Omni-conducting and omni-insulating molecules

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The source and sink potential model is used to predict the existence of omni-conductors (and omni-insulators): molecular conjugated π systems that respectively support ballistic conduction or show insulation at the Fermi level, irrespective of the centres chosen as connections. *Distinct*, *ipso*, and *strong* omni-conductors/omni-insulators show Fermi-level conduction/insulation for all *distinct* pairs of connections, for all connections via a *single* centre, and for *both*, respectively. The class of conduction behaviour depends critically on the number of non-bonding orbitals (NBO) of the molecular system (corresponding to the nullity of the graph). Distinct omni-conductors have at most one NBO; distinct omni-insulators have at least two NBO; strong omni-insulators do not exist for any number of NBO. Distinct omni-conductors with a single NBO are all also strong and correspond exactly to the class of graphs known as *nut* graphs. Families of conjugated hydrocarbons corresponding to chemical graphs with predicted omni-conducting/insulating behaviour are identified. For example, most fullerenes are predicted to be strong omni-conductors. © *2014 AIP Publishing LLC.*
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I. INTRODUCTION

Ballistic conduction on nano and mesoscopic scales is attracting ever increasing interest with the availability of new materials such as graphene sheets and flakes[1] (potentially in kilogram amounts[2]). One starting point for theoretical accounts of this type of conduction is the study of molecular conjugated structures, where electron transmission is known to be a sensitive function of, amongst others, three major factors, namely, electron energy, contact position, and underlying molecular structure. The field has a long history, and methods continue to be developed.[3] Sophisticated *ab initio* methods for obtaining detailed information on molecular conduction in particular systems have been developed (e.g., Refs. [4–9]). An alternative approach,[10–13] which we take here, is to use qualitative models to focus on generic types of conduction behaviour.

A simple approach which is capable of dealing with π systems is the graph theoretical source and sink potential (SSP) model.[13–22] The present work is concerned with this model and the information that it may give about the interaction of the factors of contact position and molecular structure. In particular, we explore the possibility that some molecular structures may display a much reduced dependence of the predicted transmission on precise positioning of the contacts. Given the difficulties of attaching "wires" with atomic resolution, such insensitivity may have some practical advantages. This motivates our definitions of *omni-conductors* and *omni-insulators* and the search for classes of chemical graphs that conform to these definitions.

A molecule will be modelled by its *molecular graph G*, which represents the carbon skeleton of a conjugated π system. *Chemical graphs* are defined as graphs that are connected and have maximum degree at most three; their vertices represent unsaturated carbon centres and their edges represent the σ-bond framework. If we set aside the dependence of transmission on energy by considering conduction to take place at the Fermi level (corresponding to the zero of energy in the Hückel/SSP model) and consider the molecule to be connected to similar left and right wires via its atoms $\bar{L}$ and $\bar{R}$, a natural question arises: Do conjugated molecular structures exist for which there is conduction (non-zero transmission) at the Fermi level for *all* choices of connections $\bar{L}$ and $\bar{R}$? An equivalent question can be asked about insulation (zero transmission).

We can imagine two types of connection of the wires to "terminal" vertices $\bar{L}$ and $\bar{R}$ in the molecular graph: either the connecting vertices are *distinct*, which is the relevant case for most applications, or they coincide, which is the so-called "*ipso*" case. The fractional transmission of a ballistic electron at the Fermi level for a given connection pair $(\bar{L}, \bar{R})$, which is here calculated within the SSP model, will be denoted $T(0)$. The combination of a graph G and a pair of contact vertices, not necessarily distinct, will be called here a *device*. Hence, from this point of view, there are in principle six interesting classes of molecular graphs and the devices related to them.

1. A molecular graph is said to be a *distinct omni-conductor* if $T(0) \neq 0$ for *all* distinct pairs of connecting vertices, $\bar{L}$ and $\bar{R}$.
2. A molecular graph is said to be an *ipso omni-conductor* if $T(0) \neq 0$ for *all* choices of single-vertex connection, $\bar{L} = \bar{R}$.
3. A molecular graph is said to be a *strong omni-conductor* if it is both a *distinct* and an *ipso* omni-conductor.

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4. A molecular graph is said to be a *distinct omni-insulator* if $T(0) = 0$ for *all* distinct pairs of connecting vertices (terminals), $\bar{L}$ and $\bar{R}$.

5. A molecular graph is said to be an *ipso omni-insulator* if $T(0) = 0$ for *all* choices of single-vertex connection, $\bar{L} = \bar{R}$.

6. A molecular graph is said to be a *strong omni-insulator* if it is both a *distinct* and an *ipso* omni-insulator.

In fact, the sixth class turns out to be empty, as we will prove, but all other classes include molecular graphs of chemical interest.

A molecule with non-bonding orbitals corresponds to a *singular* graph, and the number of non-bonding orbitals is equal to the *nullity*: the number of zero eigenvalues of the adjacency matrix of the graph. It has already been shown that the numbers of non-bonding levels of molecular graphs and subgraphs are important in defining selection rules for Fermi-level conduction of given connection pairs in general,[18] and for graphene-related molecular graphs in particular.[19] Here, it will be demonstrated that nullity is also a crucial factor in characterising omni-conductors and omni-insulators. Specifically, we will prove that *all* distinct omni-conductors have at most one non-bonding orbital whereas *all* distinct omni-insulators have at least two, and will give a complete characterisation of the nullity-one distinct omni-conductors.

The paper is arranged as follows. After a brief summary of the SSP model and graph theoretical background (Sec. II), we give a unified treatment of the selection rules for Fermi-level conduction/insulation of individual devices in terms of characteristic polynomials, nullity of graphs, and vertex types (Secs. III and IV). This leads to existence and characterisation results for the six classes of omni-conductors and insulators (Sec. V). In Sec. VI, explicit calculations for large numbers of graphs in various chemically interesting classes and infinite families are presented, with statistical information about the distribution of the different classes, leading to the conclusion (Sec. VII) that omni-conduction at the Fermi level could be a widely occurring phenomenon.

II. BACKGROUND

A. The SSP model

The SSP Hamiltonian gives a simple model of ballistic conduction of electrons through a conjugated molecule.[12,14,15] In the tight-binding approximation, calculation of the fractional transmission of an electron with given energy reduces to the solution of the Hückel problem under scattering boundary conditions, and hence to an essentially graph theoretical question, as conduction is determined by functions of the characteristic polynomials of four graphs.[13,16–19]

In the SSP model, the transmission function for a molecule that has a carbon skeleton with graph G connected to similar left and right wires via molecular vertices $\bar{L}$ and $\bar{R}$ is given by[13]

$$T(E) = \frac{4\sin^2 q\,(ut - sv)\,\tilde{\beta}^2}{|e^{-2iq}s - e^{-iq}(u+t)\tilde{\beta} + v\tilde{\beta}^2|^2}, \quad (1)$$

where E is the reduced electron energy, defined on a scale where the unit is the molecular resonance integral $|\beta|$, and the zero is the molecular coulomb integral α, which is taken here as the Fermi level. Coulomb integrals are assumed to be equal throughout the device, and the parameter $\tilde{\beta}$ is defined by the values of resonance integrals within wires ($\beta_L = \beta_R$) and between molecule and wire ($\beta_{L\bar{L}} = \beta_{R\bar{R}}$), in units of the molecular resonance integral β (which is the unit for all energies occurring in the model): $\tilde{\beta} = \beta_{L\bar{L}}^2/\beta_L = \beta_{R\bar{R}}^2/\beta_R$. Typically, $\tilde{\beta}^2 \simeq 1/2$.[13,14] The $4\sin^2 q$ factor in (1) acts to confine transmission to the conduction band of the wires. In (1) q is the wavenumber of the electron wave (defined by $E = 2\cos q$, with energy in units of $|\beta|$). The quantities s, t, u, v are the characteristic polynomials $\phi(G, E)$, $\phi(G - \bar{L}, E)$, $\phi(G - \bar{R}, E)$, $\phi(G - \bar{L} - \bar{R}, E)$ of the graphs $G, G - \bar{L}, G - \bar{R}$, and $G - \bar{L} - \bar{R}$, respectively, i.e., they are the determinants

$$
\begin{aligned}
s(E) &= |E\mathbf{I} - \mathbf{A}(G)|, \\
t(E) &= |E\mathbf{I} - \mathbf{A}(G - \bar{L})| = |E\mathbf{I} - \mathbf{A}(G)|^{\bar{L},\bar{L}}, \\
u(E) &= |E\mathbf{I} - \mathbf{A}(G - \bar{R})| = |E\mathbf{I} - \mathbf{A}(G)|^{\bar{R},\bar{R}}, \\
v(E) &= |E\mathbf{I} - \mathbf{A}(G - \bar{L} - \bar{R})| = |E\mathbf{I} - \mathbf{A}(G)|^{\bar{L}\bar{R},\bar{L}\bar{R}},
\end{aligned}
\quad (2)
$$

where $\mathbf{I}$ is the identity matrix of the appropriate dimension and $\mathbf{A}(H)$ is the adjacency matrix of a graph H. Note that G must be a connected graph if it is to represent a conjugated π system; deletion of vertices as in $G - \bar{L}$, $G - \bar{R}$, and $G - \bar{L} - \bar{R}$ may result in a disconnected graph. The superscripts on the determinants indicate deletion of a set of rows and columns, corresponding to the deletion of vertices of G. Another quantity that is important in the determination of transmission is the combination $ut - sv$, which is equal to a squared polynomial[23]

$$j^2(E) = u(E)t(E) - s(E)v(E) = (|E\mathbf{I} - \mathbf{A}(G)|^{\bar{L},\bar{R}})^2. \quad (3)$$

It can be shown that $j(E)$ is the entry at position $\bar{L}, \bar{R}$ of the adjugate matrix adj($E\mathbf{I}-\mathbf{A}$) and, if the matrix $(E\mathbf{I}-\mathbf{A})$ is invertible, then at any energy E, $j(E)$ is proportional to the $\bar{L}, \bar{R}$ entry in the inverse $(E\mathbf{I}-\mathbf{A})^{-1}$, with constant of proportionality equal to the determinant of the matrix.[24] The usual *distinct* case for a molecular device has $\bar{L} \neq \bar{R}$. In the *ipso* case, where both wires contact a single atom, $\bar{L} = \bar{R}$, polynomials t and u are identical, and v is deleted from the equations.

As $E = 2\cos q$, the full energy dependence of the transmission (1) is given by

$$T(E) = \frac{(4 - E^2)j^2\tilde{\beta}^2}{[(s - v\tilde{\beta}^2)^2 + (u+t)^2\tilde{\beta}^2] - E(s + v\tilde{\beta}^2)(u+t)\tilde{\beta} + E^2 sv\tilde{\beta}^2}, \quad (4)$$

and for transmission of electrons at the Fermi level, the limit is taken according to

$$T(0) = \lim_{E \to 0} T(E).$$

In the analysis that follows, we assume that $\tilde{\beta}^2$ is not a "special value," i.e., we assume that $\tilde{\beta} \neq 0$ and that $(s - v\tilde{\beta}^2)^2 \neq 0$ at the energy of interest. Thus, effectively, questions about the vanishing of $(s - v\tilde{\beta}^2)^2$ can be answered by inspection of $s^2 + v^2$. Physically, the claim is that even if $\tilde{\beta}$ happens to take one of the special values, there will always be a "nearby" device where it does not, and to which our generic conclusions will apply.

It is straightforward to show that the zero-energy limit of (4) is equivalent to the simpler expression

$$T(0) = \lim_{E \to 0} \frac{4j^2\tilde{\beta}^2}{[(s - v\tilde{\beta}^2)^2 + (u + t)^2\tilde{\beta}^2]}. \tag{5}$$

The question for a qualitative treatment is whether $T(0)$ is zero, or not. It has been shown[18] that the answer to this question for a given connection pattern can be decided in almost all cases simply by counting the zero eigenvalues of the graph and of its vertex-deleted subgraphs, which leads to a set of "selection-rules" for conduction. In order to exploit this insight further, and make a systematic investigation of the questions of omni-conduction and insulation, it is necessary to understand how the outcome depends on the intrinsic properties of the connecting vertices relative to the nullspace vectors. To help with this task, we introduce some notation and results from graph theory and linear algebra in Sec. II B. More detail on the mathematical arguments can be found in Ref. 25.

B. Graph theoretical notation

The eigenvalue problem for the adjacency matrix $\mathbf{A}$ of a graph is

$$\mathbf{A}\mathbf{c}^i = E_i\mathbf{c}^i, \tag{6}$$

where for some non-zero vector $\mathbf{c}^i$ the matrix has an eigenvalue E_i. For a n-vertex graph G, the n values of E_i form the *spectrum* of G. The eigenvectors $\mathbf{c}^i$ of $\mathbf{A}$ correspond to π molecular orbitals in the Hückel approximation and without loss of generality the entries $\mathbf{c}_r^i$ can be taken to be real. (Here the subscript r denotes the vertex and the superscript i the molecular orbital.) For conduction of a connected π-system G at the Fermi level, $(E = 0)$, it is critical to consider the number of non-bonding orbitals. This number is the multiplicity g_s of the zero eigenvalue in the spectrum, also called the *nullity* of the graph. A graph is *singular* if $g_s > 0$. We shall organise the eigenvectors $\mathbf{c}^i$ of the adjacency matrix such that the g_s eigenvectors in the nullspace are placed first.

A vector $\mathbf{c}$ in the nullspace of the adjacency matrix $\mathbf{A}$ is said to be a *kernel eigenvector* of G. For singular graphs the vertices can be partitioned into *core* and *core-forbidden* vertices. A *core-forbidden vertex* (CFV) corresponds to a zero entry in *every* kernel eigenvector. A vertex corresponding to a non-zero entry for *some* kernel eigenvector is a *core vertex* (CV). *Core graphs* are defined as singular graphs in which each vertex is a core vertex. A core graph of nullity one is

termed a *nut graph*. Nut graphs are connected, non-bipartite and have no vertices of degree one.[26]

The Interlacing Theorem[27] states that the eigenvalues of a vertex-deleted subgraph interlace the eigenvalues of the parent graph. As a consequence, the multiplicity (number of repetitions) of any one eigenvalue in the spectrum changes by at most one on deletion of a vertex. A necessary and sufficient condition for the nullity to *decrease* on deletion of a vertex from a graph is that the deleted vertex is a CV. Therefore, by interlacing, deletion of a CFV either leaves the nullity unchanged or increases it by one. We call a CFV *upper* where the nullity increases and *middle* where the nullity remains unchanged. In this language, a CV is said to be *lower*. Other terms are also used in the literature: the CFVs are referred to as peripheral vertices; upper vertices are variously termed maximal,[28] Parter, or rank-strong vertices;[29] middle vertices are called intermediate[28] or rank-neutral;[29] and lower vertices are also called downer or rank-weak vertices.[29] Bipartite graphs do not have middle vertices.

C. Characteristic polynomials

For a graph G of nullity g_s, the characteristic polynomial is

$$s(E) = \prod_{i=1}^{n}(E - E_i) = s_0(E)E^{g_s}, \tag{7}$$

where $s_0(E)$ is the product over the non-nullspace

$$s_0(E) = \prod_{i=g_s+1}^{n}(E - E_i). \tag{8}$$

Note that $s_0(0) \neq 0$. We will write s_0 for $s_0(E)$, s for $s(E)$, etc., where there is no ambiguity.

The other polynomials $t(E)$, $u(E)$, $j(E)$, and $v(E)$ can be expressed in terms of the eigenvector entries $\{c_{\bar{L}}^i\}$ and $\{c_{\bar{R}}^i\}$ associated with the connecting vertices $\bar{L}$ and $\bar{R}$, as described in Ref. 25. (As noted earlier, we are assuming that all eigenvector entries are real.) These polynomials are

$$t(E) = \sum_{i=1}^{n}\left(c_{\bar{L}}^i\right)^2\prod_{j\neq i}(E - E_j) = \sum_{i=1}^{n}\frac{\left(c_{\bar{L}}^i\right)^2}{E - E_i}s_0(E)E^{g_s}, \tag{9}$$

$$u(E) = \sum_{i=1}^{n}\left(c_{\bar{R}}^i\right)^2\prod_{j\neq i}(E - E_j) = \sum_{i=1}^{n}\frac{\left(c_{\bar{R}}^i\right)^2}{E - E_i}s_0(E)E^{g_s}, \tag{10}$$

$$j(E) = \sum_{i=1}^{n}\left(c_{\bar{L}}^i c_{\bar{R}}^i\right)\prod_{j\neq i}(E - E_j) = \sum_{i=1}^{n}\frac{c_{\bar{L}}^i c_{\bar{R}}^i}{E - E_i}s_0(E)E^{g_s}. \tag{11}$$

Since the first g_s eigenvectors belong to the nullspace, each polynomial can be split into two sums that differ in their

explicit dependence on E:

$$t(E) = \sum_{i=1}^{g_s} \left(c_{\bar{L}}^i\right)^2 s_0(E)E^{g_s-1} + \sum_{i=g_s+1}^{n} \frac{\left(c_{\bar{L}}^i\right)^2}{E-E_i} s_0(E)E^{g_s}$$

$$= t_b E^{g_s-1} + t_a E^{g_s}, \tag{12}$$

$$u(E) = \sum_{i=1}^{g_s} \left(c_{\bar{R}}^i\right)^2 s_0(E)E^{g_s-1} + \sum_{i=g_s+1}^{n} \frac{\left(c_{\bar{R}}^i\right)^2}{E-E_i} s_0(E)E^{g_s}$$

$$= u_b E^{g_s-1} + u_a E^{g_s}, \tag{13}$$

$$j(E) = \sum_{i=1}^{g_s} c_{\bar{L}}^i c_{\bar{R}}^i s_0(E)E^{g_s-1} + \sum_{i=g_s+1}^{n} \frac{c_{\bar{L}}^i c_{\bar{R}}^i}{E-E_i} s_0(E)E^{g_s}$$

$$= j_b E^{g_s-1} + j_a E^{g_s}. \tag{14}$$

Hence, using (3), the characteristic polynomial for the two-vertex deleted graph, $v(E)$, splits into three:

$$v(E) = v_c E^{g_s-2} + v_b E^{g_s-1} + v_a E^{g_s}, \tag{15}$$

where

$$v_a = \frac{1}{s_0}\left(u_a t_a - j_a^2\right) = \frac{1}{2}s_0 \sum_{i=g_s+1}^{n}\sum_{j=g_s+1}^{n} \frac{\left(c_{\bar{L}}^i c_{\bar{R}}^j - c_{\bar{L}}^j c_{\bar{R}}^i\right)^2}{(E-E_i)(E-E_j)}, \tag{16}$$

$$v_b = \frac{1}{s_0}(u_a t_b + u_b t_a - 2 j_a j_b) = s_0 \sum_{i=1}^{g_s}\sum_{j=g_s+1}^{n} \frac{\left(c_{\bar{L}}^i c_{\bar{R}}^j - c_{\bar{L}}^j c_{\bar{R}}^i\right)^2}{E-E_j}, \tag{17}$$

$$v_c = \frac{1}{s_0}\left(u_b t_b - j_b^2\right) = \frac{1}{2}s_0 \sum_{i=1}^{g_s}\sum_{j=1}^{g_s} \left(c_{\bar{L}}^i c_{\bar{R}}^j - c_{\bar{L}}^j c_{\bar{R}}^i\right)^2, \tag{18}$$

and in particular

$$j_a^2 = u_a t_a - s_0 v_a, \tag{19}$$

$$j_a j_b = \frac{1}{2}(u_a t_b + u_b t_a - s_0 v_b), \tag{20}$$

$$j_b^2 = u_b t_b - s_0 v_c, \tag{21}$$

so that v_a, v_b, and v_c can be derived directly from the seven quantities s_0, t_a, ... j_b. All the above expressions apply to cases with $g_s \geq 2$. For $g_s = 1$, the term in v_c is to be set to zero, and, for $g_s = 0$, only the terms in t_a, u_a, j_a, and v_a are present.

An expression for $T(E)$ can now be assembled, and its limit taken using the numerator and denominator terms from (5). The numerator is

$$4\tilde{\beta}^2 j^2 = 4\tilde{\beta}^2\left(j_a^2 E^2 + 2 j_a j_b E + j_b^2\right)E^{2g_s-2}, \tag{22}$$

TABLE I. The seven conditions for insulation.

$g_s = 0$	$j_a = 0$		
$g_s = 1$	$\begin{cases} j_b = 0 \text{ and } j_a = 0 \\ \text{or} \\ j_b = 0 \text{ and } j_a \neq 0 \end{cases}$	$\begin{cases} u_b + t_b \neq 0 \\ \text{or} \\ v_b \neq 0 \end{cases}$	,
$g_s > 1$	$\begin{cases} v_c \neq 0 \\ \text{or} \\ v_c = 0 \end{cases}$	$\begin{cases} j_b = 0 \text{ and } j_a \neq 0 \text{ and } v_b \neq 0 \text{ and } u_b + t_b \neq 0 \\ \text{or} \\ j_b = 0 \text{ and } j_a = 0 \end{cases}$	.

and the denominator is

$$(s - \tilde{\beta}^2 v)^2 + (u+t)^2 \tilde{\beta}^2$$

$$= \Big\{ E^4[(s_0 - \tilde{\beta}^2 v_a)^2 + (u_a + t_a)^2 \tilde{\beta}^2]$$

$$+ E^3[-2v_b(s_0 - v_a\tilde{\beta}^2)\tilde{\beta}^2 + 2(u_a + t_a)(u_b + t_b)\tilde{\beta}^2]$$

$$+ E^2[v_b^2 - 2v_c(s_0 - v_a\tilde{\beta}^2) + (u_b + t_b)^2]\tilde{\beta}^2$$

$$+ E[2v_b v_c]\tilde{\beta}^4 + v_c^2\tilde{\beta}^4\Big\} E^{2g_s-4}. \tag{23}$$

As both numerator and denominator may vanish at $E = 0$, it is not sufficient simply to examine whether j vanishes to determine the conduction or insulation behaviour of a device with a given pair of contacts. In general, it is necessary to delve more deeply into the cancellation behaviour of the numerator and denominator as E approaches zero.

The advantage of the present formulation for $T(E)$ is that the conductive properties of all devices based on a given molecular graph can be determined from a simple calculation of the eigenvectors and eigenvalues of G alone. No separate calculations on the n vertex-deleted graphs $G - w$ or the $n(n-1)/2$ double-deleted graphs $G - w - z$ are required. This gives the basis for an efficient computational scheme for identifying omni-conductors and omni-insulators. Conditions for insulation or conduction for a distinct pair of contact vertices in a graph with a particular nullity are easily deduced (Tables I and II); analogous conditions for ipso connections are derived by setting $v_a = v_b = v_c = 0$, $u_a = t_a$, and $u_b = t_b$.

TABLE II. The seven conditions for conduction.

$g_s = 0$	$j_a \neq 0$		
$g_s = 1$	$\begin{cases} j_b \neq 0 \\ \text{or} \\ j_b = 0 \text{ and } j_a = 0 \text{ and } u_b + t_b = 0 \text{ and } v_b = 0, \end{cases}$	$\begin{cases} u_b + t_b \neq 0 \\ \text{or} \\ v_b \neq 0 \end{cases}$	
$g_s > 1$	$\begin{cases} v_c = 0 \text{ and } j_b \neq 0 \\ \text{or} \\ v_c = 0 \text{ and } j_b = 0 \text{ and } j_a \neq 0 \text{ and } u_b + t_b = 0 \text{ and } v_b = 0. \end{cases}$	$\begin{cases} u_b + t_b \neq 0 \\ \text{or} \\ v_b \neq 0 \end{cases}$	

The reader interested only in the results could now skip to Sec. V, where the global deductions about classes of conductors are summarised, and then to Sec. VI where results for specific families of chemical graphs are described.

III. DEVICES AND VARIETIES

The various contributions u_a to v_c have different limiting behaviour, depending on the types of the contact vertices. In particular, if the characteristic polynomial of a vertex-deleted subgraph $G - w$ of a graph G (with w a generic vertex) is cast in the form

$$\phi(G - w, E) = f_b(E)E^{g_s - 1} + f_a(E)E^{g_s}, \qquad (24)$$

then the values of f_a and f_b at $E = 0$ distinguish the three types of vertex and their effect on the nullity as follows:

Vertex w	nullity of $G - w$	
Lower (CV)	is reduced by one to $g_s - 1$	$f_b(0) \neq 0$
Middle (CFV)	remains unchanged at g_s	$f_b(0) = 0$ and $f_a(0) \neq 0$
Upper (CFV)	is increased by one to $g_s + 1$	$f_b(0) = 0$ and $f_a(0) = 0$

In principle, there are 64 types of devices, depending on which of the six parameters u_b, t_b, v_b, v_c, j_a, and j_b vanish at $E = 0$, but not all combinations are possible, because of the interlacing theorem, and not all are independent, as $\bar{L}$ and $\bar{R}$ play symmetrical roles. A device with distinct connections ($\bar{L} \neq \bar{R}$) falls under one of three categories:

Category (1), both $\bar{L}$ and $\bar{R}$ are CV;
Category (2), exactly one of $\bar{L}$ and $\bar{R}$ is a CV, and the other is a CFV; and
Category (3), both $\bar{L}$ and $\bar{R}$ are CFV.

This leads us to define six main *varieties* of connection pairs:

Variety 1: two CV connections,
Variety 2a: one CV connection and one CFV middle,
Variety 2b: one CV connection and one CFV upper,
Variety 3a: two CFV upper connections,
Variety 3b: one CFV middle connection and one CFV upper,
Variety 3c: two CFV middle connections.

Varieties 1 and 2 are characterised by $t_b(0) \neq 0$ and/or $u_b(0) \neq 0$. Recall that $t_b(0) \neq 0$ iff $\bar{L}$ is a CV, and $u_b(0) \neq 0$ iff $\bar{R}$ is a CV. The varieties can be further subdivided into types distinguished by the behaviour at $E = 0$ of t, u, v, or j. A further subdivision of varieties can be based on the relative nullities of G, $G - \bar{L}$, $G - \bar{R}$, and $G - \bar{L} - \bar{R}$, which in turn are restricted by the operation of the Interlacing Theorem.

The final set of 12 device varieties is summarised in Table III, where details of the properties of the characteristic polynomials at $E = 0$, and the conclusions that can be drawn about their conduction/insulation behaviour, are also listed.

Every variety is realised in some chemical graph, and a single molecular graph may have connection pairs of several varieties. The table also gives the correspondence with the 11 cases previously used to derive the nullity-based selection rules for molecular conduction.[18] Devices with distinct connections conduct or not, depending on four selection rules based on the quantities g_s, g_t, g_u, g_v, which are the numbers of zero roots of the four characteristic polynomials s, t, u, and v, respectively. We write $s(0) = s_0 E^{g_s}$, $t(0) = t_0 E^{g_t}$, $u(0) = u_0 E^{g_u}$, and $v(0) = v_0 E^{g_v}$, where s_0, t_0, u_0, and v_0 are all non-zero. The selection rules are then as follows.[18]

Rule (i) For bipartite G, the system conducts at the Fermi level iff

$$g_s = g_v \text{ and } g_t = g_u. \qquad (25)$$

TABLE III. A characterization of devices (G, y, z). The nullity signature (g_s, g_t, g_u, g_v) lists the numbers of zero eigenvalues of the graphs G, $G - \bar{L}$, $G - \bar{R}$, and $G - \bar{L} - \bar{R}$. The 12 varieties defined from the nullity signature in the present paper are correlated with the 11 cases defined in the earlier treatment of the nullity selection rules;[18] the variety/case marked 3c(iiB) and ⋆7 corresponds to the so-called accidental situation, where all four graphs have equal nullity and $j_a(0)^2 = u_a(0)t_a(0) - s_0(0)v_a(0) = 0$, but the terms $u_a(0)t_a(0)$ and $s_0(0)v_a(0)$ are individually non-zero.

Kind	(g_s, g_t, g_u, g_v)	Variety	Case[18]	Conduction?
Two CVs		1		
	$(g_s, g_s - 1, g_s - 1, g_s - 2)$	1(i)	11	Insulation
	$(g_s, g_s - 1, g_s - 1, g_s)$	1(ii)	9	Conduction
	$(g_s, g_s - 1, g_s - 1, g_s - 1)$	1(iii)	10	Conduction
CV and CFV		2		
	$(g_s, g_s + 1, g_s - 1, g_s)$	2a	5	Insulation
	$(g_s, g_s, g_s - 1, g_s - 1)$	2b	8	Insulation
Two CFVs		3		
	$(g_s, g_s + 1, g_s + 1, g_s)$	3a(i)	2	Conduction
	$(g_s, g_s + 1, g_s + 1, g_s + 2)$	3a(ii)	1	Insulation
	$(g_s, g_s + 1, g_s, g_s + 1)$	3b(i)	3	Insulation
	$(g_s, g_s + 1, g_s, g_s)$	3b(ii)	4	Conduction
	$(g_s, g_s, g_s, g_s + 1)$	3c(i)	6	Conduction
	(g_s, g_s, g_s, g_s) and $j_a(0) \neq 0$	3c(iiA)	7	Conduction
	(g_s, g_s, g_s, g_s) and $j_a(0) = 0$	3c(iiB)	⋆7	Insulation

Rule (ii) For non-bipartite G where the four graphs G, $G - \bar{L}$, $G - \bar{R}$, and $G - \bar{L} - \bar{R}$ do not *all* have the same number of zero eigenvalues, the system conducts at the Fermi level iff

$$\min\{(g_s + g_v)/2, (g_t + g_u)/2\} = \min\{g_s, g_t, g_u, g_v\}. \tag{26}$$

Rule (iii) For non-bipartite G with equal numbers of zero eigenvalues for all of G, $G - \bar{L}$, $G - \bar{R}$, or $G - \bar{L} - \bar{R}$, i.e., $g = g_s = g_t = g_u = g_v$, the system conducts at the Fermi level iff j^2 is non-vanishing after factoring out the $2g_s$ trivial zero roots.

Rule (iv) For the *ipso* device: if G has g_s zero eigenvalues, then $T(0) = 0$ for $g_t = g_s + 1$, $0 < T(0) < 1$ for $g_t = g_s$, and $T(0) = 1$ for $g_t = g_s - 1$, i.e., the system conducts at the Fermi level iff

$$g_t \leq g_s. \tag{27}$$

(In fact, this condition is equivalent to requiring that the connection vertex is not an upper CFV.)

The extra utility of thinking about classification of vertices by CV and CFV types is that it gives a different way of detecting when and why certain cases can occur. It also leads to the possibility of deriving "super selection rules" for omni-conductors and omni-insulators that deal simultaneously with all devices based on given graphs, as will be demonstrated in Sec. V. Some relationships that link the types of the connection vertices with the conduction behaviour of the device and are easily proved include the following.

Proposition 3.1. A device with two core vertices as connections (Variety 1) is an insulator at $E = 0$ iff it is of Variety 1(i), i.e., has $g_v = g_s - 2$.

Proposition 3.2. For Variety 2 connections, i.e., with one CV and one CFV, there is no conduction at $E = 0$.

Connections of Variety 3, where both are CFV, yield more mixed results. In Variety 3c(ii), $g_v = g_s$, v_a is non-zero at $E = 0$, and two cases may occur: either $j_a \neq 0$ at $E = 0$, or j_a has more than one zero. The first case is Variety 3c(iiA), and the device conducts. The second is Variety 3c(iiB), and the device is an insulator. Both varieties are included under a single "Case 7" in the classification by nullity signature that was used in the previous treatment;[18] in the present case, 3c(iiB) corresponds to the "accidental" subcase of Case 7, where $u_0 t_0 - s_0 v_0$ vanishes.

IV. TRANSMISSION OF DEVICES

The considerations of Sec. III lead to some general conclusions based on the types of connection vertex.

A. Distinct connections

1. Graphs of nullity $g_s = 0$

A simple criterion emerges for non-singular graphs, namely, that Fermi insulation or conduction across $\bar{L}$ and $\bar{R}$

depends only on whether j_a vanishes or not at $E = 0$, as the denominator in (5) does not vanish for $g_s = 0$. Furthermore, for nullity $g_s = 0$, the entry in position $\bar{L}$, $\bar{R}$ of $(E\mathbf{I} - \mathbf{A})^{-1}$ is equal to $j_a(E)$ divided by the determinant $|E\mathbf{I} - \mathbf{A}|$.[24] Therefore,

Theorem 4.1 *A necessary and sufficient condition for conduction at $E = 0$ of a non-singular graph with connection vertices $\bar{L}$, $\bar{R}$ is that $(\mathbf{A}^{-1})_{\bar{L}, \bar{R}} \neq 0$.*

Note that as the determinant $|\mathbf{A}|$ is non-zero for a non-singular graph, we could equally well test the adjugate $adj(\mathbf{A})$.

2. Graphs of nullity $g_s = 1$

For graphs of nullity one, there is an analogous but weaker condition for conductivity, based on the adjugate matrix.

Theorem 4.2. *A sufficient condition for conduction at $E = 0$ of a device based on a graph of nullity one with connection vertices $\bar{L}$ and $\bar{R}$ is that $\bar{L}$ and $\bar{R}$ are core vertices and $adj(\mathbf{A})_{\bar{L}, \bar{R}} \neq 0$.*

Note that as the entry in $adj(\mathbf{A})$ is non-zero for every core-core pair in a graph with nullity one, this implies that *all* core-core-pairs are conducting for graphs with $g_s = 1$. Moreover, it is straightforward to show from Table III that, for $g_s = 1$, when the pair $\bar{L}$, $\bar{R}$ consists of one core and one core-forbidden vertex (hence $g_t = g_s - 1$ and $g_v = g_s$ or $g_v = g_s - 2$), the device is insulating. This case can be recognised from the adjugate, since for a CV/CFV pair the off-diagonal entry $adj(\mathbf{A})_{\bar{L}\bar{R}}$ is zero and exactly one of $adj(\mathbf{A})_{\bar{L}\bar{L}}$ and $adj(\mathbf{A})_{\bar{R}\bar{R}}$ is non-zero, with the non-zero entry corresponding to the core vertex.[30] Behaviour of devices where both $\bar{L}$ and $\bar{R}$ are core-forbidden depends on the combinations of upper and middle types, as detailed by the selection rules (Table IV).

3. Graphs of nullity $g_s > 1$

When the nullity is larger, the situation for core-core pairs is more complicated, but we do have one useful statement.

Theorem 4.3. *A device where both $\bar{L}$ and $\bar{R}$ are core vertices and $g_s \geq 2$ is insulating if the nullity of $G - \bar{L} - \bar{R}$ is $g_s - 2$, i.e., if $\bar{L}$ is a core vertex of $G - \bar{R}$ and $\bar{R}$ is a core vertex of $G - \bar{L}$.*

TABLE IV. Classification of omni-conductors and omni-insulators by class and nullity. NONE indicates classes unrealisable by connected graphs. Of the nine realisable classes, two are precisely the class of nut graphs (denoted NUT). Other realisable classes are simply marked SOME.

	Non-singular	Nullity one	Nullity $\geq$ two
Distinct omni-conductor	SOME	NUT	NONE
Ipso omni-conductor	SOME	SOME	SOME
Strong omni-conductor	SOME	NUT	NONE
Distinct omni-insulator	NONE	NONE	SOME
Ipso omni-insulator	SOME	NONE	NONE
Strong omni-insulator	NONE	NONE	NONE

The significance of this apparently technical statement derives from the fact that *all* graphs with $g_s \geq 2$ have at least one such core-core pair. The existence of this pair is easily proved using the idea of *vertex representatives* of the nullspace of a graph.[31,32] The essential idea is that for $g_s \geq 2$ it is always possible to construct g_s independent (not necessarily orthogonal or normalised) kernel eigenvectors such that when these vectors are written out as rows with core vertices occurring first, the entries for the first g_s vertices form a $g_s \times g_s$ identity matrix. A consequence of taking this special form of the vectors is that removal of any two of the chosen core vertices leads to a graph with nullity $g_v = g_s - 2$. Hence, *every* graph with $g_s \geq 2$ gives rise to at least one device with distinct connections that is insulating at the Fermi level.

Note that it is possible to find graphs with $g_s \geq 2$ where every vertex is a CV and hence every pair of connections $\bar{L}$ and $\bar{R}$ leads to insulation. Graphs of this type have been called *uniform-core* graphs.[25]

B. Ipso connections

For ipso connections, the formula for transmission (5) reduces to a single form, irrespective of the nullity of the graph:

$$T(E) = \frac{4\tilde{\beta}^2 t^2}{s_0{}^2 + 4\tilde{\beta}^2 t^2}. \qquad (28)$$

If $t_b \neq 0$ the device conducts. If $t_b = 0$ then either $t_a(0) \neq 0$, giving conduction, or $t_a(0) = 0$, giving insulation. The equivalents for ipso devices of the various statements made in Sec. III A about distinct devices are as follows.

Theorem 4.4. *A necessary and sufficient condition for conduction at $E = 0$ of a non-singular graph with connection vertices $\bar{L} = \bar{R}$ is that $(\mathbf{A}^{-1})_{\bar{L},\bar{L}} \neq 0$.*

For non-singular graphs $t = t_a(E)$, and the device conducts if and only if $t_a(0) \neq 0$. For singular graphs, the CVs and CFVs are distinguished by the value of t_b. Moreover, the value of $t_a(0)$ distinguishes between ipso connections at middle and upper vertices, for which there is conduction and insulation, respectively.

Theorem 4.5. *For an ipso connection in a singular graph, there is conduction at $E = 0$ when the connecting vertex v is a CV or a middle CFV, and conversely, insulation when the connecting vertex is an upper CFV.*

V. IMPLICATIONS FOR OMNI-CONDUCTORS AND OMNI-INSULATORS

The results described in Sec. IV can be assembled to give a global picture of the classes of omni-conductors and omni-insulators. The existence of omni-conductors could be expected, as the systems under study are conjugated, with extensive delocalisation of electrons, but the fact that omni-insulators also exist is more surprising, as an omni-insulator has mobile, delocalised electrons, and yet by definition does not conduct at the Fermi level, no matter which connection vertices are chosen.

Our general deductions from combinations of the theorems of Sec. IV will be grouped first by nullity and then by class of omni-conductor/insulator.

A. Deductions by nullity

1. Nullity $g_s = 0$

Deduction 5.1. A non-singular graph ($g_s = 0$) is a strong omni-conductor iff the inverse matrix $\mathbf{A}^{-1}$ is full (i.e., has no zero elements).

The isolated-pentagon C_{60} is one of many fullerene examples of strong omni-conductors of this type.

Deduction 5.2. A non-singular graph ($g_s = 0$) is a distinct omni-conductor iff the off-diagonal part of the inverse matrix $\mathbf{A}^{-1}$ is full.

Families of non-singular graphs that are distinct omni-conductors include the complete graphs $K_r, r \geq 2$ and the cycles $C_{2k+1}, k \geq 1$.

Deduction 5.3. A non-singular graph ($g_s = 0$) is an ipso omni-conductor iff the inverse matrix $\mathbf{A}^{-1}$ has a full diagonal.

Deductions 5.1 and 5.3 can be interpreted as saying that for a non-singular graph to be an ipso omni-conductor, each vertex must be a middle CFV.

Deduction 5.4. There are no *non-singular distinct omni-insulators (and hence* no *non-singular strong omni-insulators).*

(This is easy to see: if $\mathbf{A}^{-1}$ is diagonal, then so is $\mathbf{A}$, implying that the graph G has no edges and hence is not connected.) Non-singular *ipso* omni-insulators do exist, however, and in fact *all* ipso omni-insulators are non-singular, with each vertex being an upper CFV. For example, any non-singular bipartite graph consists entirely of *upper* core-forbidden vertices and hence is an ipso omni-insulator: this class includes all Kekulean benzenoids. A curious observation is that a graph may be *ipso* omni-insulating but *distinct* omni-conducting (a so-called *nuciferous* graph[25]), although it must be said that we know of only one example of a graph with this combination of properties. That example is K_2, the complete graph on two vertices.

2. Nullity $g_s = 1$

From Theorem 4.3, we have the following deduction.

Deduction 5.5. The distinct omni-conductors with $g_s = 1$ are exactly the nut graphs.

This follows easily from the fact that a singular graph has core vertices. If the graph has any core-forbidden vertex, there is at least one insulating device. Hence, any distinct omni-conductor must contain *only* core vertices. A graph that has only core vertices and nullity 1 is a nut graph by definition. Nut graphs are also ipso omni-conductors.

Clearly, therefore,

Deduction 5.6. The strong omni-conductors with $g_s = 1$ are exactly the nut graphs.

Note that the nut graphs are only a subset of the ipso omni-conductors with nullity 1. For example, the isolated-pentagon fullerene C_{70} has $g_s = 1$, is not a nut graph, but is an ipso omni-conductor.[33]

Deduction 5.7. There are no omni-insulators with $g_s = 1$.

This follows from the fact that any graph with $g_s = 1$ has at least two core vertices, but clearly cannot have $g_v = g_s - 2$; there is at least *one* conducting device with distinct connections, and at least *two* with ipso connections, all based on the same graph.

3. Nullity $g_s > 1$

Again from Theorem 4.3:

Deduction 5.8. There are no distinct (and no strong) omni-conductors of nullity $g_s > 1$.

We can remark that *ipso* omni-conductors with $g_s \geq 2$ exist: they may contain core vertices only, or consist of a mixture of core and middle vertices. An example is the "carbon cylinder"[34] isomer of fullerene C_{84}, which has $g_s = 3$.

Deduction 5.9. There are no ipso (and hence no strong) omni-insulators of nullity $g_s > 1$.

Equivalently, all ipso omni-insulators are non-singular. (The proof is the same as for $g_s = 1$.) However, singular distinct omni-insulators exist. They must contain only core vertices and each of the pairs of core vertices must give $g_v = g_s - 2$, implying $g_s \geq 2$.

B. Deductions by conduction class

The results listed in this section so far show that nullity one is an important dividing line between conducting and insulating regimes. Four global statements emphasising this special role of non-bonding orbitals in conduction, all of which follow from the above, are as follows.

Deduction 5.10. All distinct and strong omni-conductors have nullity $g_s \leq 1$.

Deduction 5.11. For nullity $g_s = 1$, all distinct or strong omni-conductors are nut graphs.

Deduction 5.12. All distinct omni-insulators have nullity $g_s \geq 2$.

Deduction 5.13. There are no strong omni-insulators.

Table IV reports the main theoretical conclusions of the paper as a summary of the distribution of conduction and insulation behaviour across the six classes and three nullity regimes. It can be seen that nine of the 18 combinations are impossible and nine are realisable, of which two are characterised exactly as the nut graphs. Significantly, we have examples of chemical graphs for all of the realisable combinations. Conjugated π systems with the various predicted omni-conduction or omni-insulation properties are in fact very common in chemistry.

VI. RESULTS

A. Statistics of conduction of molecular graphs

We have defined omni-conductors and omni-insulators. It remains to check their abundance amongst graphs of conjugated systems, and identify families that show these properties. Calculations implementing the rules embodied in Tables I and II were carried out for various sets of graphs. Generators geng (part of the nauty software written by B. D. McKay and available at http://cs.anu.edu.au/~bdm/), plantri,[35] CaGe,[36] fullgen,[37] and our own *ad hoc* programs were used to construct general families of graphs.

The generated datasets include chemical graphs (connected graphs with maximum degree ≤ 3), chemical trees (acyclic chemical graphs), benzenoids (subgraphs of the hexagonal tessellation of the plane with all internal faces hexagonal and without holes or handles), cubic polyhedra (planar, 3-connected graphs), fullerenes (cubic polyhedra with face sizes restricted to 5 and 6), general graphs (connected graphs without limitation of maximum degree), and general trees (acyclic general graphs).

For all sets, conductors and insulators were enumerated. