From Infection Clusters to Metal Clusters: Significance of the Lowest Occupied Molecular Orbital (LOMO)

Yuta Tsuji* and Kazunari Yoshizawa

ABSTRACT: In this paper, the nature of the lowest-energy electrons is detailed. The orbital occupied by such electrons can be termed the lowest occupied molecular orbital (LOMO). There is a good correspondence between the Hückel method in chemistry and graph theory in mathematics; the molecular orbital, which chemists view as the distribution of an electron with a specific energy, is to mathematicians an algebraic entity, an eigenvector. The mathematical counterpart of LOMO is known as eigenvector centrality, a centrality measure characterizing nodes in networks. It may be instrumental in solving some problems in chemistry, and also it has implications for the challenge facing humanity today. This paper starts with a demonstration of the transmission of infectious disease in social networks, although it is unusual for a chemistry paper but may be a suitable example for understanding what the centrality (LOMO) is all about. The converged distribution of infected patients on the network coincides with the distribution of the LOMO of a molecule that shares the same network structure or topology. This is because the mathematical structures behind graph theory and quantum mechanics are common. Furthermore, the LOMO coefficient can be regarded as a manifestation of the centrality of atoms in an atomic assembly, indicating which atom plays the most important role in the assembly or which one has the greatest influence on the network of these atoms. Therefore, it is proposed that one can predict the binding energy of a metal atom to its cluster based on its LOMO coefficient. A possible improvement of the descriptor using a more sophisticated centrality measure is also discussed.

1. INTRODUCTION

Kenichi Fukui first published a paper on the so-called frontier orbital theory of chemical reactions in 1952. His theory was supported by a series of works published by Robert Woodward and Roald Hoffmann on the conservation of orbital symmetry, the so-called Woodward–Hoffmann rules. Since then, the frontier orbital theory has been applied not only to organic chemical reactions but also to organometallic reactions and Roald Hoffmann. Usually, the frontier orbitals refer to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The two electrons occupying the HOMO are distinct from the other electrons in that they are essential to the reactivity of a molecule as they interact with the LUMO of another molecule. This simplistic picture has made it possible to develop an understanding of a variety of physicochemical properties of molecules, including thermodynamic stability, reorganization energies, and electron transmission.

In this paper, we will focus on the lowest occupied molecular orbital (LOMO). Though this orbital has not yet been found as useful as the frontier orbitals, we describe some interesting aspects of this orbital. We would respectfully like to call it the central orbital, or central molecular orbital, for some reasons. The term “frontier” literally means the part of a country which fronts or faces another country. Its opposite would be the capital or the center of the country. On the analogy of Bohr’s model, the most stable, lowest-energy electron is found in the innermost orbital, which is situated closest to the center of the atom. These grounds may rationalize our nomenclature; however, the most critical reason why we call it central will soon become clear, when we demonstrate that the orbital denotes the centrality of a network. In the chemistry literature, one may find the term “the lowest occupied molecular orbital”, but they are often a typo for the lowest unoccupied molecular orbital. As only a few exceptions, one can find the use of the term in a work by Imamura and Aoki on polyyne oligomers and a work by Erkoç and Türker on ammonia molecules encapsulated by fullerene.

In the field of chemical graph theory, some researchers have paid attention to the LOMO. For example, Bonchev and co-workers pointed out that the expansion coefficients of the
LOMO of a molecule are related with the number of self-returning walks (SRWs) on its molecular graph. Since SRWs play an important role in the characterization of the center of a graph, the LOMO coefficients may be of importance for determining atomic environments in molecules. They further developed their method based on the SRW, proposing topological atomic charges, valencies, and bond orders. Estrada and Knight suggested in their seminal book of network theory that the LOMO distribution has something to do with centrality. Recently, Redzepovic and co-workers have applied spectral graph theory to benzenoid hydrocarbons, finding that the π-electron energies of these molecules can be related with the energies of the HOMO and LOMO.

2. RESULTS AND DISCUSSION

2.1. Note for the Reader. The focus of this paper is on the use of centrality on molecules. LOMO coefficients are equivalent to a centrality measure, i.e., eigenvector centrality. In this paper, we will describe how useful the LOMO of a molecule is to find out an atom located at the center of an interatomic network.

"Centrality" is a term borrowed from network theory. Expert readers, who may be familiar with it, can skip Section 2.2 and go on to Sections 2.3 and 2.4, where we discuss the possibility that eigenvector centrality (LOMO coefficients) can be used as a descriptor for the binding energy of an atom in an atomic cluster.

Eigenvector centrality was introduced by Bonacich in 1987 for the study of social networks. One may further trace it back to his early study in 1972. Extensive studies on this centrality measure have been done in the literature. In Sections 2.2.1 and 2.2.2, using a simplistic model as an example, we demonstrate what eigenvector centrality is all about for the sake of chemists.

If one takes a look at a network theory textbook, one can find the derivation of the equations regarding eigenvector centrality, but they might be far from evident for chemists. In Sections 2.2.3 and 2.2.4, we rely on principles of quantum chemistry or quantum mechanics, which are much more familiar to chemists than network theory, to clarify the relation between LOMO and eigenvector centrality. We are sure that this paper will help the chemistry community to satisfactorily understand the significance of LOMO along with its underlying mathematical structure.

2.2. Example of the Use of Eigenvector Centrality and Its Relation to LOMO. 2.2.1. Infection Network. In December 2019, a local outbreak of pneumonia was detected in Wuhan (Hubei Province, China) and was soon identified as being caused by a new coronavirus (COVID-19). The first half of 2020 witnessed the rapid spread of COVID-19 in China and then globally. Understanding the propagation of viruses in social networks is of significant importance. On the basis of a simple model by Spizzirri, we will demonstrate how the spread of infection happens and its relation with the centrality of a network.
Figure 2 shows a simplified model of the propagation of infection in a town network. In Figure 2a, town B is connected with two towns, A and C. Suppose the first infected person appears in town B. This will result in the same number of infected people in each town connected with town B while the source of the infection in town B will recover. For a while, there will be no infected person in town B, but the infection will soon return. This time, the virus will be transferred from both town A and town C, resulting in two infected people in town B while the infected in town A and town C will recover. This process will continue.

Let us take a look at the propagation of infection in the town network shown in Figure 2b, in which every town has two neighboring towns. Again, suppose the first infected person appears in town B. The first step of the propagation is the same as that for the network detailed above. A difference emerges in the second step. The infection will return to town B from town A and town C, leading to two infected people in town B. Meanwhile, an exchange of infection will happen between town A and town C. And then the sources of infection in town A and town C will recover; however, a new infected person will appear in both towns. From then on, all of the towns will have at least one infected person, and the exchange of infection will continue in all of the pairs of neighboring towns.

2.2.2. Graph Theory. One may want to have a mathematical apparatus to deal with the evolution of the propagation of infection. Graph theory will be helpful for this purpose. In Figure 3, we show how one can mathematically represent the town networks introduced in Figure 2. The towns are converted into nodes (also called vertices) labeled using numbers (1, 2, and 3), while the roads are converted into lines called edges though in the drawing of Figure 3, there is no distinction. The network representation consisting of the nodes and the edges is called graph. Similarly, when the atoms and the bonds of a molecule are converted into nodes and edges, one can obtain a molecular graph, which has been extensively investigated in chemical graph theory.28

One of the most useful matrices associated with graph G is the adjacency matrix A(G). This matrix can be constructed such that if the ith and jth nodes are adjacent (connected), the (ij) and (ji) entries of A(G) are 1; otherwise 0. One can perceive a similarity of A(G) to the Hückel matrix. We will return to this point later.

The initial distribution of the infected population on a town network is represented by a vector of C(0) (see Figure 4).

