拓扑化学行为及其对镧系元素和锕系元素的 QSPR 应用

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摘要:提出拓扑化学行为概念,把对化合物性质最具影响力的因素归纳为拓扑生长力和拓扑阻滞力。根据该原理,利用价电子轨道能量对价电子距离矩阵进行修正。研究表明 OET(轨道能量拓扑指数)对镧系元素和锕系元素的物理化学性质具有良好的应用,尤其是对尚未借助 QSPR(定量结构性质关系)手段进行研究的光谱性质。LOO CV(留一法交叉检验)的结果验证了模型的良好稳定性和预测能力,采用的检验参数有:PRESS/SSY,SEP_{CV},R_{CV},S_{PRESS} 和 PSE,其中 PRESS/SSY 比值介于 0.000 6 和 0.114 8 之间。与文献进行比较,本文方法所得结果与之接近或更好。研究显示正是基于拓扑化学行为才有本文方法良好和较广的应用。

关键词:拓扑化学行为;价电子;QSPR;镧系元素;锕系元素
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Chemical Behavior of Topology and Its Application to QSPR of Lanthanide and Actinide

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Abstract: We introduce the chemical behavior of topology for the first time which consists of the topological growing power and the topological blocking power. On the basis of the principle, the OET (orbital-energy topological index) was proposed by revising the valence electron distance matrix with the orbital energy. The results demonstrate that OET has good application to the physicochemical properties of lanthanide and actinide, especially to the spectral properties which have not been reported by means of QSPR (quantitative structure-property relationships). The results of LOO CV (leave-one-out cross-validation) verify the good stability and predictive ability of the models using the cross-validation parameters: PRESS/SSY, SEP_{CV}, R_{CV}, S_{PRESS} and PSE with the PRESS/SSY ratio ranging between 0.000 6 and 0.114 8. Compared with the other methods, this work provides an easier way yielding results close to or better than the others. It is on the basis of the chemical behavior of topology that leads to the good and wide application of this method.

Key words: chemical behavior of topology; valence electron; QSPR; lanthanide; actinide

Since the birth of the first topological index W proposed by Wiener in 1947 [1], lots of attention have been focused on topological indexes, which are graph theoretical descriptors obtained by transforming molecular structures into the corresponding molecular graphs[2-4]. Nowadays the third generation of topological

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index has been regarded as vertex invariant expressed by real number[5]. Generally, topological indexes have played important roles in organic compounds. In contrast, the application to inorganic substances has received less attention, especially to actinide.

It is of practical importance to study QSPR for lanthanide and actinide due to their radioactivity and the absence of property data. Some researchers carried out studies of lanthanide with the help of topological indexes. For example, Wu et al.[6] developed the H_E index defined as: $H_E=1/[(1+R)S^{1/2}]$, where R is the ionic radius and S is the number of valence electrons. Feng[7] suggested the At index based on the Randic index: $^1At=\sum (E_i \times E_j)^{-0.5}$, where $E_{i(j)}=n+0.7l$. Others also studied QSPR for lanthanide[8,9]. However, to our knowledge, no one has studied QSPR for actinide. In the present study, we have been in attempts to find the inherent regularities of properties of lanthanide and actinide from the aspect of the chemical behavior of topology.

Our previous work[10~14], including successful proposition of some topological indexes, such as the ND index[12], the AEI index[13] and the QTI index[14], has considerably contributed to the proposition of the chemical behavior of topology. We deem that the topological behavior of chemistry can be divided into two aspects, which are the topological growing power and the topological blocking power. On the basis of the chemical behavior of topology encoding the inherent information of atomic structure, we proposed the novel OET index employing the orbital energy by revising the valence electron distance matrix, which has showed wide and good applications in actinide and lanthanide.

1 Principle

We consider that the properties of atoms, to a great extent, are determined by the state of valence electrons. Meanwhile the state is mainly influenced by the number and the orbital energy of the valence electrons. Therefore, the OET index can characterize such structure information because of its extending distance matrix with the orbital energy of the valence electrons.

Let $G=\{V, E\}$ be a nuclear-suppressed graph with n vertices of valence electrons, where $V(G)$ and $E(G)$ are the vertex set and edge set, respectively. $V(G)$ represents the valence electrons in a graph G, and $E(G)$ corresponds to the interactions between the valence electrons. The distance matrix DM[15] with $n \times n$ valence electrons, which is a square symmetric matrix, can be given as: $DM=[d_{ij}]_{n\times n}$, where the entries d_{ij} are the length of the shortest path between the vertices, i.e., the valence electrons in a graph G. Then the revised matrix DM_{rev} can be obtained by adding the EO_i (the orbital energy of valence electrons) values into the main diagonal of DM.

