

Visualization of Potential Energy Function Using an Isoenergy Approach and 3D Prototyping

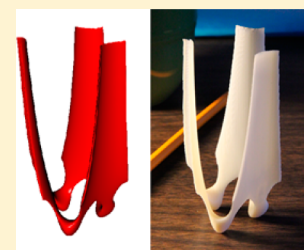
Alexander Teplukhin and Dmitri Babikov*

Chemistry Department, Marquette University, Milwaukee, Wisconsin 53201-1881, United States

S Supporting Information

ABSTRACT: In our three-dimensional world, one can plot, see, and comprehend a function of two variables at most, $V(x,y)$. One cannot plot a function of three or more variables. For this reason, visualization of the potential energy function in its full dimensionality is impossible even for the smallest polyatomic molecules, such as triatomics. This creates some barrier to understanding the interaction of atoms in a molecule. It would be beneficial to see all features of the global potential energy function at the same time (which can include deep covalent wells, transition states, shallow van der Waals wells, and reaction channels) without fixing or relaxing some degrees of freedom. In this paper, we review the isoenergy approach that allows visualization of the potential energy function of a triatomic molecule in its full dimensionality in 3D space as a volume, not as a surface. Also, we propose the use of 3D-printing capabilities to create plastic models of such isoenergy objects that can be taken into hands and inspected in detail from any perspective.

KEYWORDS: Graduate Education/Research, Physical Chemistry, Hands-On Learning/Manipulatives, Theoretical Chemistry



INTRODUCTION

The ansatz of computational chemistry is the Born–Oppenheimer approximation¹ that splits the overall molecular problem onto the electronic motion part and the nuclear motion part. The electronic part of the problem is solved first, for fixed positions of the nuclei, which provides the potential energy function V that governs the motion of nuclei. It is often said that electrons create the potential energy landscape on which for nuclei to move.² However, comparison of the potential energy function with a landscape is good only to a certain extent. When we say “landscape”, this usually means a two-dimensional potential energy surface, for example, $V(x,y)$. However, dimensionality of the potential energy function in molecules is usually higher than two; thus, the number of internal degrees of freedom for an N -atomic nonlinear molecule is $3N-6$. Even for a triatomic molecule, for example, H_2O or O_3 , the potential energy function is a function of three variables, $V(x,y,z)$, which is a hypersurface, rather than a surface.

A question of visualization of this hypersurface arises because in our three-dimensional world, one can plot, see, and comprehend a function of two variables at most, $V(x,y)$. One cannot plot a function of three or more variables. It is frustrating to realize that we are so limited in our abilities. Visualization of the potential energy function in its full dimensionality is impossible even for the smallest polyatomic molecules, the triatomics. This creates some barrier to understanding collective atomic motion in molecules, such as nonlocal vibrational modes, or trajectories of atoms in chemical reactions because all of these processes are driven by the potential energy hypersurface.

Several approaches are used to overcome this natural barrier. We can reduce dimensionality of the potential energy function

by freezing some internal degrees of freedom. This is equivalent to slicing the hypersurface and looking at one slice at a time. For example, in the case of O_3 described using valence coordinates,³ the full dimensional potential energy function is a function of three variables, $V(R_1, R_2, \alpha)$, where R_1 and R_2 are bond lengths, and α is the bending angle. If you freeze or fix the value of R_1 (e.g., equal to the equilibrium bond length in O_3), a two-dimensional potential energy surface

$$V = V(R_2, \alpha)_{R_1=R_{eq}} \quad (1)$$

is obtained that can be easily plotted and used for analysis of some processes, such as homolytic bond dissociation in ozone, $O_3 \rightarrow O_2 + O$, or inelastic scattering of oxygen atom by oxygen molecule, $O_2(j) + O \rightarrow O_2(j') + O$. This works fine, but one should be aware of limitations of this approach. For example, such a dimensionally reduced potential energy surface would be useless for analysis of the atom exchange process in ozone, which is the simplest example of a reactive process: $O_2 + O \rightarrow O + O_2$. Indeed, in this reaction, both bond lengths change (e.g., the value of R_1 growth from R_{eq} to ∞ , while the value of R_2 decreases from ∞ to R_{eq}), so freezing one of them is inappropriate.