Figure 3. Process of reducing a network to mathematical entity: graph and adjacency matrix.

Figure 4. Parallel between mathematical and graphical representations for the spread of infection on the town network shown in Figure 2a. The vector of C(0) describes the initial distribution of the infected population and the vector of AC(0) corresponds to the distribution of the infected population after a certain period of time has passed. Additionally, after the same length of time has passed, the infected population grows as represented by the vector of AC(1).

Figure 4 shows the first few steps of iterations to simulate the evolution of the infected population in the town network shown in Figure 2a. The product of AC(0) corresponds to the distribution of the infected population after a certain period of time has passed. Generally, the ith row element of the vector of AC(0) can be calculated from \( \sum a_{ij}c_{j}^{(0)} \), where \( a_{ij} \) denotes the (ij) entry of the adjacency matrix, either 0 or 1, and \( c_{j}^{(0)} \) the initial infected population at the jth node (town); therefore, the ith entry of \( AC(0) \) counts the total infected population propagated from the nodes connected with the ith node. The vector of \( C(1) \), equivalent to \( AC(0) \), can also be used as the initial population for the next step. Then, \( AC(1) \) tells how infected people are distributed over the nodes after the next.

Since the process presented in Figure 4 looks very similar to a Markov chain,29,30 we make the link to it clear briefly in the Supporting Information (SI).

Let us move on to a bit more complicated network (see Figure 5). For this network, we will try out a variety of initial populations. We will simulate how the infected population grows at each node as the virus spreads. We performed three simulations: The initial infected person appears at the node of 1 (a), at the node of 2 (b), and at the node of 3 (c). One should notice that nodes 3 and 4 are identical due to symmetry.

The results of the simulations for the growth of infected population are presented in Figure 6. Generally, one can see an exponential growth in every case. The most rapid growth is observed when the initial person is set to appear at the node of 2. The slowest growth is observed for the case where the initial person is set to appear at the node of 1. This may be because

**Figure 3.** Process of reducing a network to mathematical entity: graph and adjacency matrix.

**Figure 4.** Parallel between mathematical and graphical representations for the spread of infection on the town network shown in Figure 2a. The vector of C(0) describes the initial distribution of the infected population and the vector of AC(0) corresponds to the distribution of the infected population after a certain period of time has passed. Additionally, after the same length of time has passed, the infected population grows as represented by the vector of AC(1).

**Figure 5.** Graph representing a town network in a small county (left) and its adjacency matrix (right).
town 1 is rural whereas town 2 is urban in the county. Or one could say that town 1 is “frontier”, whereas town 2 is “central”.

Figure 6 shows that the initial distribution of infected people will affect the pattern of the growth of the number of infected people. But we demonstrate in Figure 7 that the ratio of the population does not vary after a sufficiently long time has passed whatever the initial distribution was. At every iteration step, the number of infected people at each node was divided by the number of infected people at the node with the largest number of infected people of the four, resulting in Figure 7. Thus, in this figure, the maximum value does not exceed 1. At the very beginning, the ratios oscillate greatly, but they converge soon. Remarkably, this figure shows that different initial distributions converge to the same distribution. This can be proved mathematically as will be shown later.

This simulation implies one can make a distinction of the towns in a county. Based on the converged distribution of the ratio of infected people, the towns can be ranked. Town 2 holds the largest number of infected people of the four while the ratio of infected people in town 1 stays low. The ratios of towns 3 and 4 fall in between. The distinction of the towns is likely to be traced back to the extent to which the town is urbanized. Thus, the ratios shown in Figure 7 can be used as a measure of centrality of the nodes in a network. This is the eigenvector centrality.24,31 The reason why the name includes “eigenvector” will become clear soon.

As more sophisticated models for epidemics on networks, instead of the one presented above, one may use two fundamental models known in the literature:32–34 Susceptible-Infected-Susceptible (SIS) and Susceptible-Infected-Recovered (SIR) models, which are extensions of the classical models used in epidemiology that consider the influence of the topology of a network on the propagation of an epidemic, where the spreading of an infectious disease on the network have been modeled representing individuals as nodes and the contacts between them as edges. To better incorporate the dynamical process of the spread of epidemics into the model, one needs to consider a ratio of the infection birth rate and the infection death rate, which is called the epidemic threshold and determines whether an infection becomes epidemic or not.34,35

2.2.3. Chemical Graph Theory. It is time to start chemistry. Not only infection networks but also molecules can be viewed as a graph. A simple undirected graph is used for the description of molecules, in which the nodes correspond to the atoms in the molecule and the edges correspond to the chemical bonds.36 Such a graph is termed the molecular graph. π-conjugated compounds, whose π-electronic structures are well described with the simple Hückel model, have been a good target for the application of graph theory because there is a one-to-one correspondence between the Hückel Hamiltonian (Hückel matrix) and the adjacency matrix.37,38 The relation between the Hückel Hamiltonian \( H \) and the adjacency matrix \( A \) can be written as

\[
H = \alpha I + \beta A
\]  

where \( I \) denotes the identity matrix and \( \alpha \) and \( \beta \) represent the Coulomb and resonance integrals for \( sp^2 \)-hybridized carbon

Figure 6. Growth of the number of infected people at each node of the network shown in Figure 5; node 1: blue, node 2: orange, and node 3 (equivalent to node 4): gray. The images on the right indicate the growth of infected population representing the initial distribution of the infected population. The initial infected person appears at the first node (a), second node (b), and third node (c).

Figure 7. Evolution of the ratio of the number of infected people at each node shown in Figure 6; node 1: blue, node 2: orange, and node 3 (equivalent to node 4): gray. The ratios at the 30th iteration step are shown explicitly. The images on the right represent the initial distribution of the infected population. The initial infected person appears at the first node (a), second node (b), and third node (c).
atoms and C(sp²)–C(sp²) bonds, respectively. By setting α and β to 0 and 1, respectively, the Hückel Hamiltonian can be reduced to the adjacency matrix. One should note that α corresponds to the energy origin of the eigenvalue spectrum while β the energy unit of the spectrum, so the arbitrariness of setting the values of α and β does not undermine the essential features of the spectrum.

In Figure 8a, one can see a process of reducing a chemical structure to a graph representation. The π-conjugated molecule of triafulvene includes four sp² carbon atoms and four C(sp²)–C(sp²) bonds, which are, respectively, converted into nodes and edges in the so-called Hückel graph (hydrogen-depleted graph). The Hückel graph for triafulvene shares the same network structure as the infection network simulated in the previous section. We will see a remarkable correspondence between the simulation of the evolution of the infected population on the network and the electronic structure of triafulvene.

Figure 9 shows the central orbital—LOMO—of triafulvene calculated with the Hückel method. For comparison, the eigenspectrum of triafulvene is reproduced below but we will use the Hamiltonian and the adjacency matrix for graph theory and 

![Graph](https://example.com/graph.png)

Figure 8. (a) Process of reducing the chemical structural formula for triafulvene to the Hückel graph. (b) Hückel Hamiltonian for triafulvene and the adjacency matrix for the Hückel graph.