The new topological index OET is defined as the following:

$$OET=\lg\lambda_{max} \quad (1)$$

Where λ_{max} is the maximum eigenvalue of DM_{rev}. For example, the valence electron state of Nd is $4f^4(6)6s^2(5.49)$[16]. According to the method introduced above, the nuclear-suppressed graph and the extended matrix DM_{rev} of Nd can be given as the following:

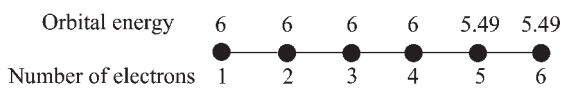


Fig.1 Description of valence electron state of Nd

$$DM_{rev}=\begin{bmatrix} EO_1 & L_{12} & L_{12}+L_{23} & L_{12}+L_{23}+L_{34} & L_{12}+L_{23}+L_{34}+L_{45} & L_{12}+L_{23}+L_{34}+L_{45}+L_{56} \\ L_{12} & EO_2 & L_{23} & L_{23}+L_{34} & L_{23}+L_{34}+L_{45} & L_{23}+L_{34}+L_{45}+L_{56} \\ L_{12}+L_{23} & L_{23} & EO_3 & L_{34} & L_{34}+L_{45} & L_{34}+L_{45}+L_{56} \\ L_{12}+L_{23}+L_{34} & L_{23}+L_{34} & L_{23}+L_{34} & EO_3 & L_{45} & L_{45}+L_{56} \\ L_{12}+L_{23}+L_{34}+L_{45} & L_{23}+L_{34}+L_{45} & L_{34}+L_{45} & L_{45} & EO_5 & L_{56} \\ L_{12}+L_{23}+L_{34}+L_{45}+L_{56} & L_{23}+L_{34}+L_{45}+L_{56} & L_{34}+L_{45}+L_{56} & L_{45}+L_{56} & L_{56} & EO_6 \end{bmatrix}$$

$$=\begin{bmatrix} 6.00 & 1 & 2 & 3 & 4 & 5 \\ 1 & 6.00 & 1 & 2 & 3 & 4 \\ 2 & 1 & 6.00 & 1 & 2 & 3 \\ 3 & 2 & 1 & 6.00 & 1 & 2 \\ 4 & 3 & 2 & 1 & 5.49 & 1 \\ 5 & 4 & 3 & 2 & 1 & 5.49 \end{bmatrix}$$

Consequently, the OET index of Nd equals to lg17.912 3, that is 1.253 2. The OET indexes of lanthanide and actinide are listed in Table 1. Due to the unavailable data of the orbital energy of Md, No and Lr, the OET values of 12 actinides were computed. The OET indexes were calculated in Matlab 7.0 (Math Work). For statistical and graph analyses, they were implemented with the help of Excel (Microsoft Corp.), SPSS13.0 (SPSS, Inc.) and Origin7.0 (OriginLab.).

Table 1　Orbital and energy and OET indexes of lanthanide and actinide

No.	Element	Orbital and energy / eV	OET	No.	Element	Orbital and energy / eV	OET
1	La	$5d^1(5.75)6s^2(5.58)$	0.92 51	15	Lu	$4f^{14}(12)5d^1(6.6)6s^2(7)$	2.044 2
2	Ce	$4f^1(6)5d^1(6)6s^2(5.47)$	1.037 7	16	Ac	$6d^1(5.17)7s^2(6.30)$	0.937 1
3	Pr	$4f^3(6)6s^2(5.42)$	1.147 4	17	Th	$6d^2(6.08)7s^2(6.10)$	1.051 2
4	Nd	$4f^4(6)6s^2(5.49)$	1.253 2	18	Pa	$5f^2(6)6d^1(5.89)7s^2(6)$	1.154 6
5	Pm	$4f^5(6)6s^2(5.55)$	1.351 5	19	U	$5f^3(6)6d^1(6.05)7s^2(6.1)$	1.259 0
6	Sm	$4f^6(6)6s^2(5.63)$	1.442 7	20	Np	$5f^4(6)6d^1(6.0)7s^2(6.2)$	1.356 0
7	Eu	$4f^7(6)6s^2(5.67)$	1.526 9	21	Pu	$5f^6(6.0)7s^2(6.06)$	1.444 9
8	Gd	$4f^7(6)5d^1(6)6s^2(6.14)$	1.606 2	22	Am	$5f^7(6.0)7s^2(5.99)$	1.528 1
9	Tb	$4f^9(6)6s^2(5.85)$	1.677 6	23	Cm	$5f^7(11)6d^1(6)7s^2(6.2)$	1.640 2
10	Dy	$4f^{10}(6)6s^2(5.93)$	1.745 2	24	Bk	$5f^9(12)7s^2(6.23)$	1.717 9
11	Ho	$4f^{11}(6)6s^2(6.02)$	1.808 3	25	Cf	$5f^{10}(9)7s^2(6.30)$	1.763 3
12	Er	$4f^{12}(6)6s^2(6.10)$	1.867 6	26	Es	$5f^{11}(9)7s^2(6.42)$	1.824 3
13	Tm	$4f^{13}(7)6s^2(6.18)$	1.923 3	27	Fm	$5f^{12}(15)7s^2(6.50)$	1.908 3
14	Yb	$4f^{14}(7)6s^2(6.25)$	1.979 5				