Another known method of reducing dimensionality of the potential energy hypersurface is to relax some degrees of freedom. For example, in the case of ozone, one could relax the value of the bending angle α by minimizing energy for each pair of chosen values of R_1 and R_2 , which produces a two-dimensional potential energy surface:⁴

$$V = V(R_1, R_2)_{\alpha=f(R_1, R_2)} \quad (2)$$

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Such surface can be easily plotted and used to visualize the reactive atom exchange process, $\text{O}_2 + \text{O} \rightarrow \text{O} + \text{O}_2$, but again, it is limited to the reaction path only, and some important information is missing. Namely, the zero-point energy of vibration is entirely lost.⁴ The processes of O-atom permutation and pseudorotation^{5,6} are also impossible to see on such a dimensionally reduced potential energy surface.

It would be beneficial to see all features of the global potential energy function at the same time, which can include deep covalent wells, transition states, shallow van der Waals wells (usual in the channel regions), and the entrance/exit reaction channels themselves. It would be nice to have a method that allows visualization of the potential energy function in its full dimensionality, without reductions, at least for triatomic molecules. Seemingly simple, triatomic molecules still hold many puzzles, and their theoretical description is still challenging, particularly from standpoint of quantum molecular dynamics. Calculations of precise rotational–vibrational spectra, highly excited delocalized states near dissociation threshold, and scattering resonances above the threshold are just few examples. On the practical side, triatomic molecules play crucial roles in Earth's atmosphere, environment, and interstellar medium.^{7–9}

In this paper, we review the isoenergy approach introduced earlier by one of us^{10,11} that allows visualization of the potential energy function of a triatomic molecule in its full dimensionality in 3D space as a volume, not as a surface. With this alternative method of presentation, the potential energy wells look like “chambers”, while the transition state regions look like narrow “passages” between them, all in 3D space; reaction channels look like “tunnels”. Most importantly, we propose the use of 3D printing capabilities to create handy models of such isoenergy objects that can be taken into hands and inspected in detail from any perspective. Our own experience with such 3D models shows that they are rather useful in teaching and even in research.

■ ISOENERGY APPROACH

Isosurfaces are routinely used to visualize molecular orbitals or electronic densities. In those cases, a small, minimal value ρ_{\min} of the electron density ρ is chosen, and a surface is built in 3D-space (x,y,z) that connects all points in space with $\rho = \rho_{\min}$, the isosurface. Points with $\rho < \rho_{\min}$ are outside of the isosurface, and this part of space is made transparent to the observer. Points with $\rho > \rho_{\min}$ are inside of the isosurface, and they are invisible to the observer. They can be made visible by plotting another isosurface with a larger value of ρ_{\min} .

Our approach to visualizing the potential energy function of a triatomic molecule is very similar, but it is inverted in a sense. Namely, a large, maximum value of the potential energy V_{\max} is chosen based on physical considerations. This can be a thermal energy of a chemical reaction, collision energy of a trajectory, or energy eigenvalue of a quantum state. Then, a 3D potential energy function $V(x,y,z)$ is visualized as follows: all points in 3D space with $V > V_{\max}$ are made transparent to the observer. This part of the configuration space is inaccessible to the motion of nuclei in a chemical process we consider (at least classically, neglecting the tunneling effects); thus, it is assumed to be unimportant (or less important), and that is why it is made transparent. In contrast, all points in 3D configuration space with $V < V_{\max}$ are made opaque because they are accessible to the motion of nuclei. The Cartesian variables (x,y,z) in physical 3D-space are used to represent some internal

vibrational coordinates used for theoretical description of a molecule. For example, this may be the valence coordinates (R_1, R_2, α) , the normal mode coordinates $(\zeta_1, \zeta_2, \zeta_3)$, or the hyperspherical coordinates (ρ, θ, φ) that we prefer for several reasons.^{12–15}

By using this method, an observer can see the potential energy function as a continuous volume structure in 3D space, as shown in Figure 1, where we applied the isoenergy approach

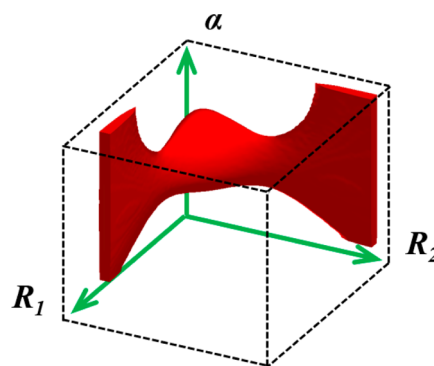


Figure 1. Isoenergy volume for O_3 molecule using valence coordinates. V_{\max} is chosen at the dissociation threshold of O_3 , which allows one to see the covalent well, the transition states, and the van der Waals interaction regions.