Thanks to the Hermitian property, one can even form the initial wave function such that \( |Ψ(0)\rangle = c_1|ψ_1\rangle + c_2|ψ_2\rangle + c_3|ψ_3\rangle + \cdots + c_N|ψ_N\rangle \) (2)

When we remind ourselves that the Schrödinger equation states that \( i\hbar \frac{d}{dt} |ψ\rangle = \hat{H} |ψ\rangle \), where \( e_i \) denotes the eigenvalue of the molecular orbital of \( |ψ_i\rangle \), eq 3 leads to

\[
\hat{H} |Ψ(0)\rangle = c_1\hat{H}|ψ_1\rangle + c_2\hat{H}|ψ_2\rangle + c_3\hat{H}|ψ_3\rangle + \cdots + c_N\hat{H}|ψ_N\rangle
\]

Using this, we define a new wave function as follows

\[
|Ψ(1)\rangle = \hat{H} |Ψ(0)\rangle = c_1e_1|ψ_1\rangle + c_2e_2|ψ_2\rangle + c_3e_3|ψ_3\rangle + \cdots + c_Ne_N|ψ_N\rangle
\]

This process corresponds to the step of updating \( C(0) \) to \( C(1) \) in Figure 4. By repeating this procedure \( n \) times, we arrive at

\[
|Ψ(n)\rangle = \hat{H}^n |Ψ(0)\rangle = c_1e_1^n|ψ_1\rangle + c_2e_2^n|ψ_2\rangle + c_3e_3^n|ψ_3\rangle + \cdots + c_Ne_N^n|ψ_N\rangle
\]

Suppose that the absolute value of \( e_1 \) is the largest of the \( N \) eigenvalues. By parenthesizing \( |Ψ(n)\rangle \) with \( e_1^n \), one obtains

\[
|Ψ(n)\rangle = e_1^n\left(c_1|ψ_1\rangle + c_2\frac{e_2}{e_1}|ψ_2\rangle + c_3\frac{e_3}{e_1}|ψ_3\rangle + \cdots + c_N\frac{e_N}{e_1}|ψ_N\rangle\right)
\]

This is very important because it indicates a normalized value such that the largest amplitude becomes 1.
Since the absolute value of $\epsilon_1$ is the largest, $\lim_{n \to \infty} c_i^n = 0$; therefore, $\psi^{(n)}$ converges to $\epsilon_1^0 \psi_1$. Note that $\epsilon_1^0 \psi_1$ is just a coefficient of the eigenvector of $\psi_1$, so the normalization of $\epsilon_1^0 \psi_1$ results in $\psi_1$. This suggests that by multiplying an arbitrary wave function (or an arbitrary vector) from the left by the Hamiltonian (or adjacency matrix) repeatedly, one can converge the wave function to an eigenvector of the Hamiltonian, i.e., $\psi_1$. This means that whatever the initial distribution is, the process yields the same distribution. This process is well known in mathematics as the power method.42

Next thing we need to do is to check whether $\psi_1$ is the LOMO. Since the LOMO is the most stable orbital, there is no wave function node. This is the eigenvector whose all components have the same sign.43 The Perron–Frobenius theorem guarantees that when all of the elements of a matrix are positive (positive matrix), the largest eigenvalue of the matrix is not degenerate and all of the elements of the corresponding eigenvector (a.k.a. Perron–Frobenius vector) have the same sign.44 Any other eigenvector does not show this property due to orthogonality. Some of the elements must have the opposite sign. From this theorem, it is clear that $\psi_1$ is the LOMO because all of the LOMO coefficients have the same sign and the eigenvalue corresponding to $\psi_1$, namely, $\epsilon_1$, is the largest.

Someone versed in this theorem may worry about the distinction between the positive matrix and non-negative matrix. Actually, the adjacency matrix is not the positive matrix because it includes some zeros. By adding a small perturbation to the adjacency matrix, one can convert it to a positive matrix from the non-negative matrix. If the perturbation is substantially small, the eigenvalues and eigenvectors are hardly affected. This point is discussed further in the SI.

For a detailed mathematical proof of the Perron–Frobenius theorem, one can consult the mathematical literature, but here we provide a proof of a certain kind from the point of view of quantum mechanics, which may be helpful for chemists. A matrix version of the Schrödinger equation reads,

$$H \mathbf{C} = \mathbf{C} \epsilon$$

(8)

where

$$
\mathbf{C} = 
\begin{bmatrix}
C_{11} & C_{12} & \cdots & C_{1N} \\
C_{21} & C_{22} & \cdots & C_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
C_{N1} & C_{N2} & \cdots & C_{NN}
\end{bmatrix}
$$

(9)

and $\epsilon = \text{diag}(\epsilon_1, \epsilon_2, \ldots, \epsilon_N)$, where $\text{diag}(\ldots)$ denotes a diagonal matrix in which the $i$th element in the parentheses corresponds to its $(i,i)$ entry. Note that in the Hückel method, the overlap matrix is approximated by the identity matrix, so it does not appear in eq 8. The $(ij)$ entry of $\mathbf{C}$ corresponds to the $j$th MO expansion coefficient at site (atom) $i$. The molecular orbital of $\psi_j$ is equivalent to the column vector of $\mathbf{C}_j = [C_{ij}, C_{ij}, \ldots C_{ij}]^T$. Using $\mathbf{C}_j$ eq 8 can be rewritten as

$$H \mathbf{C}_j = \epsilon_j \mathbf{C}_j$$

(10)

If one uses the adjacency matrix of $\mathbf{A}$ instead of $\mathbf{H}$, eq 10 can be changed into

$$\mathbf{A} \mathbf{C}_j = \lambda_j \mathbf{C}_j$$

(11)

The relation between $\epsilon_j$ and $\lambda_j$ is $\epsilon_j = \alpha + \beta \lambda_j^{27}$ By setting $\alpha$ to the origin of energy, we have $\epsilon_j = \beta \lambda_j$. $\mathbf{A}$ has the dimension of $N \times 1$ because $\mathbf{A}$ and $\mathbf{C}_j$ have the dimensions of $N \times N$ and $N \times 1$, respectively. $\mathbf{C}_j$ is a column vector. Its $i$th row element is $\sum_k a_{ik} \beta_{jk}$, where $[\beta_{jk}]$ denotes the $k$th row of the vector of $\mathbf{C}_j$, which is equal to $C_{ij}$. Of course, $\lambda_j \mathbf{C}_j$ is also a column vector. Its $i$th row element is $\lambda_j [\beta_{jk}]$, which is equal to $\lambda_j C_{ij}$. Therefore, we obtain

$$\lambda_j \mathbf{C}_j = \sum_k a_{ik} \beta_{jk} \mathbf{C}_j$$

(12)

Suppose the $i$th eigenvector corresponds to the LOMO. The following equality holds true

$$\left| \lambda_i \right| C_{il} = \sum_k a_{ik} \left| \beta_{jk} \right| C_{jl}$$

(13)

This is because all of the $i$th MO expansion coefficients have the same sign. One should also note that $a_{ij} \geq 0$. As mentioned above, if we are allowed to add a small positive number to each nonzero entry of $\mathbf{A}$ as a perturbation, we have $a_{ij} > 0$, and we assume this in the following.

For the $m$th eigenvector, where $m \neq i$, in contrast, we have

$$\left| \lambda_m \right| C_{ml} = \sum_k a_{ik} \left| \beta_{jk} \right| C_{kl} < \sum_k a_{ik} \left| \beta_{jk} \right| C_{jl}$$

(14)

because some of the coefficients have the different sign from the rest. Only the LOMO is allowed to let all of the coefficients have the same sign. This is not the case for the other orbitals, which have to be orthogonal to the LOMO.

By multiplying both sides of the inequality in eq 14 by $C_{il}$ and summing them up over $i$, we have $\sum_i \left| \lambda_m \right| C_{ml} C_{il} < \sum_i \left| a_{ik} \right| C_{il} \left| \beta_{jk} \right| C_{jl}$. By interchanging $i$ and $k$ on the right-hand side of this inequality, we get $\sum_i \left| \lambda_m \right| C_{ml} C_{il} < \sum_i \left| a_{ik} \right| C_{il} \left| \beta_{jk} \right| C_{jl}$. Since $\mathbf{A}$ is a symmetric matrix, $a_{ij} = a_{ji}$. Using this equality and changing the order of summation, $\sum_i \left| \lambda_m \right| C_{ml} C_{il} < \sum_i \left| a_{ik} \right| C_{il} \left| \beta_{jk} \right| C_{jl}$. Using eq 13 on the right-hand side of this inequality, $\sum_i \left| \lambda_m \right| C_{ml} C_{il} < \sum_i \left| \lambda_m \right| C_{ml} \left| C_{il} \right|$ is obtained. This leads to

$$\left| \lambda_m \right| < | \lambda_i |$$

(15)

This inequality states that the eigenvalue associated with the LOMO, i.e., $| \lambda_i |$, is larger than any other eigenvalues. Note that the $m$th eigenvector is an arbitrary one. This is an outcome of the application of the Perron–Frobenius theorem in conjunction with the basic principles in quantum mechanics to the Hückel matrix or the adjacency matrix.

