nonlinear triatomic molecule, which is the number of internal degrees of freedom, $3N - 6$, with N being the number of atoms. For example, familiar to every chemist are the *valence* coordinates $\{r_1, r_2, \gamma,\}$ which consist of two bond lengths in ABC and the angle between the two bonds. Another well-known coordinates are the *normal-mode* coordinates $\{\xi_1, \xi_2, \xi_3,\}$ which represent the collective motion of all three atoms leading to symmetric stretching, asymmetric stretching and bending of ABC. When the motion of atoms in a molecule is treated with quantum mechanics the vibrational wave function depends on these coordinates, $\psi(r_1, r_2, \gamma)$, and the vibrational Hamiltonian operator $\hat{H}$ in the Schrodinger equation acts on these coordinates, $\hat{H}\psi = E\psi$. It is important to note, however, that neither the valence nor the normal-mode coordinates are employed for accurate numerical studies of triatomics, because the simple valence coordinates result in the extremely complicated Hamiltonian operator [11], while the normal-mode representation is an approximation which breaks down at higher levels of vibrational excitation and/or for anharmonic potentials.

Although a search for the best coordinates still continues [12], several coordinates have been identified as convenient and have been used extensively in molecular calculations. Namely, the Jacobi coordinates $\{R, r, \Theta\}$ are probably the most popular, where r is the bond length of a diatomic fragment of the molecule, say BC, while R is the distance from A to the center-of-mass of BC, and Θ is the angle between them (see Figure 1). The Hamiltonian operator is rather simple in these coordinates and they work well in many cases, particularly for description of molecular vibrations in ABC (see Figure 2) or non-reactive elastic and inelastic scattering of A + BC [13]. However, there are situations when Jacobi coordinates are not the best choice. For example, if only the A + BC arrangement diatomic basis is used, and the ABC motion is floppy and anharmonic with vibrational character very different than that of BC, then the calculation of the ABC spectra may converge slowly or not at

all. Besides the bound states, Jacobi coordinates are also used for description of chemical reactions like A + BC → AB + C [14] but in this case their intrinsic drawback shows up. It appears that a set of Jacoby coordinates introduced for the entrance channel of reaction, A + BC (see Figure 3a), becomes inappropriate for the exit channel of the reaction, AB + C. Indeed, at large AB + C separation the diatomic fragment AB is not described by any internal coordinate, but corresponds to numerically unstable geometry described by a very small value of angle $\Theta \to 0$ and large value of $r \to 2R$ (see Figure 3b). As a consequence, the convergence of calculations could be very poor again.
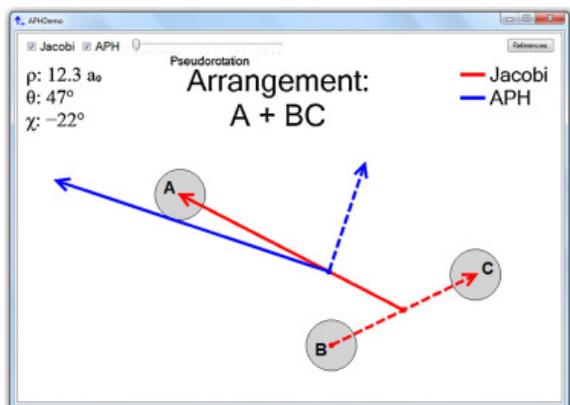

Fig. 1. Screenshot of the APHDemo application. Checkboxes in the upper-left corner allow displaying Jacobi (red) or APH (blue) vectors, or both simultaneously. The values of hyperspherical variables $\{\rho, \vartheta, \chi\}$ are conveniently displayed. User can drag atoms with a mouse. Instantaneous arrangements of atoms are automatically labeled as "ABC", in the case of a molecule or transient species, or "A + BC", *etc.*, in the asymptotic case of chemical reagents/products.
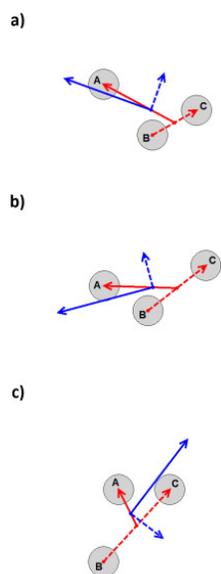