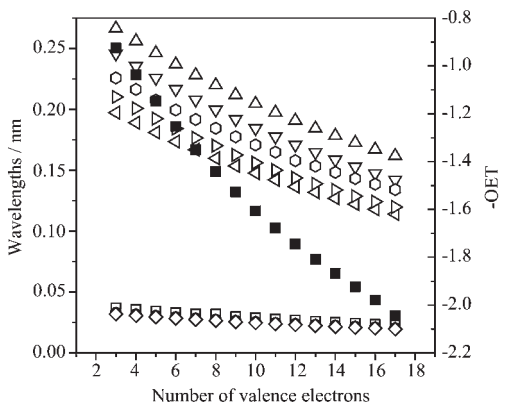
2　Results and discussion

2.1　Relationships between OET and properties of lanthanide

To our knowledge, no study on the property of X-ray spectra of lanthanide has been reported using topological index. It is important to investigate the properties of them due to the radioactivity. As a starting point, we tested the performance of OET with the help of the properties of X-ray spectra of lanthanide, which are the wavelengths of X-ray emission spectra of $K\alpha_1$, $K\beta_1$, $L\alpha_1$, $L\beta_1$ and the wavelengths of X-ray absorption edges of K, L_{I}, L_{II}, L_{III}, respectively[17].

In that properties of atoms are closely correlated with their valence electrons, what is the relationship between them? The answer may lie in Fig.2, which is the plot of the number of valence electrons versus the wavelengths of lanthanide.

From Fig.2, we can see that the wavelengths and the OET index to some extent show the similar regularities. Consequently, we think that the relationship between them may be described as the following:



■, □, ○, △, ▽, ◇, ◁, ▷, ⬡, represent −OET, the wavelengths of X-ray emission spectra of $K\alpha_1$, $K\beta_1$, $L\alpha_1$, $L\beta_1$, and the wavelengths of X-ray absorption edges of K, L_{I}, L_{II}, L_{III}, respectively

Fig.2　Plot of number of valence electrons versus wavelengths and −OET

$$\text{Property}=a\text{OET}+b \quad (2)$$

Where a is the contribution coefficient of the OET index and b is a constant.

One can observe that the models have good applications to the spectral properties of 15 lanthanide

in terms of the statistical results of the models in Table 2: correlation coefficients (R), F values (F), and standard errors (S). Meanwhile, the relationships between the properties and the indexes in the literature are under investigation. Much better results can be obtained in the present paper compared with that of the H_E index[6] and the ^{1}At index[7] for the same data set according to the R values.

Table 2 Statistical results of relationships between OET and properties of lanthanide

No.		a	b	N	F	S	R	R_1[6]	R_2[7]
1	$K\alpha_1$	−0.127 9	0.492 5	15	2 262	0.003 6	0.997 1	0.956 9	0.995 8
2	$K\beta_1$	−0.113 2	0.434 6	15	11 859	0.001 4	0.999 5	0.963 8	0.995 8
3	$L\alpha_1$	−0.941 3	3.546 0	15	20 427	0.008 7	0.999 7	0.965 8	0.995 0
4	$L\beta_1$	−0.931 1	3.330 8	15	20 038	0.008 7	0.999 7	0.963 8	0.995 8
5	K	−0.110 3	0.422 3	15	12 448	0.001 3	0.999 5	0.963 8	0.995 8
6	L_{I}	−0.751 3	2.675 9	15	26 131	0.006 1	0.999 8	0.966 7	0.994 6
7	L_{II}	−0.814 2	2.862 1	15	24 929	0.006 8	0.999 7	0.967 1	0.994 3
8	L_{III}	−0.825 9	3.028 1	15	28 914	0.006 4	0.999 8	0.967 5	0.994 1