Since all of the LOMO coefficients have the same sign, it is clear from eq 12 that $\lambda_j > 0$. Eq 15 can be read as

$$-\lambda_i < \lambda_m < \lambda_j$$

(16)

When we return to the Hückel energy scale, eq 16 is converted into

$$\lambda \beta \phi < \epsilon_m < -\lambda \beta \phi$$

(17)

where $\lambda \beta \phi$ is the Hückel energy of the LOMO. One should note that $\beta < 0$.

2.2.5. Example. Let us look at an example of the LOMO. In Figure 10, we show the LOMO of calicene. The energy of the LOMO is $2.36 \beta$, so the Perron–Frobenius theorem guarantees that the other orbitals fall in a range of $2.36 \beta < \epsilon < -2.36 \beta$. This is indeed satisfied as can be seen from the eigenspectrum shown in Figure 10.
We turn to the LOMO coefficients of calicene. The largest amplitude is found on the C7 atom while the smallest on the C2 and C3 atoms. This implies that the C7 atom is the center of the molecule whereas the C2 and C3 atoms are located farthest from the center. Thus, one can discriminate an atom from another depending on the topological distance from the center of the molecule.

The LOMO coefficient corresponds to eigenvector centrality. This is not the only way to assess the centrality of a node in a graph. An important alternative would be degree centrality, which is defined as the number of edges incident upon a node. In the chemical terminology, degree centrality is the same as the coordination number. When counting the coordination number for a carbon atom in a molecule represented by the Hückel graph, we do not take hydrogen atoms into account because they are not incorporated in the Hamiltonian at the Hückel level. The carbon atoms in calicene can be divided into two groups using the degree centrality (coordination number): the first group includes the C7 and C8 atoms, whose coordination number is 3. The other carbon atoms are classified into the second group: they have the coordination number of 2. That all of the carbon atoms except for C7 and C8 have the same centrality when relying on the method of degree centrality may run counter to our intuition for the network.

A major drawback of degree centrality is that it only takes into account local information. For example, a node with a few important neighbors may have more global influence than a node with many less important neighbors. Thus, one uses eigenvector centrality as a refinement of degree centrality. Generally, eigenvector centrality can be used to measure the influence of a node in a network. A recursive definition of eigenvector centrality, in which the eigenvector centrality of a vertex is defined as being proportional to the sum of the eigenvector centrality of the vertices to which it is connected, is also helpful for understanding the importance of eigenvector centrality. This is a way one can understand what the LOMO is all about.

2.3. Molecular Graph as a Network for Electron Flow.

What walks on the networks detailed in the former part of this paper (Sections 2.2.1 and 2.2.2) may be a human being or virus. In contrast, on the molecular graph, electrons are transported. Chemical graph theory has recently been found useful for understanding how electrons flow in molecules. This is reminiscent of the theory elaborated by Bonchev and co-workers mentioned in the introductory part of this paper.

What Bonchev and co-workers presented in the chemistry literature can be written as follows

\[ C_{i,LOMO}^2 = \lim_{k \to \infty} \frac{\text{SRW}_{i}^k}{\sum \text{SRW}_{i}^k} \]  

where \( C_{i,LOMO}^2 \) is the square of the LOMO coefficient at atom \( i \) and \( \text{SRW}_{i}^k \) denotes the number of self-returning walks (SRWs) of length \( k \) starting and ending at atom \( i \). It should be noted that in the mathematics literature, this equation can be traced back to Wei’s work in 1952, noted by Berg in 1958, and later reproduced by Cvetković, Rowlinson, and Simić in their book.

In Figure 11, the enumeration of SRWs is exemplified by the counting of SRW_1^4 for the graph corresponding to triafulvene.

SRWs are also of importance in the method of moments, which has been applied to a variety of solids to establish relationships between geometric and electronic structures.

Since \( \sum \text{SRW}_{i}^k \) corresponds to the total number of SRWs of length \( k \) on the molecular graph, the right-hand side of eq 18 can be viewed as the limit for the relative number of SRWs. Bonchev and co-workers proposed that SRW_4 in the molecular graph can be interpreted as electron motion near atom \( i \). Thus, LOMO coefficients are expected to have something to do with the relative frequencies of such electron motion. This further can be correlated with Feynman’s idea of accounting for all possible electron paths. Nagao, Nishikawa, and Aono demonstrated that the transition amplitude in the Feynman path integral method can be obtained by summing contributions from all independent trajectories. Each SRW in a molecular graph would be interpreted as an independent Feynman’s electron trajectory.

2.4. Atom Binding Energy.

As has been clarified in the previous sections, LOMO coefficients will be helpful for identifying an atom in a molecule where electrons frequently visit: The larger the LOMO coefficient of an atom, the more frequently electrons pass by the atom. Also, according to network theory, the larger the LOMO coefficient of an atom, the more likely it is to be influential in the network. Based on these facts, we have conceived that the binding energy of an atom to a host (another atom, molecule, solid, or surface) may be correlated with the LOMO coefficient of the atom. The LOMO coefficient is likely to be a good descriptor for the prediction of the binding energy. This is because the binding energy can be traced back to the electronic communication between the atom and those of the host.

In the remaining part of this paper, we will see a correlation between the binding energy of a metal atom to its cluster and the LOMO coefficient of the corresponding atom. Since the theory of LOMO coefficients have been developed relying on the simple Hückel theory, we investigate s-block metal clusters, whose electronic structures are expected to be well described.
Fan et al.\textsuperscript{62} found that lithium ions are likely to diffuse on graphene, an anode material for lithium-ion batteries, and as the lithium content increases, small lithium clusters can be formed thereon. Such nanoclusters can potentially nucleate Li dendrites, leading to device failure. Based not only on such a practical point of view but also on fundamental interest, Li clusters have attracted researchers’ attention.\textsuperscript{63–65} Also, high-spin Li clusters have caught the attention of theoreticians because of their novel bonding motifs.\textsuperscript{66–68}

Before we take a look at the LOMO coefficients of these clusters, we need to obtain their structures. The prediction of the structure of the ground state of a cluster, which corresponds to the global minimum of the potential energy surface, is a difficult task. Generally, the number of local minima increases exponentially as the size of the cluster increases.\textsuperscript{69}

The implementation of an evolutionary approach known as particle swarm optimization (PSO) capable of finding the global minimum of the potential energy surface of clusters was reported by Call et al.\textsuperscript{70} The PSO algorithm was originally proposed by Kennedy and Eberhart in 1995, inspired by the social behavior of flocks of birds and fish.\textsuperscript{71} Recently, Ma and co-workers have developed a crystal structure analysis by particle swarm optimization (CALYPSO) methodology, which has made it possible to apply the PSO algorithm to the global optimization of extended systems.\textsuperscript{72–74} The CALYPSO method has been developed so that it can also be applied to cluster structure prediction.\textsuperscript{75}

In this study, to effectively obtain stable lowest-energy structures of Li\textsubscript{n}, Be\textsubscript{n}, Na\textsubscript{n}, and Mg\textsubscript{n} clusters, we used CALYPSO\textsuperscript{72–74} in conjunction with the periodic density functional theory (DFT) code of Vienna ab initio simulation package (VASP) 5.4.4.\textsuperscript{76,77} The number of structures produced at each step—population—was set to 10. The number of CALYPSO steps—generations—was fixed to 10. The first generation was generated randomly. For the next generation, 20% of the population were generated randomly while the others were generated on the basis of the previous generation using a local version of PSO algorithm with Metropolis criterion.\textsuperscript{75}

All of the structures generated were locally optimized using VASP. Since VASP employs periodic boundary conditions, an orthorhombic unit cell with a dimension of 15 Å × 15 Å × 15 Å or larger was built and the cluster was located at its center so that the vacuum surrounding the cluster could be regarded as thick enough to avoid interactions between the cluster and its replica in the neighboring cell.