to the potential energy function of O_3 molecule expressed in the simplest valence coordinates, $V(R_1, R_2, \alpha)$. The bond lengths R_1 and R_2 of O_3 are plotted along x and y , while the value of the bending angle α is plotted along z . The ranges of coordinates in Figure 1 are $1.0 \leq R \leq 5.5 a_0$ and $75^\circ \leq \alpha \leq 180^\circ$. This covers the deep covalent well region seen in the middle of Figure 1 as a “lobe”, two transition states seen as the “bottlenecks”, and two shallow van der Waals interaction regions—the “wings”. If the vibrational energy of O_3 is low, the motion of its nuclei is restricted to the covalent well inside of the lobe only (the minimum energy point is at $R_1 = R_2 = 2.4 a_0$ and $\alpha = 117^\circ$). The transition state point, the bottleneck, can be reached by adding more vibrational energy to O_3 in order to stretch one of its bonds to $R = 3.5 a_0$. Since two bonds in O_3 are equivalent, one can stretch either R_1 or R_2 , which produces a symmetric structure in Figure 1 with two bottlenecks. Outside the transition state, when $R > 3.5 a_0$, O_3 transforms into a van der Waals complex between O and O_2 . Imagine that one could label the terminal atoms in O_3 using isotopes, which would produce $^{17}\text{O}^{16}\text{O}^{18}\text{O}$. Then, two possible van der Waals complexes would be $^{17}\text{O}\cdots^{16}\text{O}^{18}\text{O}$ and $^{17}\text{O}^{16}\text{O}\cdots^{18}\text{O}$, formed in the left and right wings in Figure 1, respectively. Note also that these wings cover a wide range of α , which means that the van der Waals complex is floppy, with large-amplitude bending motion allowed. In contrast, the lobe is compact along α , which means that bending the covalently bound O_3 results in significant energy increase (reflected by transparent areas below and above the lobe in Figure 1) and does not lead to any transition state. It is quite amazing that all of these features of the potential energy function can be seen in Figure 1.

It is also instructive to inspect the cut-outs of the volume structure in Figure 1. One example is shown in Figure 2, where the part of potential energy function with $\alpha > 117^\circ$ is removed. The remaining piece exhibits a slice with a color map that corresponds to dimensionally reduced 2D potential energy surface $V(R_1, R_2)$ with the bending angle fixed at $\alpha = 117^\circ$.

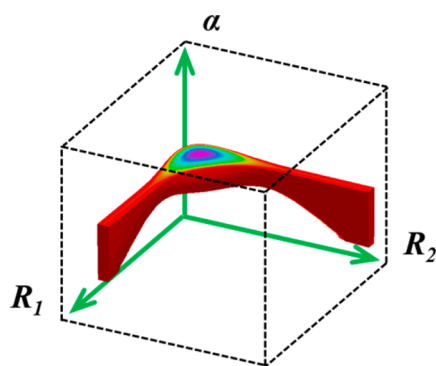


Figure 2. Slice through the covalent O_3 well of the isoenergy volume structure from Figure 1. Gradient of potential in the well is reflected by the color change. The minimum energy point is seen.

Here, one can see a large gradient of potential, reflected by color change, with violet showing the minimum energy point of the covalent well. This slice is what is usually called the potential energy surface. Clearly, many features of the potential energy function discussed in the previous paragraph are missing if only this 2D slice is examined.

The shape of isoenergy volume for the potential energy function of O_3 expressed in the valence coordinates $V(R_1, R_2, \alpha)$ is relatively easy to understand (Figures 1 and 2) mainly because these coordinates are often used to represent the familiar molecular parameters, such as chemical bonds and bending angle. The isoenergy approach becomes even more useful in the cases when we have to deal with less intuitive coordinates such as hyperspherical coordinates discussed in the next section.

GLOBAL POTENTIAL IN THE HYPERSPHERICAL COORDINATES

Hyperspherical coordinates (ρ, θ, φ) have a number of advantages over other choices.^{12–14} The most important is, perhaps, the simplicity of the rotational–vibrational Hamiltonian operator,^{12,13} but this advanced topic is not covered here. Relevant to visualization of the potential energy function $V(\rho, \theta, \varphi)$ is the ability of the hyperspherical coordinates to describe, on equal footing, different arrangements of atoms in a triatomic molecule and different dissociation channels, emphasizing molecular symmetry globally, through the entire physical range of molecular shapes.¹⁴

For example, one must realize that the images of Figures 1 and 2 represent only a small part of the global potential energy function. When the values of bond lengths are increased even further, beyond $R = 5.5 a_0$, the dissociation channels of ozone $^{17}\text{O}^{16}\text{O}^{18}\text{O}$ onto $^{17}\text{O} + ^{16}\text{O}^{18}\text{O}$ and $^{17}\text{O}^{16}\text{O} + ^{18}\text{O}$ are observed. Furthermore, for the large-amplitude vibrational motion, the third dissociation channel, which gives $^{17}\text{O}^{18}\text{O} + ^{16}\text{O}$, is also relevant as well as two ozone isomers (or isotopomers), $^{16}\text{O}^{17}\text{O}^{18}\text{O}$ and $^{16}\text{O}^{18}\text{O}^{17}\text{O}$, with isotopically substituted central atoms. The global potential energy function of O_3 describes all of these features (three wells connected to three dissociation channels through six transition states), and the question of its visualization is not a trivial one. This problem is emphasized here. A more detailed description of hyperspherical coordinates can be found elsewhere.^{12–15}

Figure 3 illustrates the potential energy function of ozone molecule^{10,16,17} using the hyperspherical coordinates, $V(\rho, \theta, \varphi)$,^{12–15} and the isoenergy approach introduced in the

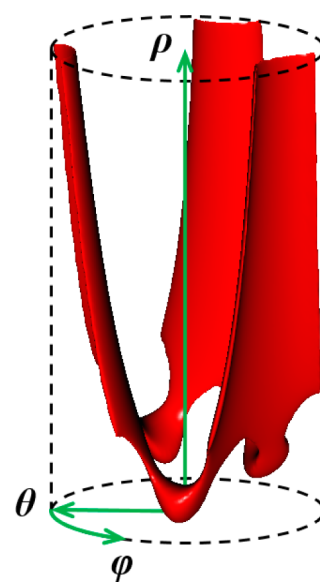


Figure 3. Global view of the isoenergy surface for $\text{O}_3 \rightarrow \text{O}_2 + \text{O}$. Hyperspherical coordinates are used. V_{max} is chosen at the quantum dissociation threshold of O_3 , which allows the dissociation channels to be seen. The range is $\rho < 15 a_0$.

previous section. The coordinates are assigned in a cylindrical-style, with hyper-radius ρ plotted along z and hyperangles θ and φ plotted in the (x, y) plane as shown in Figure 3. We can see that in the range of small ρ , the potential energy function exhibits three lobes that correspond to three possible isomers of O_3 . At large values of ρ , we see three tunnels that describe three possible channels of dissociation to $\text{O}_2 + \text{O}$. The six bottlenecks (transition states) in the intermediate range of ρ interconnect all of these features into a single volume structure in 3D. Thus, the overall structure is rather complex, which makes a good case for 3D printing (discussed in the next section). Clearly, a plane figure cannot express all aspects of this object.

By analyzing Figure 3, it helps to keep in mind that hyper-radius ρ reflects the overall size of a triatomic system, while hyper-angles θ and φ determine its shape. For a triatomic molecule, for example, O_3 , the low-amplitude vibrational motion along ρ , θ , and φ corresponds to three familiar normal modes: symmetric-stretching, bending, and asymmetric-stretching, respectively. At the same time, the large-amplitude motion along φ leads to isomerization (permutation of O atoms within O_3), while the large-amplitude motion along ρ leads to dissociation of O_3 onto $\text{O}_2 + \text{O}$. As for numerical values of hyperspherical variables, it is useful to remember that $\theta = 0^\circ$ corresponds to equilateral triangle configurations, and $\theta = 90^\circ$ corresponds to collinear geometries; all isosceles triangle configurations are described by $\varphi = 0^\circ, 60^\circ, 120^\circ$, etc. For example, in Figure 3, the three equivalent minima are at $\rho = 4.05 \text{ Bohr}$, $\theta = 51.3^\circ$, and $\varphi = 60^\circ, 180^\circ$, and 300° . Three dissociation channels lead to $\rho \rightarrow \infty$, $\theta \rightarrow 90^\circ$, and $\varphi \rightarrow 0^\circ, 120^\circ$, and 240° . The six bottlenecks (transition states) are at $\rho = 5.63 \text{ Bohr}$, $\theta = 68.8^\circ$, and $\varphi = \pm 26^\circ, 120^\circ \pm 26^\circ$, and $240^\circ \pm 26^\circ$. The reader is encouraged to try our desktop application,¹⁴ written with a goal of facilitating the understanding of connection between the APH coordinates and molecular geometry.

We stress one more time that no degrees of freedom are frozen or relaxed here. The surface is available for inspection in its full dimensionality. The only restriction is V_{max} , but every

chemical problem has some characteristic physical energy limit, so this cannot be regarded as a disadvantage. Quite opposite, this is an advantage that allows one to focus on chemically important parts of the potential energy function. For example, in Figures 1–3, the value of V_{\max} is chosen at quantum dissociation threshold of ozone that corresponds to $\text{O}_3 \rightarrow \text{O}_2(\nu = 0) + \text{O}$ limit. This is equal to vibrational zero-point energy of O_2 , which is set to 787.380 cm^{-1} .¹⁸

3D PRINTING

With inexpensive 3D prototyping (or additive manufacturing), it is possible to create a plastic model of the potential energy function. The 3D printing of a 2D potential energy surface was proposed by Lolur and Dawes.¹⁹ For O_3 , they fixed the diatomic bond distance R_1 and printed a 2D function $V(R_2, \alpha)$ represented in a usual way, by a surface. We combined our isoenergy approach with 3D printing.

We wrote a Matlab²⁰ script to generate a stereolithography (STL) file ready to feed to a 3D printer. The script itself is rather short, about 20 lines, because there are free external functions available that make all the hard work automatic. Input for this script is a 1D potential energy data array of real numbers of the length $L \times M \times N$. Other inputs include the values of L , M , and N ; the value of V_{\max} ; and the names of input and output files. The script and examples of input and output files are provided in the Supporting Information.

When this script is executed, the input array is first transformed by the “reshape” function into a 3D grid of dimensions $L \times M \times N$. Next, a Matlab subroutine “isosurface” creates a triangulated surface by interpolation. After that, the routine “smoothpatch” is called to make the isosurface even smoother. Finally, the routine “stlwrite” writes the triangulated mesh (see Figure 4) to the STL file. All of the third-party functions, the stlwrite, smoothpatch, etc., are available on MathWorks website.

The resultant plastic model of 3D potential energy function of ozone is shown in Figure 5. It looks identical to the computer model of Figure 3, except for the color. Unfortunately, the 3D printing facility at Marquette University had only one color available, white. The actual size of the plastic model is $2 \times 2 \times 4$ in. The cost of a model of this size was initially estimated at \$80; however, since very little time and material were actually spent, we were not charged anything. This is because such a model contains a lot of empty space and little occupied space due to V_{\max} .

TEACHING INTERATOMIC INTERACTIONS AND REACTION DYNAMICS USING 3D-PRINTED ISOENERGY MODEL

The plastic model of isosurface makes it straightforward to discuss various features of a complicated potential energy function (e.g., the one for ozone molecule) since all of them can be seen at the same time. For example, in Figure 5, one can easily discern a compact deep covalent well, a narrow transition state region, and a dissociation channel. A wide and shallow van der Waals interaction region is also indicated. Furthermore, the clear connection between these features allows easy visualization of many molecular processes. For example, one can talk about the ozone formation reaction, in which the reactant $\text{O} + \text{O}_2$ enter through one of the channels, pass through the van der Waals region where the intermediate species $\text{O} \cdots \text{O}_2$ are formed,²¹ and then through the transition state, and end up

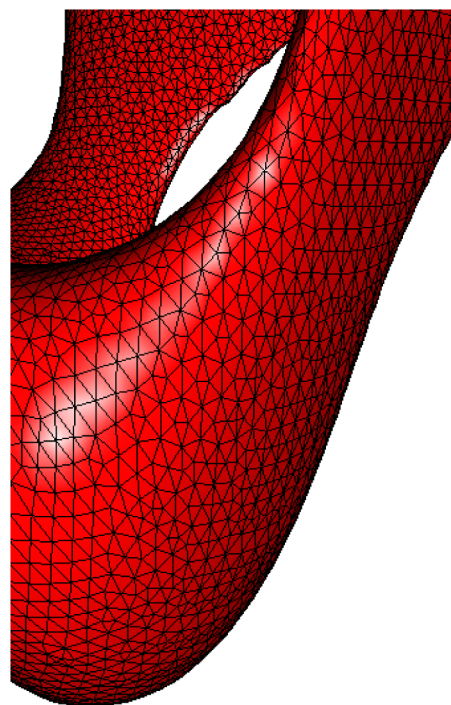


Figure 4. Triangulated mesh representing ozone isoenergy surface (the covalent well and the transition state region).