Besides the s pectral properties, OET has been proved to have good applications to the other properties of lanthanide, which are the cumulative formation constant of $Ln(TAA)_3$ with HTTA in CCl_4 ($\lg K_1$)[18], the stability constant of coordination with NTA ($\lg K_2$)[19], the stability constant of coordination with 1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid ($\lg K_3$)[19], the stability constant of coordination with EDTA ($\lg K_4$)[8], the hydration energy (ΔQ)[19], the standard electrode potential of Ln^{3+}/Ln ($-\varphi_+^{\ominus}$)[20], the standard electrode potential of $Ln(OH)_3$/Ln ($-\varphi^{\ominus}$)[20], the solubility of hydroxide (pK_m)[6], the Pauling electronegativity (X_P)[8], the effective nuclear charge (Z^*)[8], the ionic radius of Ln^{3+} (r_+)[6], the lattice energy of $LnO_{1.5}$ (U)[20], the dissolution enthalpy of anhydrous chloride in water ($-\Delta_f H_1$)[8], the standard enthalpy of formation of sulfate ($-\Delta_f H_2$)[8], the standard free energy of formation of sulfate ($\Delta_f G_1$)[8], and the hydration energy of metal ion Ln^{3+} (ΔH)[6], respectively. Presented in Table 3 are the statistical results of the 16 properties. In terms of the regression results,

Table 3 Statistical results of relationships between OET and properties of lanthanide

No.		a	b	N	F	S	R	R_1[6]	R_2[7]
1	$\lg K_1$	2.912 7	10.109 2	15	1 074	0.117 5	0.994 0	0.975 5	0.985 5
2	$\lg K_2$	1.611 1	9.075 7	14	227	0.139 4	0.974 6	0.956 7	0.973 9
3	$\lg K_3$	4.275 7	12.291 4	14	807	0.196 4	0.992 6	0.954 0	0.994 0
4	$\lg K_4$	3.734 4	11.905 5	15	425	0.239 4	0.985 1	0.930 8	0.995 5
5	ΔQ	92.427 2	723.985 4	15	1 224	3.491 7	0.994 7	0.950 9	0.997 6
6	$-\varphi_+^{\ominus}$	−0.226 7	2.732 6	15	248	0.019 0	0.974 7	0.924 3	0.986 5
7	$-\varphi^{\ominus}$	−0.150 1	3.037 5	15	255	0.012 4	0.975 5	0.924 0	0.987 5
8	pK_m	0.992 6	4.219 0	14	178	0.090 8	0.967 9	0.946 0	0.974 1
9	X_P	0.153 7	0.952 3	15	1 680	0.005 0	0.996 2	0.951 2	0.996 5
10	Z^*	1.884 2	9.118 7	15	831	0.086 4	0.992 3	0.936 4	1.000 0
11	r_+	−18.683 7	123.167 4	15	4 893	0.353 1	0.998 7	0.966 2	0.995 1
12	U	403.074 5	5 870.404 0	14	688	18.774 6	0.991 4	0.955 6	0.993 6
13	$-\Delta_f H_1$	82.538 63	54.883 03	15	291	6.400 7	0.978 4	0.928 7	0.979 1
14	$-\Delta_f H_2$	−114.555	4 304.419 0	13	188	10.454 6	0.972 0	0.918 3	0.986 2
15	$\Delta_f G_1$	−129.106	3 794.890 0	13	235	10.540 5	0.977 4	0.924 0	0.990 3
16	ΔH	319.484 4	3 077.129 0	10	1 191	11.314 0	0.996 7	0.978 4	0.990 5

the OET index is much better than the H_E index, and is close to the ^{1}At index. Compared with the QTI index[14], the OET index is superior in correlating with the spectral properties in Table 2. By contrast, the QTI index performs better on correlating with some physicochemical properties in Table 3. The reason may come from the following: (1) the OET index reveals the structural information of the number of valence electrons and the orbital energy, which encodes the important information of the properties, especially the spectral properties. (2) the QTI index reflects the structural information from the aspects of the main quantum number, azimuthal quantum number, spin quantum number and orbital energy of the valence electrons, which encodes more information despite the time-consuming computation.

2.2 Relationships between OET and properties of actinide

Moreover, to testify the reasonability of the method, the relationships between OET and properties of actinide were developed according to equation (**2**). Models were conducted between OET and the wavelengths of X-ray emission spectra of $K\alpha_1$, $K\beta_1$, $L\alpha_1$, $L\beta_1$[17], the wavelengths of X-ray absorption edges of K, L_I, L_II, L_III[17], the photon energy of $K\alpha_1$, $K\beta_1$, $L\alpha_1$, $L\beta_1$[21], and the excitation energy of K, L_I, L_II, L_III[21] of actinide. The correlation results in Table 4 demonstrate statistical significance of the models with all R over 0.99. In addition, OET has good application to other properties, such as the wavelengths and the excitation energy of $M\,\text{Ⅰ}$, $M\,\text{Ⅱ}$, $M\,\text{Ⅲ}$, $M\,\text{Ⅳ}$, $M\,\text{Ⅴ}$, which further indicates the wide potential of the method proposed in the current study.