The generalized gradient approximation (GGA) was adopted with the functional described by Perdew, Burke, and Ernzerhof (PBE).\textsuperscript{80} The Kohn–Sham equations were solved with a plane-wave basis set using the projector-augmented wave (PAW) method.\textsuperscript{81,82} The cutoff energy for the plane-wave basis set was set to 300 eV. The break conditions for the electronic self-consistent-field (SCF) loop and the optimization loop were set to 1.0 × 10\textsuperscript{−4} and 1.0 × 10\textsuperscript{−3} eV, respectively. Only one point was used for the Brillouin zone sampling. Spin-polarization calculations were performed for all of the systems.

The most stable structure thus found was singled out as the initial configuration for the reoptimization with more accurate convergence criteria. The cutoff energy was increased to 500 eV. A tighter SCF convergence criterion of 1.0 × 10\textsuperscript{−5} eV was used. The all band simultaneous update of wave functions\textsuperscript{83} was selected for the algorithm for SCF. The atoms in the cluster were relaxed until the forces on them become less than 0.05 eV/Å.

Figure 12 shows optimized structures of some Li clusters. The atomic coordinates of these clusters are shown in the SI.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{Optimized structures of Li\textsubscript{5} (a), Li\textsubscript{8} (b), and Li\textsubscript{10} (c). The LOMO coefficients for the 2s atomic orbitals on symmetrically distinct atoms calculated at the level of the extended Hückel method are indicated. The point group of each cluster is shown in parentheses.}
\end{figure}

The structures of the Li\textsubscript{5} and Li\textsubscript{10} clusters seem consistent with what were reported in preceding studies.\textsuperscript{63,65} As for the Li\textsubscript{8} cluster, a D\textsubscript{4h} structure is reported in the literature,\textsuperscript{63,64} while our CALYPSO calculation pointed to the C\textsubscript{3v} structure. The VASP-calculated energy of the C\textsubscript{3v} structure is almost the same as that of the D\textsubscript{4h}, but the C\textsubscript{3v} was found slightly lower in energy by 0.04 eV. The coexistence of multiple Li\textsubscript{n} isomers at room temperature was suggested by Fournier et al. based on their DFT calculations.\textsuperscript{84}

These clusters in Figure 12 were optimized at the level of DFT, while the extended Hückel method was used for the generation of the LOMO coefficients. The reader who has read thus far surely appreciates the value of the Hückel method. However, the metal clusters cannot be dealt with in the framework of the simple Hückel method, so we adopted the extended Hückel method.\textsuperscript{85} The standard extended Hückel parameters were taken from the literature\textsuperscript{86} and those used in...
this study were tabulated in the SI. For the extended Hückel calculation, Yet Another extended Hückel Molecular Orbital Package (YaeHMOP) was used.\textsuperscript{87} The off-diagonal elements of the Hamiltonian were evaluated using the Wolfsberg–Helmholz approximation.\textsuperscript{88} The proportional constant in this approximation was set to 1.75 as was suggested by Hoffmann.\textsuperscript{85}

Following the convention, four Slater-type basis functions of 2s, 2p\textsubscript{\textit{x}}, 2p\textsubscript{\textit{y}}, and 2p\textsubscript{\textit{z}} were used for the Li atoms. The contributions of the 2p orbitals to the LOMO were found negligibly small. Their coefficients are always lower than 0.05. The LOMO coefficients shown in Figure 12 are those for the 2s basis functions.

For the visualization of the metal clusters, we use VESTA.\textsuperscript{89} In Figure 12, bonds are drawn between Li atoms separated by 3.1 Å or less. The distance of 3.1 Å corresponds to the double geometry of the M\textsubscript{15} cluster, whose energy is \( R^2 \) = 1.00. The proportional constant in this approximation was set to 1.75 as was suggested by Hoffmann.\textsuperscript{85}

In the Li8 cluster, one can perceive a correlation between the binding energy and the LOMO coefficient. Without using the LOMO coefficients, one may rank the centrality of the Li atoms in the Li\textsubscript{8} cluster based on the coordination number. However, things are not so simple when moving to a more complicated cluster.

In the Li\textsubscript{8} cluster, the Li7 atom has the coordination number of 7 whereas that of the others is 1. Thus, there is no doubt that the Li\textsubscript{7} atom has the highest centrality, whereas the other atoms, namely, the peripheral atoms, share the lowest centrality. Nevertheless, we see a variation in the LOMO coefficients for the peripheral atoms. This implies that the centrality may vary from atom to atom even if these atoms have the same coordination number.

Complicated as the geometry of the Li\textsubscript{10} cluster is, one may manage to recognize the correspondence between the coordination number and the centrality. Such a problem as the one we have seen in the Li\textsubscript{8} cluster will not arise.

Let us take a look at whether the LOMO coefficient is correlated with the binding energy of an atom in a cluster. We define the binding energy for the metal cluster with a composition of M\textsubscript{\textit{n}} as follows

\[
E_{\text{bind}} = E(M) + E(M_{n-1}) - E(M_n)
\]

where \( E(M) \) and \( E(M_n) \) are the energies of the M atom to be removed and the parent M\textsubscript{\textit{n}} cluster, respectively. The removal of the M atom results in the M\textsubscript{\textit{n-1}} cluster, whose energy is expressed as \( E(M_{n-1}) \). For this energy calculation, the geometry of the M\textsubscript{\textit{n-1}} cluster was kept fixed to the same as that adopted in the parent cluster structure. These energies were obtained from the calculations at the DFT level with VASP.

In Figure 13, one can see correlations between the binding energy for a Li atom in the Li clusters and the LOMO coefficient of its 2s orbital. The coefficients of determination \( R^2 \) calculated for these plots are very high, approaching 1. This appears to be a justification of the idea that the LOMO coefficient could be a good descriptor for the atom binding energy in atom assemblies.

If the number of points in these plots was less than 3, any plots would result in the \( R^2 \) value of 1, which would hinder one from clarifying whether or not there is a correlation between them. This is why the metal clusters consisting of at least three or more symmetrically distinct atoms were singled out for analysis.

In the clusters of Li\textsubscript{8} and Li\textsubscript{10}, the correspondence between the measures of centrality based on the coordination number and the LOMO coefficient and the binding energy is apparent. One would argue that such a geometrical feature as the coordination number might be sufficient for the prediction of the binding energy. However, the Li\textsubscript{8} cluster would oppose this argument. Owing to the lack of correspondence between the two measures of centrality in this cluster, this system begs for further analysis.

Since all of the peripheral Li atoms in the Li\textsubscript{8} cluster have the coordination number of 1, they are expected to be equally bound to the cluster as long as we rely on the centrality measure of the coordination number. However, the binding energies of these atoms vary. As another factor which affects the binding energy, the distance of the atom measured from the center of the cluster occurs to us.