Fig. 2. Examples of atom arrangements due to low-amplitude vibrational motion in the triatomic ABC system and their description using Jacobi (red) and APH (blue) vectors. Note that three physically different arrangements correspond to congruent triangles. Lengths of APH vectors remain the same, which emphasizes symmetry. Jacobi vectors do not have this advantage.
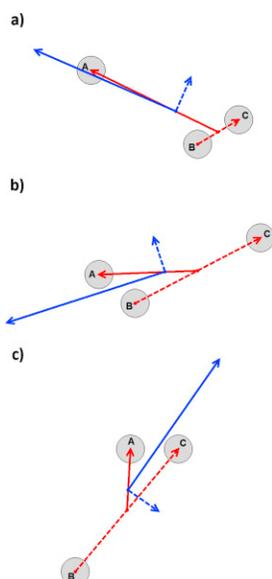
Fig. 3. Examples of atom arrangements due to high-amplitude vibrational motion leading to A + BC, AB + C and AC + B reagents/products, and their description using Jacobi (red) and APH (blue) vectors. Note that in the product channels AB + C and AC + B the Jacobi vectors defined for the reactant channel A + BC become inappropriate. In contrast, the APH coordinates always adjust to the instantaneous arrangement of atoms.

This is inconvenient and it would often be beneficial to use some other coordinates that threat all the reaction channels on equal footing. Such coordinates were developed by Pack and Parker and are known as *adiabatically-adjusting principal-axes hyperspherical* (APH) coordinates [15], [16], [17]. They adjust smoothly from one arrangement of atoms to another arrangement and describe well not only the reagent channel A + BC, but also the product channel AB + C, and even the second product channel AC + B (in the cases when the second product channel is chemically relevant, see Figure 3c). Furthermore, the Hamiltonian operator is simple in the APH coordinates [16].

Advantages of the APH coordinates for triatomic systems are known [16] and several examples can be drawn from the recent literature where molecular simulations successfully employ the APH coordinates. For example, spectroscopy of O_3, N_3, H_3, Ar_3, Ne_3, Ne_2H, HeNeH molecules [4], [7], [18], [19], [20], [21], [22], molecular ions N_3^+, H_3^+, D_3^+, HCO^+, DCO^+, H_3^-, D_2H^-, H_2D^- [1], [9], [10], [23], and pseudo-triatomic $Cl\!-\!\!-\!CH_3\!-\!\!-\!Br$ [24], have been studied using the APH coordinates. The exchange reactions $H + O_2 \leftrightarrow OH + O$, $O + H_2 \leftrightarrow OH + H$, $O + O_2 \leftrightarrow O_2 + O$, $H + H_2 \leftrightarrow H_2 + H$, $F + H_2 \leftrightarrow FH + H$, $D + H_2 \leftrightarrow DH + H$, $H + D_2 \leftrightarrow HD + D$, and $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$ [2], [3], [7], [17], [24], [25], [26], [27], [28] have also been studied using the APH coordinates. Still, one should admit that the APH coordinates are much less popular, compared to the simpler but more limited Jacobi coordinates.

One reason for this is that the formalism of adiabatic adjustment is mathematically involved [16] which creates a barrier to understanding, particularly by students at the beginning of their computational research projects. In order to simplify introduction to the APH coordinates we created an interactive desktop application APHDemo that allows seeing a triatomic system on the screen, dragging atoms by mouse from one arrangement to another and watching how the APH coordinates adjust continuously, for example, from the reagent channel to the product channel, through the reaction intermediate. The Jacobi coordinates can also be made visible for comparison, which allows understanding better their drawbacks, and emphasizing advantages of the APH coordinates.

The major area of application of this program is, probably, in the educational process. We created several animations that illustrate typical examples of vibrational dynamics and can be used in the classroom presentation of the APH coordinates. However, this tool may also be rather handy to those who plan employing the APH coordinates in their research, particularly to graduate to students and postdocs.

2. APH coordinates

Pack and Parker [16] emphasized a link between the simple Jacoby coordinates and the APH coordinates, and described transformation from Jacobi to APH. It is convenient to introduce vector notation {**R**, **r**} in addition to {R, r, Θ}. Here $R = |\mathbf{R}|$, $r = |\mathbf{r}|$, while angle Θ can be easily determined from coordinates of vectors **R** and **r**. Next step is to introduce the *mass-scaled* Jacobi coordinates {S, s, Θ}, or {**S**, **s**} in matrix notation, as follows:

(1)

$$S = d\mathrm{R}, s = d^{-1}\mathrm{r}.$$

Here

(2)

$$d = \left[\frac{m}{\mu}\left(1 - \frac{m}{M}\right)\right]^{1/2}$$

is a scaling factor, where m is the mass of atom that defines the arrangement (*e.g.*, atom A for arrangement A + BC), μ is a three-body reduced mass and M is a total mass:

(3)

$$\mu = \left[\frac{m_A m_B m_C}{M}\right]^{1/2}, M = m_A + m_B + m_C.$$

The mass-scaled Jacobi vectors {**S**, **s**} do not differ much from the original Jacobi vectors {**R**, **r**} because for natural triatomic molecules the value of scaling factor is always close to one, $d \approx 1$.

The next step is to define a set of new coordinates {**Q**, **q**} obtained by rotation of {**S**, **s**} as follows:

(4)

$$\begin{pmatrix} Q \\ q \end{pmatrix} = \mathsf{T} \begin{pmatrix} S \\ s \end{pmatrix},$$

where **T** is a kinematic rotation matrix that depends on kinematic rotation angle χ, so, **T**(χ). The value of χ is chosen such that vector **Q** would point along one of the *principal axes* of inertia for ABC, namely, the one with the smallest moment of inertia. Thus, in the reagent channel A + BC vector **Q** would approach vector **S**, but in the product channels AB + C or AC + B vector **Q** would significantly deviate from the Jacobi vector **S**. Pack and Parker [16] showed analytically that such value of χ maximizes the value of $Q = |\mathbf{Q}|$ and changes *adiabatically* (smoothly) between the various atom arrangements.

The last step is to convert a set of three coordinates {Q, q, χ} into a set of three *hyper-spherical* variables {ρ, ϑ, χ} called APH coordinates, and to establish analytic transformation between Jacobi coordinates {S, s, Θ} and the APH coordinates {ρ, ϑ, χ}. Pack and Parker showed that:

(5)

$$\rho = (S^2 + s^2)^{1/2}$$

$$\tan\theta = \frac{[(S^2 - s^2)^2 + (2S \cdot s)^2]^{1/2}}{2Ss\sin\Theta}$$

$$\tan(2\chi) = \frac{2S \cdot s}{S^2 - s^2}$$

The variable ρ, called hyperradius, represents the overall "size" of the ABC system, while two hyperangles ϑ and χ define "shape" of the ABC. For low-amplitude vibrational motion in a triatomic molecule the APH coordinates are similar to the normal-mode coordinates: ρ describes symmetric stretching, while ϑ and χ are responsible for the bending motion and asymmetric stretching, respectively. However, for large-amplitude vibrational motion ρ describes dissociation (*e.g.*, to A + BC), ϑ describes vibration of the diatomic product (*e.g.*, BC), while χ describes permutations of atoms or pseudo-rotation (*e.g.*, A–B–C to C–A–B and to B–C–A, see Ref. [1]).

3. APHdemo application

APHDemo is a desktop Windows application developed to demonstrate the essence of APH coordinates. It allows readers to see how the adjustment of APH coordinates occurs in response to the motion of atoms in ABC. The window screenshot is shown in Figure 1. The original Jacobi vector pair {**R**, **r**} for the arrangement A + BC is shown in red. The APH vector pair {**Q**, **q**} is shown in blue. Solid lines correspond to **R** and **Q**, while dashed lines correspond to **r** and **q**. All vectors lie in the plane of the triatomic molecule. The values of APH variables {ρ, ϑ, χ} are printed in the top-left corner. User can move atoms A, B or C with computer mouse and turn on and off the coordinate sets to show (Jacoby or APH, or both) using checkboxes. In addition, a track bar is available to animate a pseudo-rotational collective motion of all three atoms.

Dragging atoms allows going through all possible configurations of ABC. Figure 2 illustrates the low-amplitude molecular vibrations, when three interatomic distances are all comparable. Three frames of the figure correspond to three possible cases of one atom (A, B or C) being slightly further from the other two atoms, for an arbitrary shape of ABC. We see that here the Jacobi coordinates (red) are quite appropriate for description of all three cases. However, the APH coordinates (blue) have one advantage. Notice that we intentionally chosen the three shapes in Figure 2 being congruent. Jacobi coordinates do not "see" this equivalence and describe three shapes by somewhat different values of $R = |\mathbf{R}|$ and $r = |\mathbf{r}|$. In contrast, the APH coordinates "recognize" the equivalence and describe all three arrangements by the same values of $Q = |\mathbf{Q}|$ and $q = |\mathbf{q}|$. This has important applications in spectroscopy, where symmetry is the factor determining the allowed state-to-state transitions [1].

Figure 3 summarizes important concepts for the large-amplitude motion of atoms, when one atom is far from the other two (in the entrance/exit channel of a reaction). We see that in the reagent channel A + BC the APH vectors {**Q**, **q**} are similar to Jacobi vectors {**R**, **r**} and either coordinates describe the triatomic system well (see Figure 3a). Namely, both **q** and **r** describe vibration of the diatomic reagent (the BC distance), while both **Q** and **R** describe collision of the two reagents (the A-BC separation). However, in the product channels neither of Jacoby vectors describes the diatomic product (see Figure 3b and 3c). Indeed, in the product channels |**r**| becomes very large and describes separation of two products (AB–C or AC–B distances), while $R \to r/2$, so that asymptotically the vector **R** becomes obsolete. In contrast, the APH vectors {**Q**, **q**} remain meaningful even in the product channels. From Figure 3 we see that vector **q** always remains small and always describes the diatomic fragment, either reagent or product, depending on the channel. At the same time, vector **Q** always remains large and plays a role of the universal reaction coordinate. This is a clear and significant advantage of the APH coordinates.

One other capability of the APHDemo is to illustrate pseudo-rotational motion. During this process all three atoms in ABC move on circles of the same radius, but with phase shifts of 120° with respect to each other (see the Abstract graphic). Using the track-bar at the top of the APHDemo window (see Figure 1), user can initiate the trajectory of such collective motion. During pseudorotation the APH vectors {$\mathbf{Q}$, $\mathbf{q}$} simply rotate around the center of mass of ABC, which corresponds to the change of hyperangle χ only, with no changes of ρ and ϑ. One can see that it takes two full turns of the atoms in order for the APH vectors {$\mathbf{Q}$, $\mathbf{q}$} to return into their original position. This corresponds to the range of hyperangle $-180° < \chi < +180°$, which includes both roots of χ, as it was emphasized by Parker and Pack [16]. This last property has important implications in dynamics around the conical intersections and in theoretical treatment of the geometric phase effect [18], [29].

4. How this application can be used for research and in classroom

The users of APHDemo are encouraged to try various arrangements of atoms in ABC. When the atoms are being moved, the set of blue vectors {$\mathbf{Q}$, $\mathbf{q}$} will stretch/compress but also rotate, while the set of red vectors {$\mathbf{R}$, $\mathbf{r}$} will primarily stretch/compress with little to no rotation. For some arrangements the APH vectors {$\mathbf{Q}$, $\mathbf{q}$} will become quite similar to Jacobi vectors {$\mathbf{R}$, $\mathbf{r}$}, but they will be very different for other arrangements, as discussed above. We created several representative animations that can be downloaded from Supporting Information. Those include trajectories for the local and normal mode vibration of ABC, for non-reactive scattering of A + BC, for reactive process A + BC → AB + C, and for pseudo-rotation in A–B–C. In addition, with APHDemo it becomes easier to understand what shapes correspond to the limiting values of the APH hyperangles. For example, the equilateral configuration of ABC corresponds to $\vartheta = 0°$, while linear ABC is described by $\vartheta = 90°$. Isosceles shapes correspond to $\chi = 0°, \pm60°, \pm120°$. All these arrangements can be easily explored using our interactive tool, and the corresponding values of ρ, ϑ and χ can be read from the top-left corner of the screen (see Figure 1).

In addition to just visualization, the APHDemo can help in explaining, and potentially discovering new reaction mechanisms and pathways, such as roaming. It could be rather useful for mode assignment of vibrational states in both Jacobi and APH coordinates, as the user could simply drag back-and-forth any atom and observe corresponding changes of the coordinates.

The application was written in C# using Math.NET Numerics library [30] to perform vector operations. APHDemo requires Microsoft.NET Framework 4.5 [31], usually available in standard installation. The executable file is also available for download *via* Supporting Information. It is sufficient to download this file (*e.g.*, to a Desktop of a PC) and run it with double-click of the mouse.

5. Conclusion

The APHDemo application has been developed to visualize the process of adiabatic-adjustment of the APH coordinates to the shape of a triatomic system during molecular vibrations or chemical reaction. It helps to understand physical meaning of the APH coordinates without going into complicated math, and emphasizes their advantages over Jacobi coordinates. Simply by dragging atoms with a mouse the user can go through all possible arrangements of three particles, tracking orientations of the vectors and reading values of the adjusting coordinates. This demonstrational application will be very helpful for those who decided to use APH coordinates in their research, particularly for graduate students and postdocs. We plan implementing this interactive tool at Marquette University in the computational chemistry graduate course, a part of curriculum for the Physical Chemistry and/or Chemical Physics programs.

As for future prospects, this application can serve as a foundation for a software to visualize trajectories or wave functions in APH coordinates. Such software may help plotting time-independent vibrational wave functions, or visualizing motion of a wave packet from time-dependent calculations, or even showing trajectories from classical calculations. Addition of these features will make our application even more useful for computational

research on triatomic molecules, including spectroscopy and dynamics. In principle, this application should work on Linux under the free and open source Wine software [32]. Such Linux version of APHDemo will also be developed in the future.

Acknowledgments

Appendix A. Supplementary data

Download all supplementary files included with this article

The following are the supplementary data to this article:

Download : **Download video (2MB)**

Download : **Download video (5MB)**

Download : **Download video (3MB)**

Download : **Download video (2MB)**

References

[1] D. Babikov, V.A. Mozhayskiy, A.I. Krylov. **The photoelectron spectrum of elusive cyclic-N_3 and characterization of the potential energy surface and vibrational states of the ion.** *J. Chem. Phys*., 125 (2006), p. 84306

[2] G. Quéméner, B.K. Kendrick, N. Balakrishnan. **Formation of molecular oxygen in ultracold O + OH collisions.** *Phys. Rev. A*, 79 (2009), p. 022703

[3] G. Quéméner, B.K. Kendrick, N. Balakrishnan. **Quantum dynamics of the H + O_2 → O + OH reaction.** *J. Chem. Phys*., 132 (2010), p. 14302

[4] H. Lee, J.C. Light. **Vibrational energy levels of ozone up to dissociation revisited.** *J. Chem. Phys*., 120 (2004), p. 5859

[5] D. Babikov, B.K. Kendrick, R.B. Walker, P. Fleurat-Lessard, R. Schinke, R.T. Pack. **Metastable states of ozone calculated on an accurate potential energy surface.** *J. Chem. Phys*., 18 (2003), p. 6298

[6] D. Babikov, B.K. Kendrick, R.B. Walker, R. Schinke, R.T. Pack. **Quantum origin of an anomalous isotope effect in ozone formation.** *Chem. Phys. Lett*., 372 (2003), p. 686

[7] D. Babikov, B.K. Kendrick, R.B. Walker, P. Fleurat-Lessard, R. Schinke, R.T. Pack. **Formation of ozone: metastable states and anomalous isotope effect.** *J. Chem. Phys*., 119 (2003), p. 2577

[8] D. Babikov. **Entrance channel localized states in ozone: possible application to helium nanodroplet isolation spectroscopy.** *J. Chem. Phys*., 119 (2003), p. 6555

[9] V. Kokoouline, C.H. Greene. **Unified theoretical treatment of dissociative recombination of D_{3h} triatomic ions: application to H_3^+ and D_3^+.** *Phys. Rev. A*, 68 (2003), p. 12703

[10] N. Douguet, V. Kokoouline, C.H. Greene. **Theoretical rate of dissociative recombination of HCO^+ and DCO^+ ions.** *Phys. Rev. A*, 77 (2008), p. 064703

[11] M. Lara, A. Aguado, M. Paniagua, O. Roncero. **State-to-state reaction probabilities using bond coordinates: application to the Li+HF(v, j) collision.** *J. Chem. Phys*., 113 (2000), p. 1781

[12] G. Katz, K. Yamashita, Y. Zeiri, R. Kosloff. **The Fourier method for tri-atomic systems in the search for the optimal coordinate system.** *J. Chem. Phys*., 116 (2002), p. 4403

[13] A. Semenov, D. Babikov. **Mixed quantum/classical theory of inelastic scattering in space-fixed and body-fixed reference frames.** *J. Chem. Phys*., 139 (2013), p. 174108

[14] Z. Sun, X. Lin, S. Lee, D.H. Zhang. **A Reactant-coordinate-based time-dependent wave packet method for triatomic state-to-state reaction dynamics: application to the H + O$_2$ reaction.** *J. Phys. Chem. A*, 113 (2009), p. 4145

[15] R. Pack. **T Coordinates for an optimum CS approximation in reactive scattering.** *Chem. Phys. Lett.*, 108 (1984), p. 333

[16] R.T. Pack, G.A. Parker. **Quantum reactive scattering in three dimensions using hyperspherical (APH) coordinates.** *Theory J. Chem. Phys.*, 87 (1987), p. 3888

[17] J. Crawford, G.A. Parker. **State-to-state three-atom time-dependent reactive scattering in hyperspherical coordinates.** *J. Chem. Phys.*, 138 (2013), p. 54313

[18] D. Babikov, B.K. Kendrick. **The infrared spectrum of cyclic-N$_3$: theoretical prediction.** *J. Chem. Phys.*, 133 (2010), p. 174310

[19] V. Kokoouline, C.H. Greene. **Photofragmentation of the H$_3$ molecule, including Jahn-Teller coupling effects.** *Phys. Rev. A*, 69 (2004), p. 032711

[20] M. Márquez-Mijares, *et al.* **A theoretical investigation on the spectrum of the Ar trimer for high rotational excitations.** *J. Chem. Phys.*, 130 (2009), p. 154301

[21] H. Suno. **Hyperspherical slow variable discretization method for weakly bound triatomic molecules.** *J. Chem. Phys.*, 134 (2011), p. 064318

[22] H. Suno. **A theoretical study of Ne$_3$ using hyperspherical coordinates and a slow variable discretization approach.** *J. Chem. Phys.*, 135 (2011), p. 134312

[23] M. Ayouz, O. Dulieu, J. Robert. **Resonant states of the H$_3^-$ molecule and its isotopologues D$_2$H$^-$ and H$_2$D$^-$.** *J. Phys. Chem. A*, 117 (2013), p. 9941

[24] C. Hennig, S. Schmatz. **Rotational effects in complex-forming bimolecular substitution reactions: a quantum-mechanical approach.** *J. Chem. Phys.*, 131 (2009), p. 224303

[25] G.B. Pradhan, N. Balakrishnan, B.K. Kendrick. **Ultracold collisions of O(^{1}D) and H$_2$: the effects of H$_2$ vibrational excitation on the production of vibrationally and rotationally excited OH.** *J. Chem. Phys.*, 138 (2013), p. 164310

[26] G.B. Pradhan, J.C. Juanes-Marcos, N. Balakrishnan, B.K. Kendrick. **Chemical reaction versus vibrational quenching in low energy collisions of vibrationally excited OH with O.** *J. Chem. Phys.*, 139 (2013), p. 194305

[27] S. Adhikari, A.J.C. Varandas. **The coupled 3D wave packet approach for triatomic reactive scattering in hyperspherical coordinates.** *Comput. Phys. Commun.*, 184 (2013), p. 270

[28] B.K. Kendrick, R.T. Pack, R.B. Walker, E.F. Hayes. **Hyperspherical surface functions for nonzero total angular momentum. I. Eckart singularities.** *J. Chem. Phys.*, 110 (1999), p. 6673

[29] X. Li, D.A. Brue, B.K. Kendrick, J.D. Blandon, G.A. Parker. **Geometric phase for collinear conical intersections. I. Geometric phase angle and vector potentials.** *J. Chem. Phys.*, 134 (2011), p. 64108

[30] C.M. Rüegg. **Math.NET Numerics.** (2014) Available from: http://numerics.mathdotnet.com (accessed July 2014)

[31] Microsoft. **.NET Framework 4.5.** (2014) Available from: http://www.microsoft.com (accessed July 2014)

[32] A. Julliard. **Wine.** (2014) Available from: https://www.winehq.org/ (accessed August 2014)