Table 4　Statistical results of relationships between OET and properties of actinide

No.		a	b	F	S	R	No.		a	b	F	S	R
1	$K\alpha_1$	−0.034 7	0.169 5	3 830	0.000 6	0.998 7	9	$K\alpha_1$	30.372 5	60.783 5	674	1.234 6	0.992 7
2	$K\beta_1$	−0.030 3	0.149 4	4 000	0.000 5	0.998 8	10	$K\beta_1$	33.977 7	69.177 2	683	1.372 0	0.992 8
3	$L\alpha_1$	−0.229 1	1.197 9	3 982	0.003 8	0.998 7	11	$L\alpha_1$	3.816 1	8.882 0	770	0.145 2	0.993 6
4	$L\beta_1$	−0.226 9	1.004 6	4 306	0.003 7	0.998 8	12	$L\beta_1$	6.203 0	9.539 5	595	0.268 4	0.991 7
5	K	−0.029 3	0.143 8	3 818	0.000 5	0.998 7	13	K	35.535 7	71.549 2	686	1.432 4	0.992 8
6	L_I	−0.179 2	0.794 8	4 560	0.002 8	0.998 9	14	L_I	7.828 7	12.061 1	621	0.331 7	0.992 0
7	L_II	−0.188 7	0.828 9	4 729	0.002 9	0.998 9	15	L_II	7.667 5	11.455 8	611	0.327 5	0.991 9
8	L_III	−0.193 1	0.964 7	4 347	0.003 1	0.998 9	16	L_III	5.163 2	10.765 7	757	0.198 1	0.993 5

1~8: wavelengths; 9~12: photon energy; 13~16: excitation potential.

2.3 Model validation

Regression models with good fitting but no predictive ability are sometimes chance correlations and often show some pathological features like overfitting, and involvement of noisy variables. Therefore, it is necessary to testify the significance and validity of the models. To achieve that, the LOO CV method was used, which has been proved to be practical and reliable. The parameters of the LOO CV method can play important roles in assessing the performance of models[22~24] which are PRESS/SSY ratio, SEP (standard error of prediction), R_{CV}^2 (cross-validation correlation coefficient), S_{PRESS} (uncertainty of prediction) and PSE (predictive square error).

In general, the SEP_{CV} values of the jack-knifed approach should be slightly larger than the SEP values of the mono-variable models. Meanwhile, the stability and reliability of the models can be statistically showed by the results that all the R and SEP values of the mono-variable models are close to their R_{CV} and SEP_{CV} values of the LOO CV. In addition, PRESS is of significance in determining the real predictive error of the models. The PRESS value less than SSY demonstrates much better predictive power than chance as well as statistical significance. In this work, all the conducted models have PRESS $\ll$ SSY indicating predictive power of excellence and statistical significance. Furthermore, the PRESS/SSY ratio is important in estimating the confidence interval of the properties. For a reliable model, the PRESS/SSY ratio should be <0.6. If the PRESS/SSY ratio is <0.1, the model is excellent. Except pK_m, the PRESS/SSY ratios

of the properties in the paper are smaller than 0.1 ranging between 0.000 6 and 0.072 5, which show the good stability and reliability of the models. Finally, two useful cross-validated parameters come S_{PRESS} and PSE which are helpful in deciding uncertainty of prediction. The lower value of S_{PRESS} and PSE, the better is the predictive power which indicates that the model has excellent correlation ability. On the basis of S_{PRESS} and PSE values, once again one can see that the models have the relativity and predictability of excellence. The parameters in Table 5~7 verify the good stability and reliability of the models proposed in this study.

Table 5 Parameters of mono-variable models and leave-one-out cross-validation of lanthanide

No.		SEP	SEP_{CV}	R	R_{CV}	PRESS	PRESS/SSY	S_{PRESS}	PSE
1	$K\alpha_1$	0.003 3	0.003 7	0.997 1	0.996 3	0.000 2	0.007 3	0.004 0	0.003 7
2	$K\beta_1$	0.001 3	0.001 5	0.999 5	0.999 3	0.000 0	0.001 3	0.001 5	0.001 4
3	$L\alpha_1$	0.008 1	0.009 5	0.999 7	0.999 6	0.001 4	0.000 9	0.010 2	0.009 5
4	$L\beta_1$	0.008 1	0.009 6	0.999 7	0.999 6	0.001 4	0.000 9	0.010 3	0.009 6
5	K	0.001 2	0.001 5	0.999 5	0.999 3	0.000 0	0.001 4	0.001 5	0.001 4
6	L_{I}	0.005 7	0.006 6	0.999 8	0.999 7	0.000 7	0.000 7	0.007 1	0.006 6
7	L_{II}	0.006 4	0.007 4	0.999 7	0.999 6	0.000 8	0.000 7	0.008 0	0.007 4
8	L_{III}	0.006 0	0.007 0	0.999 8	0.999 7	0.000 7	0.000 6	0.007 5	0.007 0

Table 6 Parameters of mono-variable models and leave-one-out cross-validation of lanthanide