The center of the Li\textsubscript{8} cluster is the Li\textsubscript{7} atom. How far a Li atom is from the center of the cluster is shown in Figure 14a.

\[
E_{\text{bind}} = E(M) + E(M_{n-1}) - E(M_n)
\]
scatter plot of the distance vs. the binding energy is generated as shown in Figure 14b, where one cannot see any correlation. This means that the binding energies of the Li atoms in the Li8 cluster cannot be predicted only on the basis of the geometrical features. It is the LOMO coefficient that is helpful for predicting the binding energy.

The results for the other clusters are presented in the SI. Here, just briefly, one can, by and large, observe a good correlation between the LOMO coefficient and the binding energy for the Be\(_n\), Na\(_n\), and Mg\(_n\) clusters, too. For the clusters of Na\(_5\) and Mg\(_{10}\), the highest \(R^2\) value of 1 was marked (see Figure 15a,b). The lowest \(R^2\) value was seen in the analysis of Mg\(_8\) cluster (see Figure 15c).

All in all, these structures look consistent with those reported in the literature.\(^91\)\(^{-}^93\) Given that higher correlations are found for the clusters with higher symmetry, the symmetry of the cluster may also have something to do with the binding energy.

We should mention that there is also a problem in the use of eigenvector centrality (LOMO), which problem is that this centrality has the same value for all of the nodes in a regular graph, i.e., a graph in which all of the nodes have the same degree.\(^94\) This may be particularly serious in the case of atomic clusters whose constituting atoms all have the same coordination number. The Mg\(_8\) cluster may fall into this class because all of the atoms have the same coordination number of three.

In the Mg\(_8\) cluster, it is easy to see that for instance, Mg1 participates in one triangle while Mg5 in two, so they are not equivalent. At the simple Hückel level, eigenvector centrality (LOMO) does not distinguish such important structural differences. However, at the extended Hückel level, since not only the through-bond interaction but also the through-space interaction is included, the atoms are ranked as shown in Figure 15c. Nevertheless, the relatively lower \(R^2\) value of 0.73 for the Mg\(_8\) cluster suggests a need for amelioration.

In 2005, Estrada and Rodríguez-Velázquez\(^94\) proposed a measure of centrality whereby nodes are ranked according to their participation in different network subgraphs. This is called subgraph centrality, which is defined for the \(i\)th node in a graph represented by the adjacency matrix of A as

\[
S_i = [\exp(A)]_i = \sum_{k=1}^{N} C_{ik}^2 \exp(\lambda_k) \tag{20}
\]

The use of subgraph centrality was later contextualized in molecular systems.\(^95,\)\(^96\) Estrada and co-workers proved a theorem that opens for extending this context in a quantum chemical context, which allowed the use of Hermitian matrices such as those used in quantum chemistry.\(^95\)

By assuming a simple relation between the Hamiltonian and adjacency matrices, namely, H = \(-A\),\(^96\) subgraph centrality for the \(i\)th atom in an atomic cluster may be calculated from

\[
S_i = \sum_{\mu \in \mu} \sum_{k=1}^{N} C_{ik}^2 \exp(-\varepsilon_k) \tag{21}
\]

where \(C_{ik}\) is the \(k\)th MO expansion coefficient associated with basis function \(\mu\) centered on the \(i\)th atom and \(\varepsilon_k\) is the \(k\)th MO energy at the extended Hückel level. Using this centrality, the \(R^2\) value for the correlation in the Mg\(_8\) cluster is increased to 0.76 (see the SI).
3. CONCLUSIONS

The importance of electrons with the highest energy in a molecule or empty orbitals that can accept them is well received in chemistry. On the other hand, the nature of the lowest-energy electrons in a molecule or the orbital that holds them, namely, the lowest occupied molecular orbital (LOMO), has not been given much attention, but we had the audacity to name it the central orbital, exploring the possibility of its use.

Thanks to graph theory, we have learned that LOMO quantifies which atoms have the greatest effect on a network of atoms. LOMO pinpoints which atom is the most important in an aggregate of atoms, or cluster. On the other hand, in an aggregate of atoms, how strong the interaction between one atom and another can also be a measure of centrality. We investigated the relationship between the LOMO coefficient of an atom in a cluster and its binding energy using some s-block metal clusters as examples, and found that there is a fairly good correlation between them. Using a more sophisticated centrality measure such as subgraph centrality, one may further improve the correlation.

There is an urgent need to develop descriptors for predicting adsorption energy in catalytic chemistry because machine learning for catalytic informatics and catalyst development has been active in recent years and seeking for them.97–99 We hope that the utility of LOMO as a descriptor for the binding energy as well as centrality, as revealed in the present study, will provide some hints for these studies.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04913.

Link between the process shown in Figure 4 and Markov chain; effects of a small perturbation added to the Hückel matrix on the molecular orbital energies and distributions; relation between the Perron–Frobenius theorem and Frost’s rule; extended Hückel parameters used in this study; results for Be4, N4, and Mg3 clusters; the use of subgraph centrality; and atomic coordinates of the optimized cluster structures (PDF)

AUTHOR INFORMATION

Corresponding Author
Yuta Tsuji — Institute for Materials Chemistry and Engineering and IRCCS, Kyushu University, Fukuoka 819-0395, Japan; orcid.org/0000-0003-4224-4532; Email: yuta@ms.ifoc.kyushu-u.ac.jp

Author
Kazunari Yoshizawa — Institute for Materials Chemistry and Engineering and IRCCS, Kyushu University, Fukuoka 819-0395, Japan; orcid.org/0000-0002-6279-9722

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.0c04913

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank two anonymous reviewers for their helpful comments. This work was supported by KAKENHI grants (numbers JP17K14440 and JP17H03117) from the Japan Society for the Promotion of Science (JSPS) and the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) through the MEXT projects Integrated Research Consortium on Chemical Sciences, Cooperative Research Program of Network Joint Research Center for Materials and Devices and Elements Strategy Initiative to Form Core Research Center, and by JST-CREST JPMJCR15PS and JST-Mirai JPMJMI18.A2. The computations in this work were primarily performed using the computer facilities at the Research Institute for Information Technology, Kyushu University. Y.T. is grateful for a JSPS Grant-in-Aid for Scientific Research on Innovative Areas (Discrete Geometric Analysis for Materials Design, grant number JP20H04643, and Mixed Anion, grant number JP19H04700).

REFERENCES

(1) Fukui, K.; Yonezawa, T.; Shingu, H. A Molecular Orbital Theory of Reactivity in Aromatic Hydrocarbons. J. Chem. Phys. 1952, 20, 722–725.
(2) Hoffmann, R.; Woodward, R. B. Orbital Symmetries and endo-exo Relationships in Concerted Cycloaddition Reactions. J. Am. Chem. Soc. 1965, 87, 4388–4389.
(3) Hoffmann, R.; Woodward, R. B. Conservation of Orbital Symmetry. Acc. Chem. Res. 1968, 1, 17–22.
(4) Woodward, R. B.; Hoffmann, R. The Conservation of Orbital Symmetry. Angew. Chem., Int. Ed. Engl. 1969, 8, 781–853.
(5) Houk, K. N. Frontier Molecular Orbital Theory of Cycloaddition Reactions. Acc. Chem. Res. 1975, 8, 361–369.
(6) Hoffmann, R. Theoretical Organometallic Chemistry. Science 1981, 211, 995–1002.
(7) Hoffmann, R. Solids and Surfaces: A Chemist’s View of Bonding in Extended Structures; Wiley-VCH: Weinheim, 1988.
(8) Carissan, Y.; Hagebaum-Reignier, D.; Goudard, N.; Humbel, S. HuLiS Code: Lewis embedded in Hückel Theory. http://www.huls.free.fr (accessed August 5, 2020).
(9) Carissan, Y.; Hagebaum-Reignier, D.; Goudard, N.; Humbel, S. Hückel-Lewis Projection Method: A “Weights Watcher” for Mesomeric Structures. J. Phys. Chem. A 2008, 112, 13256–13262.
(10) Kumar, S. A.; Bhaskar, B. L. Computational and Spectral Studies of 3,3’-(propane-1,3-diy1)bis(7,8-dimethoxy-1,3,4,5-tetrahydro-2H-benzo[d]azepin-2-one). Helyon 2019, 5, No. e02420.
(11) Chen, H.-Y.; Chao, I. Effect of Perfluorination on the Charge-Transport Properties of Organic Semiconductors: Density Functional Theory Study of Perfluorinated Pentacene and Sexithiophene. Chem. Phys. Lett. 2005, 401, 539–545.
(12) Yoshizawa, K. An Orbital Rule for Electron Transport in Molecules. Acc. Chem. Res. 2012, 45, 1612–1621.
(13) “frontier, n. and adj.” OECD Online. Oxford University Press, June 2020. Web. 5 August 2020.
(14) Sanghera, P. Quantum Physics for Scientists and Technologists: Fundamental Principles and Applications for Biologists, Chemists, Computer Scientists, and Nanotechnologists; Wiley-Interscience: Hoboken, 2011.
(15) Imamura, A.; Aoki, Y. Helical Molecular Orbitals Around Straight-Chain Polyyne Oligomers as Models for Molecular Devices. Chem. Phys. Lett. 2013, 590, 136–140.
(16) Erkoç, Ș.; Türker, L. Ammonia Deposition in Fullerenes (NH3)n@C60. J. Mol. Struct.: THEOCHEM 2003, 640, 57–61.
(17) Bonchev, D.; Kier, L. B.; Mekenyan, O. Self-Returning Walks and Fractional Electronic Charges of Atoms in Molecules. Int. J. Quantum Chem. 1993, 46, 635–649.
(18) Bonchev, D.; Seitz, W. A.; Gordeva, E. Relative Atomic Moments as Squared Principal Eigenvector Coefficients. J. Chem. Inf. Model. 1995, 35, 237–242.
(19) Gutman, I.; Bonchev, D.; Seitz, W. C.; Gordeva, E. Complementing the Proof of the Limit of Relative Atomic Moments. J. Chem. Inf. Model. 1995, 35, 894–895.
(20) Barysh, M.; Bonchev, D.; Mekenyan, O. Graph Center, Self-Returning Walks, and Critical Pressures of Alkanes. MATCH 1986, 20, 125–140.
(21) Bonchev, D.; Gordeeva, E. Topological Atomic Charges, Valencies, and Bond Orders. J. Chem. Inf. Model. 1995, 35, 383–395.
(22) Estrada, E.; Knight, P. A. First Course in Network Theory; Oxford University Press: New York, 2015.
(23) Redzepovic, I.; Furtula, B.; Gutman, I. MATCH Commun. Math. Comput. Chem. 2020, 84, 229–237.
(24) Bonachich, P. Power and Centrality: A Family of Measures. Am. J. Sociol. 1987, 92, 1170–1182.
(25) Bonachich, P. Factoring and Weighting Approaches to Clique Identification. J. Math. Sociol. 1972, 2, 113–120.
(26) Dong, E.; Du, H.; Gardner, L. An Interactive Web-Based Dashboard to Track COVID-19 in Real Time. Lancet Infect. Dis. 2020, 20, S33–S34.
(27) Spiziri, L. Justification and Application of Eigenvector Centrality. Algebra Geom. Eig. Netw. 2011, Retrieved from https://www.math.washington.edu/~morrow/336_11/papers/leo.pdf (accessed August 5, 2020).
(28) Trinajstic, N. Chemical Graph Theory; CRC Press: Boca Raton, 1992.
(29) Sharma, R.; Shah, S.; Shankar, A. Algebra I: A Basic Course in Abstract Algebra; Pearson: London, 2011.
(30) Chennubhotla, C.; Jepson, A. Hierarchical Eigensolver for Transition Matrices in Spectral Methods. In Advances in Neural Information Processing Systems; Saul, L. K.; Weiss, Y.; Bottou, L., Eds.; MIT Press: Cambridge, 2005; Vol. 17, pp 273–280.
(31) Dehmer, M., Ed., Structural Analysis of Complex Networks; Birkhäuser: Boston, 2011.
(32) Estrada, E. Graph and Network Theory. In Mathematical Tools for Physicists; Grinfeld, M., Ed.; J. Wiley: Weinheim, 2014; pp 111–157.
(33) Keeling, M. J.; Eames, K. T. D. Networks and Epidemic Spreading in Random Rectangular Networks. Phys. Rev. E 2016, 94, No. 052316.
(34) Keeling, M. J.; Eames, K. T. D. Networks and Epidemic Models. J. R. Soc. Interface 2005, 2, 295–307.
(35) Estrada, E.; Meloni, S.; Sheerin, M.; Moreno, Y. Epidemic Spreading in Random Rectangular Networks. Phys. Rev. E 2016, 94, 052316.
(36) Gomez, S.; Arenas, A.; Borge-Holthoefer, J.; Meloni, S.; Moreno, Y. Discrete-Time Markov Chain Approach to Contact-Based Disease Spreading in Complex Networks. Europhys. Lett. 2010, 89, 38009.
(37) Dehmer, M.; Emmert-Streib, F., Eds., Quantitative Graph Theory: Mathematical Foundations and Applications; Chapman and Hall/CRC: Boca Raton, 2014.
(38) Estrada, E. Back to the Origins. Using Matrix Functions of Hückel Hamiltonian for Quantum Interference. In Quantum Chemistry at the Dawn of the 21st Century; Chakraborty, T.; Carbo-Dorca, R., Eds; Apple Academic Press: Oakville, 2018; pp 445–468.
(39) Bonchev, D.; Mekenyan, O., Eds. Graph Theoretical Approaches to Chemical Reactivity; Kluwer Academic Publishers: Dordrecht, 1994.
(40) Bonchev, D. Chemical Graph Theory: Introduction and Fundamentals, Vol. 1; CRC Press: Boca Raton, 1991.
(41) George, A. B.; Weber, H. J.; Harris, F. E. Mathematical Methods for Physicists. In A Comprehensive Guide; Academic Press: Cambridge, 2013.
(42) Monahan, J. F. Numerical Methods of Statistics; Cambridge University Press: New York, 2011.
(43) Lee, J. G. Computational Material Science: An Introduction; CRC Press: Boca Raton, 2012.
(44) Masuda, N.; Lambiotte, R. A Guide to Temporal Networks; World Scientific: London, 2016.
(45) Bapat, R. B. Graphs and Matrices; Springer Hindustan Book Agency: London, 2010.
(46) Albright, T. A.; Burdett, J.; Whangbo, M.-H. Orbital Interactions in Chemistry, 2nd ed.; Wiley: Hoboken, 2013.
(47) Li, X.; Shi, Y.; Gutman, I. Graph Energy; Springer: New York, 2012.
(48) Boudin, F. In A Comparison of Centrality Measures for Graph-Based Keyphrase Extraction, Proceedings of the Sixth International Joint Conference on Natural Language Processing, 2013; pp 834–838.
(49) Erciyes, K. Complex Networks: An Algorithmic Perspective, 1st ed.; CRC Press: Boca Raton, 2014.
(50) Sah, C. S.; Kasim, S.; Fudzee, M. F.; Ping, J. M.; Mohamad, M. S.; Saedduin, R. R.; Ismail, M. A. An Enhanced Topologically Significant Directed Random Walk in Cancer Classification Using Gene Expression Datasets. Saudi J. Biol. Sci. 2017, 24, 1828–1841.
(51) Iyer, S.; Killingback, T.; Sundaram, B.; Wang, Z. Attack Robustness and Centrality of Complex Networks. PLoS One 2013, 8, No. e59613.
(52) Tsuji, Y.; Estrada, E.; Movassagh, R.; Hoffmann, R. Quantum Interference, Graphs, Walks, and Polynomials. Chem. Rev. 2018, 118, 4887–4911.
(53) Tsuji, Y.; Estrada, E. Influence of Long-Range Interactions on Quantum Interference in Molecular Conduction. A Tight-Binding (Hückel) Approach. J. Chem. Phys. 2019, 150, No. 204123.
(54) Morikawa, T.; Narita, S.; Klein, D. Molecular Electric Conductance and Long-Bond Structure Counting for Conjugated-Carbon Nano-Structures. Chem. Phys. Lett. 2005, 402, 554–558.
(55) Wei, T. H. The Algebraic Foundations of Ranking Theory Theses; Cambridge Univ.: Cambridge, 1952.
(56) Berge, C. Théorie Des Graphes Et Ses Applications; Dunod: Paris, 1958.
(57) Cretković, D.; Rowlinson, P.; Simić, S. Eigenspaces of Graphs; Cambridge Univ. Press: Cambridge, 1997.
(58) Burdett, J. K.; Lee, S. Moments and the Energies of Solids. J. Am. Chem. Soc. 1985, 107, 3050–3063.
(59) Stacey, T. E.; Fredrickson, D. C. Structural Acid–Base Chemistry in the Metallic State: How μ3-Neutralization Drives Interfaces and Helices in Ti23Mn25. Inorg. Chem. 2013, 52, 8349–8359.
(60) Feynman, R. P.; Hibbs, A. R. Quantum Mechanics and Path Integrals; McGraw-Hill: New York, 1965.
(61) Nagao, H.; Nishikawa, K.; Aono, S. The Hückel Model by Means of the Path Integral Method. Chem. Phys. Lett. 1992, 190, 97–103.
(62) Fan, X.; Zheng, W. T.; Kuo, J. L.; Singh, D. J. Adsorption of Single Li and the Formation of Small Li Clusters on Graphene for the Anode of Lithium-Ion Batteries. ACS Appl. Mater. Interfaces 2013, 5, 7793–7797.
(63) Brito, B. G. A.; Cândido, L.; Rabelo, J. N. T.; Hai, G.-Q. Binding Energies of Small Lithium Clusters: A Comparison of Different Theoretical Calculations. Chem. Phys. Lett. 2014, 616-617, 212–216.
(64) Kushwaha, A. K.; Nayak, S. K. Wobbled Electronic Properties of Lithium Clusters: Deterministic Approach through First Principles. Phys. E 2018, 97, 368–374.
(65) Cheng, L.; Yang, J. New Insight into Electronic Shells of Metal Clusters: Analogues of Simple Molecules. J. Chem. Phys. 2013, 138, No. 141101.
(66) Glukhotsev, M. N.; von Ragé Schleyer, P. Polyatomic Molecules without Electron-Pair Bonds: High-Spin Trigonal, Tetrahedral, and Octahedral Lithium Clusters. Isr. J. Chem. 1993, 33, 455–466.
(67) Danovich, D.; Shal, S. Bonding with Parallel Spins: High-Spin Clusters of Monovalent Metal Atoms. Acc. Chem. Res. 2014, 47, 417–426.
(68) Donoso, R.; Rüssler, J.; Llano-Gil, S.; Fuentealba, P.; Cárdenas, G. J. Chem. Phys. 2016, 145, No. 094301.
(69) Stillinger, F. H. Exponential Multiplicity of Inherent Structures. Phys. Rev. E 1999, 59, 48–51.
(70) Call, S. T.; Zubarev, D. Y.; Boldyrev, A. I. Global Minimum Structure Searches via Particle Swarm Optimization. J. Comput. Chem. 2007, 28, 1177–1186.
(71) Eberhart, R.; Kennedy, J. A New Optimizer Using Particle Swarm Theory. In *Proceedings of the Sixth International Symposium on Micro Machine and Human Science*; Ieee, 1995; pp 39–43.

(72) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. Crystal Structure Prediction via Particle-Swarm Optimization. *Phys. Rev. B* 2010, 82, No. 094116.

(73) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. CALYPSO: A Method for Crystal Structure Prediction. *Comput. Phys. Commun.* 2012, 183, 2063–2070.

(74) Gao, B.; Gao, P. Y.; Lu, S. H.; Lv, J.; Wang, Y. C.; Ma, Y. M. Interface Structure Prediction via CALYPSO Method. *Sci. Bull.* 2019, 64, 301–309.

(75) Lv, J.; Wang, Y. C.; Zhu, L.; Ma, Y. M. Particle-Swarm Structure Prediction on Clusters. *J. Chem. Phys.* 2012, 137, No. 084104.

(76) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* 1993, 47, 558–561.

(77) Kresse, G., Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal-Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B* 1994, 49, 14251–14269.

(78) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* 1996, 6, 15–50.

(79) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* 1996, 54, 11169–11186.

(80) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868.

(81) Blochl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* 1994, 50, 17953–17979.

(82) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* 1999, 59, 1758–1775.

(83) Kresse, G.; Furthmüller, J. VASP the Guide; http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html (accessed August 5, 2020).

(84) Fournier, R.; Bo Yi Cheng, J.; Wong, A. Theoretical Study of the Structure of Lithium Clusters. *J. Chem. Phys.* 2003, 119, 9444–9454.

(85) Hoffmann, R. An Extended Hückel Theory. I. Hydrocarbons. *J. Chem. Phys.* 1963, 39, 1397–1412.

(86) Alvarez, S. *Table of Parameters for Extended Hückel Calculations*; Universitat de Barcelona: Barcelona, Spain, 1993.

(87) Landrum, G. A.; Glassy, W. V. *YaeHMOP* program is freely available on the web site: http://yaehmop.sourceforge.net/ (accessed August 5, 2020).

(88) Wölfersberg, M.; Helmhholz, L. J. The Spectra and Electronic Structure of the Tetrahedral Ions MnO$_4^{−}$, CrO$_4^{−}$, and ClO$_4^{−}$. *J. Chem. Phys.* 1952, 20, 837–843.

(89) Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl. Crystallogr.* 2011, 44, 1272–1276.

(90) Sharma, R. *Chemistry of Chemical Bonding: Discovery* Publishing House: New Delhi, 2007.

(91) Kronik, L.; Vasiliev, I.; Jain, M.; Chelikowsky, J. R. Ab initio Structures and Polarizabilities of Sodium Clusters. *J. Chem. Phys.* 2001, 115, 4322–4332.

(92) Jellinek, J.; Acioli, P. H. Magnesium Clusters: Structural and Electronic Properties and the Size-Induced Nonmetal-to-Metal Transition. *J. Phys. Chem. A* 2002, 106, 10919–10925.

(93) Xia, X.; Kuang, X.; Lu, C.; Jin, Y.; Merino, G.; Xing, X.; Herrmann, A. Deciphering the Structural Evolution and Electronic Properties of Magnesium Clusters: An Aromatic Homonuclear Metal Mg17 Cluster. *J. Phys. Chem. A* 2016, 120, 7947–7954.

(94) Estrada, E.; Rodríguez-Velázquez, J. A. Subgraph Centrality in Complex Networks. *Phys. Rev. E* 2005, 71, No. 056103.

(95) Estrada, E.; Rodríguez-Velázquez, J. A.; Randić, M. Atomic Branching in Molecules. *Int. J. Quantum Chem.* 2006, 106, 823–832.

(96) Estrada, E.; Hatano, N. Statistical-Mechanical Approach to Subgraph Centrality in Complex Networks. *Chem. Phys. Lett.* 2007, 439, 247–251.