A General Strategy for Determining Atom Connecting Positions

Sky(Yixiang) Zhang, Hai Xiao, and Jun Li

Department of Chemistry, Tsinghua University, Beijing, 100084, P.R. China

E-mail: haixiao@tsinghua.edu.cn; junli@tsinghua.edu.cn

Abstract

The construction of images used in chain-of-state(CoS) methods for transition state(TS) locating and minimum energy path(MEP) searching needs initial and final state prepared in advance. However, while exploring a chemical reaction with CoS methods, the final state is generally unknown and constructed with human feeling and experience, which is low efficient and time wasting. We purpose here a new concept called atom connecting position(ACP) which correlates with final state construction. And a general method is presented for determining ACPs based on spherical optimization and VSEPR theory without manual interfering. Several examples are testified to prove the validity and robustness of the method, while regular VSEPR model suiting may fail under these circumstances.

1 INTRODUCTION

Initial and final state should be prepared before doing transition state(TS) locating and minimum energy path(MEP) searching using chain-of-state(CoS) methods like nudge elastic band(NEB) method. Generally speaking, with a chemical reaction described in the MEP,
the initial state is obtainable, whereas the final state is usually unknown and should be constructed artificially. Since there could be bond reforming and atom transfer in MEP, determining suitable positions for the transferred atom to be positioned is really important for final state construction. These positions are referred to as atom connecting positions (ACPs). However, determination of these positions needs chemical insight and manual intervention, because these positions correlate with geometry structure as well as electronic structure.

Using valence shell electron pair repulsion (VSEPR) shape model is a good start, since the ACPs determined by chemical insight are generally based on the repulsion of connected atoms (and lone pairs). But using of VSEPR shape model directly is not only hard and tedious, but also would fail under some situations. Firstly, VSEPR shape model can only be used when the transferred atom connect to another atom, but it could also connect with multiple atoms, like Fe atom connecting to 6 carbons on C$_{60}$ and Carbon Nanotube. Exception would also happen when the atoms are not chemically connected, like metal surface and Au$_{20}$ cluster, in which atoms are packing together. Choosing connected atoms is tricky since it’s difficult to classify two atoms to be connected or not when they are weakly connected.

Besides, there are almost 18 different kinds of VSEPR shape models and variations. Suiting the connected atoms and lone pairs to the specific shape like Linear, Trigonal, Tetrahedral or Octahedral is not easy, either, especially when there exists distortion. Even if controlling with a threshold, different thresholds may give out different results, downgrading the robustness of the method. Therefore, we need to purpose a general and robust method for determining ACPs connecting with not only specific atom as a center, but a virtual center like the center of a benzene ring. This center is referred as kernel because it may not be the position of specific atom.

Tracing back the beginning of VSEPR and rethinking the motivation, we found that the main idea of VSEPR is to find out the low-repulsion positions around the kernel. Actually, we
believe the ACPs are actually these low-repulsion positions. This leads us to a constrained optimization problem. To optimize the positions locating on the spherical surface centered at the kernel and sample all possible positions, we may get all ACPs satisfy the necessity. By introducing spherical optimization(SOPT) method,\textsuperscript{8} we formulated the framework of VSEPR-SOPT, which turns the chemical insight into a robust and efficient algorithm.

2 METHODS

2.1 Spherical Optimization

The detail of spherical optimization(SOPT) has been described by Abashkin, Y. and Russo, N.,\textsuperscript{8} so we will introduce it briefly. Considering two atom system with \( N \) atoms and noted as \( x \) and \( y \) with root-mean-square deviation of distance as \( R \), the constrained optimization problem is described as

\[
\min_{\vec{x}} E = E(x_1, x_2, ..., x_n) \\
\text{s.t.} \quad (x_1 - y_1)^2 + (x_2 - y_2)^2 + ... + (x_n - y_n)^2 = R^2
\]  

(1)

where \( n = 3N \) is the total degrees of freedom. \( x \) and \( y \) are also named as target and anchor, since \( x \) will be optimized and \( y \) is fixed during the optimization. The energy function is rewritten by including the constraint and eliminate \( x_n \),

\[
E' = E(x_1, x_2, ..., x_{n-1}, f(x_1, x_2, ..., x_{n-1}, R))
\]  

(2)

and the force is rewritten as
\[ F'_i = -\frac{\partial E'}{\partial x_i} = -\left( \frac{\partial E}{\partial x_i} + \frac{\partial E}{\partial x_n} \frac{\partial x_n}{\partial x_i} \right) = F_i - F_n \frac{x_i - y_i}{x_n - y_n} \] (3)

where \( F \) is the force obtained from electronic structure calculation, and \( F' \) is a \( n - 1 \) vector. Thus, we convert this particular constrained optimization with \( n \) variables to a regular optimization problem with \( n - 1 \) variables. More details of the algorithm are neglected and can be found elsewhere.

### 2.2 VSEPR-SOPT Model

Combining SOPT with VSEPR is tricky, since the target and anchor used in SOPT are not real system, and the energy function remains unknown.

Firstly, let’s consider locating one ACP on the sphere centered at kernel. Locating multiple ones can be regarded as locating ACP one after another. Positions on the sphere centered at kernel with radius \( R = L \) is the collection of possible positions. Here \( L \) is the length between kernel and the position on the sphere, which is given by user or get from database. So the target system is constructed with a pseudo atom positioned on the sphere, and the anchor system contains only the position of kernel.

The energy of the system is hard to determine since the system is not real, and the formula of VSEPR repulsion is unknown. Besides, we expect the calculation to be as fast as possible without introducing too much parameters. Considering the formula is to describe repulsion and inspired by Lennard-Jones potential, we believe the repulsion energy between a pair of atoms can be described as \( \frac{1}{r^n} \). It turned out \( n = 4 \) will give out the best results. For molecular system, the energy function would be
\[
E(\vec{x}) = \sum_{l=1}^{N} \frac{1}{|\vec{r}_i - \vec{x}|^4}
\]  

(4)

where \( N \) is the total number of atoms in real system, \( \vec{x} \) is the position of pseudo atom and \( \vec{r}_i \) is the position of \( i^{th} \) atom in real system. Noted that no external parameter is introduced in the function, which seems weird. But the results turned to be good enough.

For periodic system, the contribution of replicas should be counted. Therefore, another 8 neighbor cells are counted. The energy function is

\[
E(\vec{x}) = \frac{1}{N} \sum_{i,j,k} \sum_{l=1}^{N} \frac{1}{|\vec{r}_l + i\vec{a} + j\vec{b} + k\vec{c} - \vec{x}|^4}
\]  

(5)

where \( \vec{a}, \vec{b}, \vec{c} \) are unit vectors of the cell. With the formula of energy function, SOPT now is able to be utilized for finding ACPs.

For \( M \) ACPs, we just need to make the target system contains \( M \) pseudo atoms, and duplicate kernel \( M \) times in anchor system, adjust the radius of the sphere \( R = L\sqrt{M} \). Interactions between pseudo atoms should be added to the energy function

\[
E(\vec{x}_1, \vec{x}_2, ..., \vec{x}_M) = \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{1}{|\vec{r}_i - \vec{x}_j|^4} + \sum_{i,j=1,i\neq j}^{M} \frac{1}{|\vec{x}_i - \vec{x}_j|^4}
\]  

(6)

The rest part is the same. And for periodic system, the formula will be modified as stated above. Since the simplicity of the procedure, the execution of the algorithm is really fast. The time is estimated to be less than 1s for 100 optimizations in Python code.
2.3 Position Sampling on Spherical Surface

In order to acquire all possible ACPs on the sphere, we need to sample all positions on the sphere and run VSEPR-SOPT one by one. Therefore, a sampling algorithm should be introduced. Using polar coordinate system and sampling $\theta$ and $\phi$ uniformly is simple and convenient, but the sampling density around the pole is much higher than that around the equator. However, a uniform sampling on the spherical surface is expected. Here we use one of the methods introduced by Cory Simon.\footnote{Cory Simon} By generating three standard normally distributed numbers $X$, $Y$, $Z$ to form a vector $V = [X,Y,Z]$ and normalize it, the vector is uniformly distributed on the surface of sphere. Normally, sampling 100 times is adequate for covering the entire surface, but it can be increased if necessary.

2.4 Flowchart of VSEPR-SOPT

We provide the flowchart for the algorithm of VSEPR-SOPT below,

1. Input the system, kernel position, number of lone-pairs ($N_l$) and number of ACPs needed ($N_n$).
2. Add a pseudo atom to the system and construct energy function.
3. Sampling on the sphere $N_s$ times with the algorithm described above, optimize the pseudo atoms system with the potential described in Eq.6 with SOPT.
4. Repeat step 2-3 $N_l$ times to get all positions of lone-pairs.
5. Repeat step 2-3 $N_n$ times to get all ACPs needed with lone-pairs positions fixed.

3 RESULTS

Here we use the notation A@B to refer to the system A with B as the kernel, e.g. CH$_2$O@C means molecular system CH$_2$O, and the carbon is the kernel. It worth mentioning that the
center of a ring can be kernel as well. The kernel will be noted as circle in these situations. In the following, we tested several kinds of system, including small molecules (CH$_4$, CH$_2$O), clusters (Au$_{20}$, C$_{60}$), complicated molecular system (complicated Au$_6$ cluster) and heterogeneous system (CeO$_2$-based single atom catalyst (SAC)). In the related figures, ACPs are labeled with pseudo atoms in violet, and only kernel (or kernel related) atoms and pseudo atoms are in ball-stick format and other atoms are in line format. The B3LYP functional with default parameters in Gaussian 09 are used in all DFT calculations and geometry optimization if not specified. 6-31G(d) basis sets are used for C, O, H and LANL2DZ are used for Au, Fe.

3.1 CH$_4$ and CH$_2$O System

VSEPR-SOPT results of CH$_4$@C, CH$_4$@H are shown in Fig.1a and 1b. For CH$_4$@C, all 4 face centers of the tetrahedral are acquired, and for CH$_4$@H, linear shape is implied and the other end is acquired as ACP. Results of CH$_2$O@C, CH$_2$O@O are shown in Fig.2a and 2b. For CH$_2$O@C, a trigonal bipyramidal is displayed and the positions off the CH$_2$ plane are acquired. However, for CH$_2$O@O, the lone-pairs’ positions acquired violates the chemical rule, since we expect the lone-pairs to be in the plane of CH$_2$O, but the positions given by VSEPR-SOPT are off the plane. This is due to the free sampling of the spherical surface and the absence of electronic structure. But the result is still acceptable. The results shown here satisfy chemical insights in general, and the weakness is endurable.

3.2 Au$_{20}$ Cluster System

Au$_{20}$ cluster has 3 kinds of Au: Au along the edges (Au$_e$), Au at the apexes (Au$_a$) and Au at the center of each face (Au$_c$). ACP for Au$_{20}$ with each kind of Au atom acquired by VSEPR-SOPT are shown in Fig.3a-3c. For each kind of Au atom, only one position is identified as
ACP. To show the correctness of the result, we further testified geometry structure of CO absorbed on Au$_{20}$ with DFT calculation, as shown in Fig. 4a-4c. The results given by DFT match the VSEPR-SOPT results astonishingly.

However, suiting these kinds of Au atom with regular VSEPR shape model is hard or even impossible, since these Au atoms are not connecting with chemical bonds but packing together. It’s really difficult to determining the VSEPR shape for these Au atoms. For a Au$_a$ atom, 3 Au atoms are coordinated, while the angles are only 60° instead of 120° to suit a Triangle model or 90° to suit a Octahedral model. For a Au$_c$ atom, 6 Au atoms are coordinated in a strange shape which doesn’t belong to any VSEPR model. And Au$_c$ atom is coordinated with 9 Au atoms, which is far beyond the range of VSEPR shape model. This may cause failure for regular VSEPR model, whereas the result given by VSEPR-SOPT match our chemical insight and the reality remarkably.
3.3 \textit{C}_{60} \text{ and Carbon Nanotube}(CNT) \text{ System}

For \textit{C}_{60} \text{ and CNT}, all carbon atoms are equivalent, but the ACPs can be inside or outside the cage/tube. In these cases, center of a carbon circle can also be kernel, and these circles are equivalent as well. So we use both carbon and the center of circle to be the kernel. Using VSEPR-SOPT, we can identify the ACPs on \textit{C}_{60} easily, as shown in Fig.5a and 5b. TiC\textit{C}_{60} presented Sun, Qiang, et al.\cite{11} is optimized with PAW method implemented in VASP. The result shown in Fig.5c agrees with the circle kernel situation very well.

As for CNT, the same setups are executed. The VSEPR-SOPT results with carbon and circle as kernel are shown in Fig.6a and 6b. Fe-CNT system is optimized by DFT and presented in Fig.6c. DFT result shows that Fe is just above the center of the carbon circle, as what we acquired with VSEPR-SOPT.

For \textit{C}_{60} system and CNT system, ACPs acquired by VSEPR-SOPT are not only chemically meaningful, but also satisfy the DFT calculation results. Whereas for regular VSEPR shape model suiting, it would be really hard since the kernel here is not an individual atom but the center of a circle. The geometry optimization procedure may cost more comparing with
VSEPR-SOPT we presented here.

![Figure 5: C₆₀ system](image)

(a) C₆₀ @C  
(b) C₆₀ @circle  
(c) TiC₆₀

3.4 Complicated Au₆ Cluster

Au₆ cluster is a very large cluster system, which contains 6 equivalent Au atom, 6 P atom, 2 N atom and 20 phenyl groups(Fig.7). Environment of the Au atom is very complicated. One Au atom is not only connecting with one N and P, but connecting with other Au atoms weakly, the phenyl groups around the atom have influence as well. Therefore, it’s impossible to determine the VSEPR shape of Au atom. However, with the help of VSEPR-SOPT, acquiring the ACPs is really easy, as shown in Fig.8. Noted that the VSEPR-SOPT does not need the connection relationship at all, which is critical for regular VSEPR shape model. This example proves the robustness of the method.
Figure 7: Au₆ cluster

Figure 8: Au₆ cluster@Au by VSEPR-SOPT
3.5 CeO$_2$-based Single Atom Catalyst

CeO$_2$-based single atom catalyst could be used as heterogeneous catalysis, like CO$_2$ reduction and CO oxidation. Au$_1$/CeO$_2$ has been reported and the geometry optimizations are implemented with VASP, as shown in Fig.9. CO can be regarded as ACP detector in this example. It’s worth mentioning that this system is a periodic system. So the energy formula of periodic system should be used. The VSEPR-SOPT result is shown in Fig.10. And the ACP acquired agrees well with the position of carbon mentioned in the article. This example shows the validity of our method in heterogeneous systems.

Figure 9: Au$_1$/CeO$_2$-CO

Figure 10: Au$_1$/CeO$_2$ ACPs
4 SUMMARY AND DISCUSSION

In this article, we purposed a general method for locating atom connecting positions (ACPs) of a system with kernel, where the kernel can be atom or the center of a ring. The basic idea is to generalize VSEPR model to a constrained geometry optimization problem. With the help of spherical optimization (SOPT), the chosen energy function and sampling method, all ACPs are acquirable and satisfy chemical insight basically. Several typical systems are testified, like small molecules (CH$_4$, CH$_2$O), simple clusters (Au$_{20}$, C$_{60}$), complicated molecular system (complicated Au$_6$ cluster) and heterogeneous system (Au$_1$/CeO$_2$ single atom catalyst). In all systems except CH$_2$O@O, chemical insight is satisfied rigorously, while for CH$_2$O@O, chemical insight is partially satisfied as well and the result is acceptable. These examples demonstrate the validity and robustness of the method. And the method can be useful in reaction searching and reaction network construction.

Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 21590792, 91426302, and 2143005) to J.L. and the Thousand Talents Plan for Young Scholars to H.X. The calculations were performed using the supercomputers at the Computational Chemistry Laboratory of Department of Chemistry under Tsinghua Xuetang Talents Program. We thank Biao Yang from Tsinghua University for providing the structure of Au$_6$ cluster.

References

(1) Henkelman, G. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *Journal of Chemical Physics* **2000**, *113*,
9978–9985.

(2) JNSSON, H.; MILLS, G.; JACOBSEN, K. W. *Classical and Quantum Dynamics in Condensed Phase Simulations*; pp 385–404.

(3) Sheppard, D.; Xiao, P.; Chemelewski, W.; Johnson, D. D.; Henkelman, G. A generalized solid-state nudged elastic band method. *The Journal of Chemical Physics* 2012, 136, 074103.

(4) Sheppard, D.; Terrell, R.; Henkelman, G. Optimization methods for finding minimum energy paths. *Journal of Chemical Physics* 2008, 128, 385–404.

(5) Sheppard, D.; Henkelman, G. Paths to which the nudged elastic band converges. *Journal of Computational Chemistry* 2011, 32, 1769–1771.

(6) Sheppard, D.; Xiao, P.; Chemelewski, W.; Johnson, D. D.; Henkelman, G. A generalized solid-state nudged elastic band method. *Journal of Chemical Physics* 2012, 136, 385–404.

(7) Mackay, R. A.; Henderson, W. *Introduction to modern inorganic chemistry*; CRC Press, 2017.

(8) Abashkin, Y.; Russo, N. Transition state structures and reaction profiles from constrained optimization procedure. Implementation in the framework of density functional theory. *Journal of Chemical Physics* 1994, 100, 4477–4483.

(9) Simon, C. Generating uniformly distributed numbers on a sphere. Website, 2015; [http://corysimon.github.io/articles/uniformdistn-on-sphere/](http://corysimon.github.io/articles/uniformdistn-on-sphere/).

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.;
Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox”, D. J. Gaussian 09 Revision E.01. Gaussian Inc. Wallingford CT 2009.

(11) Sun, Q.; Wang, Q.; Jena, P.; Kawazoe, Y. Clustering of Ti on a C60 surface and its effect on hydrogen storage. *Journal of the American Chemical Society* **2005**, *127*, 14582–14583.

(12) He, X.; Wang, Y.; Jiang, H.; Zhao, L. Structurally Well-Defined Sigmoidal Gold Clusters: Probing the Correlation between Metal Atom Arrangement and Chiroptical Response. *Journal of the American Chemical Society* **2016**, *138*, 5634–5643, PMID: 27070415.

(13) Liu, J.-C.; Wang, Y.-G.; Li, J. Toward Rational Design of Oxide-Supported Single-Atom Catalysts: Atomic Dispersion of Gold on Ceria. *Journal of the American Chemical Society* **2017**, *139*, 6190–6199, PMID: 28406020.