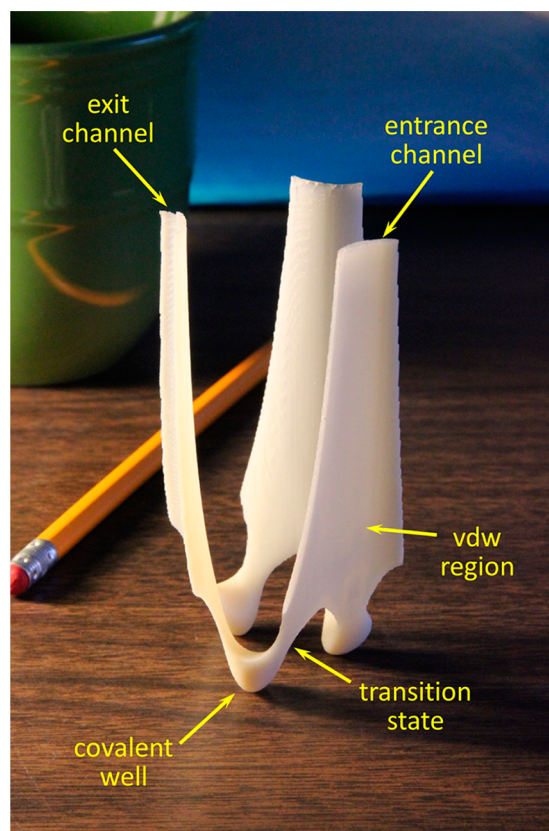


Figure 5. Photo of the prototyped potential energy function of ozone on a desktop. Chemically important features are subscribed for clarity.

in one of the covalent wells (see Figure 5), which correspond to formation of stable O_3 . Or, one can talk about the atom-exchange process, in which the reagent $\text{O} + \text{O}_2$ enter through one of the channels, passes through all the features discussed

above, and exits in the other product channel (leading to $A + BC \rightarrow AB + C$). Also, in the case of ozone, the plastic model emphasizes permutation symmetry of the potential energy function: one can see the presence of three energetically equivalent covalent wells, different only by atom permutations (ABC, BCA, and CAB), and three dissociation channels ($A + BC$, $B + CA$, and $C + AB$). Even such intricate processes as pseudorotational motion are easily represented by the plastic model. During pseudorotation in O_3 , the system moves from one covalent well to the next and the next, passing through transition states and the van der Waals regions between them.

The instructor can bring such plastic model (or models for several molecules) to the class and hand it out to students to take closer look during the discussion of potential energy functions, for example, the discussion outlined in the previous paragraph. This can be done simultaneously with projection of the 3D computer model of the structure on a screen. Even in the research we do on the ozone molecule,^{4,21,22} we found it very useful to have a plastic model on the desktop. It showed to be handy in optimizing a process of grid generation for numerical representation of vibrational wave functions and computing the action of Hamiltonian operator on such wave functions.

CONCLUSION

Our approach to visualize the potential energy function is quite different from the commonly used, which offers additional opportunities in teaching and research. It makes use of the computer graphics and 3D prototyping and reaches the purpose of visualizing all features of the potential energy function for triatomic molecules in full dimensionality, without freezing or relaxing any degrees of freedom. This is achieved by employing the isoenergy approach. Here, we considered the ozone molecule, but our approach is general and can be used to visualize any potential energy function. Our MATLAB code, available through the Supporting Information, can be used by students and postdocs to produce a plastic isoenergy model of the potential energy function they develop. Application to any triatomic molecule is straightforward, and we plan to prototype the potential energy functions of SO_2 and S_3 .

ASSOCIATED CONTENT

Supporting Information

Matlab script to generate a STL file; input and output files for the grid $128 \times 128 \times 128$. This material is available via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: dmitri.babikov@mu.edu.

Notes

The authors declare no competing financial interest.

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