No.		SEP	SEP_{CV}	R	R_{CV}	PRESS	PRESS/SSY	S_{PRESS}	PSE
1	$\lg K_1$	0.109 9	0.132 7	0.994 0	0.991 2	0.264 0	0.017 6	0.142 5	0.132 7
2	$\lg K_2$	0.130 7	0.155 2	0.974 6	0.963 1	0.337 3	0.072 5	0.161 1	0.155 2
3	$\lg K_3$	0.181 5	0.216 0	0.992 6	0.989 6	0.652 9	0.020 7	0.224 1	0.216 0
4	$\lg K_4$	0.221 8	0.254 4	0.985 1	0.980 5	0.970 4	0.038 6	0.273 2	0.254 4
5	ΔQ	3.249 4	3.737 2	0.994 7	0.993 0	209.500 0	0.013 9	4.014 4	3.737 2
6	$-\varphi_+^{\ominus}$	0.017 8	0.019 9	0.974 7	0.968 1	0.005 9	0.062 8	0.021 4	0.019 9
7	$-\varphi^{\ominus}$	0.011 6	0.013 7	0.975 5	0.965 6	0.002 8	0.067 7	0.014 7	0.013 7
8	pK_m	0.088 6	0.113 4	0.967 9	0.940 9	0.180 0	0.114 8	0.117 7	0.113 4
9	X_P	0.005 2	0.005 8	0.996 2	0.994 0	0.000 5	0.012 0	0.006 2	0.005 8
10	Z^*	0.082 4	0.097 3	0.992 3	0.988 7	0.141 9	0.022 5	0.104 5	0.097 3
11	r_+	0.329 7	0.383 0	0.998 7	0.998 2	2.200 0	0.003 6	0.411 4	0.383 0
12	U	17.355 5	21.710 8	0.991 4	0.986 5	6 599.000 0	0.026 8	22.530 3	21.710 8
13	$-\Delta_t H_1$	5.975 3	6.770 5	0.978 4	0.972 0	687.600 0	0.055 2	7.272 7	6.770 5
14	$-\Delta_t H_2$	6.234 4	7.021 6	0.972 0	0.967 4	640.940 0	0.064 2	7.633 3	7.021 6
15	$\Delta_t G_1$	5.975 3	6.770 5	0.977 4	0.972 0	687.600 0	0.055 2	7.272 7	6.770 5
16	ΔH	10.315 0	12.186 1	0.996 7	0.995 2	1 485.000 0	0.009 7	13.624 4	12.186 1

Table 7 Parameters of mono-variable models and leave-one-out cross-validation of actinide

No.		SEP	SEPCV	R	R_{CV}	PRESS*	PRESS/ SSY	S_{PRESS}	PSE
1	$K\alpha_1$	0.000 5	0.000 7	0.998 7	0.996 3	0.000 01	0.007 4	0.001 0	0.000 9
2	$K\beta_1$	0.000 5	0.000 6	0.998 8	0.998 1	0.000 004	0.003 9	0.000 6	0.000 6
3	$L\alpha_1$	0.003 5	0.004 3	0.998 7	0.998 1	0.000 2	0.003 8	0.004 7	0.004 3
4	$L\beta_1$	0.003 3	0.004 1	0.998 8	0.998 3	0.000 2	0.003 5	0.004 5	0.004 1
5	K	0.000 4	0.000 6	0.998 7	0.997 9	0.000 004	0.004 2	0.000 6	0.000 6
6	L_{I}	0.002 6	0.003 1	0.998 9	0.998 5	0.000 1	0.003 1	0.003 3	0.003 0
7	L_{II}	0.002 6	0.003 2	0.998 9	0.998 5	0.000 1	0.003 0	0.003 5	0.003 2
8	L_{III}	0.002 8	0.003 4	0.998 9	0.998 3	0.000 1	0.003 4	0.003 7	0.003 4

Continued Table 7

9	$K\alpha_1$	1.127 0	1.433 4	0.992 7	0.988 1	24.655 0	0.023 6	1.570 2	1.433 4
10	$K\beta_1$	1.252 5	1.592 5	0.992 8	0.988 3	30.432 1	0.023 3	1.744 5	1.592 5
11	$L\alpha_1$	0.132 5	0.168 4	0.993 6	0.990 0	0.340 3	0.020 7	0.184 5	0.168 4
12	$L\beta_1$	0.245 0	0.311 8	0.991 7	0.986 5	1.1665	0.026 8	0.341 5	0.311 8
13	K	1.307 6	1.662 6	0.992 8	0.988 3	33.168 9	0.023 2	1.821 2	1.662 6
14	L_{I}	0.302 8	0.385 2	0.992 0	0.987 1	1.781 0	0.025 7	0.422 0	0.385 2
15	L_{II}	0.298 9	0.380 3	0.991 9	0.986 9	1.735 9	0.026 1	0.416 6	0.380 3
16	L_{III}	0.180 8	0.229 7	0.993 5	0.989 4	0.633 1	0.021 0	0.251 6	0.229 7

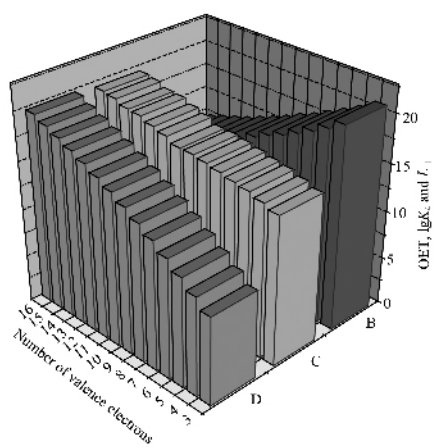
*: to avoid PRESS=0, PRESS of $K\alpha_1$, $K\beta_1$, K are replaced by 0.000 01, 0.000 004 and 0.000 004.

2.4 Chemical behavior of topology

The good proposition of the OET index attributes to the suggestion of the chemical behavior of topology. We deem that the chemical behavior of topology can be divided into the topological growing power and the topological blocking power. Generally, the topological growing power indicates the increase of properties and activities, and the topological blocking power demonstrates the decrease of properties and activities. However, the topological growing power and blocking power are combined together in some cases because of the complexity of structures of substances. Therefore, information of the chemical behavior of topology sometimes dose not show obvious regularities.

In the present research, the physicochemical properties increase or decrease with the number of valence electrons (N_{E}). Accordingly, N_{E} can be a descriptor indicating the topological growing power and the blocking power. In that OET encodes the information of N_{E}, the successful suggestion of the OET index comes from the fact that the OET index efficiently describes the topological growing and the blocking power based on the chemical behavior of topology.

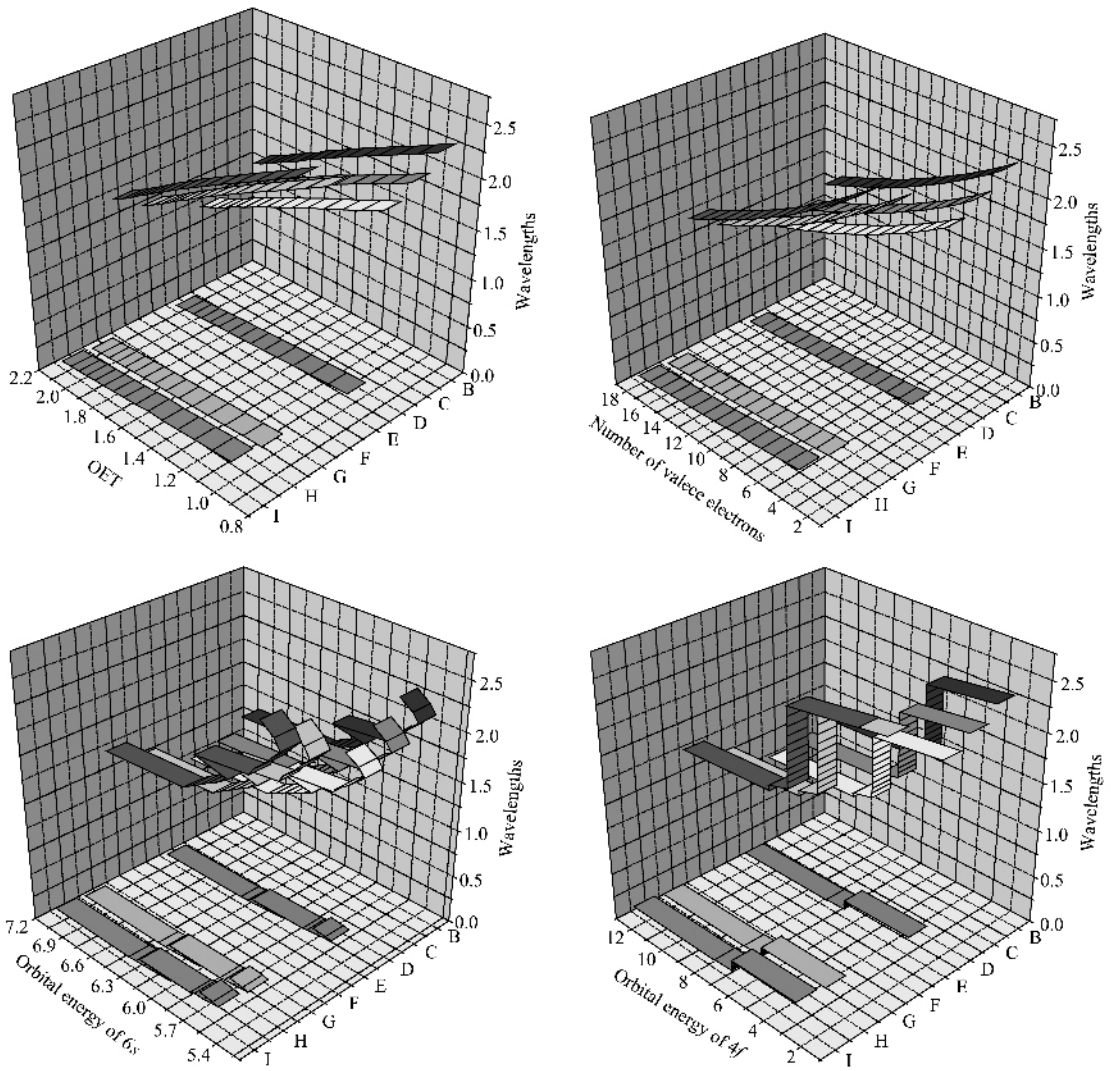
For instance, $\lg K_4$ of lanthanide increases with the increasing N_{E} while the OET index also increases with the increasing N_{E}, which indicates the topological growing power. For L_{II} of lanthanide, it decreases with the increasing N_{E}, so does the OET index, which shows the topological blocking power. Fig.3, which is the three-dimensional graph of N_{E} versus OET, $\lg K_4$ and L_{II}, demonstrates the topological growing power and blocking power. To get better results of compare, OET and L_{II} are replaced by OET × 10 and L_{II} × 10 in the figure.



B, C and D represent $L_{\mathrm{II}} \times 10$, $\lg K_4$ and OET × 10, respectively

Fig.3 Three-dimensional graph of demonstration of topological growing power and blocking power

There is another problem concerning the high correlation of OET with various properties. What if, instead of OET, N_{E} or energy of valence electrons is used to build the models? Therefore, the relationships were conducted between the wavelengths of $K\alpha_1$, $K\beta_1$, $L\alpha_1$, $L\beta_1$, K, L_{I}, L_{II}, L_{III} of lanthanide and the corresponding values of OET, N_{E}, E_{6s} (orbital energy of 6s), E_{4f} (orbital energy of 4f). To illustrate it better, we employ the topological planeness for measuring the quality of descriptors in explaining the variances of the properties. The higher planeness, the more inherent information the descriptor encodes, and the better ability of explaining the variances of properties it possesses. The order of the planeness in Fig.4 is: OET> N_{E}>E_{6s}>E_{4f}, which indicates OET is the better descriptor in explaining the regularities of these properties compared with the other ones. The planeness of OET is



I, H, G, F, E, D, C and B of the graph represent the wavelengths of X-ray emission spectra of $K\alpha_1$, $K\beta_1$, $L\alpha_1$, $L\beta_1$, and the wavelengths of X-ray absorption edges of K, L_{I}, L_{II}, L_{III} of lanthanide, respectively

Fig.4 Three-dimensional graph of the topological planeness of lanthanide

better than that of N_E, which is in the accordance with the fact that N_E is not the most dominant factor in determining these properties despite its importance. Compared with E_{4f}, E_{6s} is the more influential factor for explaining the variances of the properties. For instance, the R^2 (coefficient of determination of the models) is 0.999 0, 0.991 2, 0.722 3 and 0.414 5 of the model between the wavelengths of K of lanthanide and OET, N_E, E_{6s}, E_{4f}, the order of which is the same as that of the planeness indicating the reasonability of the topological planeness. Besides the wavelengths of $K\alpha_1$, $K\beta_1$, $L\alpha_1$, $L\beta_1$, K, L_{I}, L_{II} and L_{III}, the planeness of the other properties is similar to what indicates in Fig.4. Virtually, the topological planeness is another evidence of the success of the index OET based on the chemical behavior of topology. It is the combination of the number and the orbital energy of the valence electrons that leads to the good planeness of OET, which verifies our assumption that the properties of atoms are mainly dominated by the number of valence electrons and the orbital energy.

3 Conclusions

Because of the radioactivity as well as the lack of property data of lanthanide and actinide, the investigation of QSPR for them is of practical

importance. Based on the chemical behavior of topology of atoms, the most influential factors in determining the properties consist of the topological growing power and the topological blocking power. The topological planeness testifies the reasonability of the chemical behavior of topology and demonstrates the different roles what OET, N_E, E_{6s} and E_{4f} play in explaining the variances of the properties. Additionally, the OET indices have excellent discrimination ability of the atoms. Compared with the other studies, this work provides an easier way yielding better results, especially for the study on the spectral properties of atoms. It is on the basis of the chemical behavior of topology that leads to the good application of the OET index to the properties of lanthanide and actinide, which provides a practically potential tool for QSPR study on other substances.

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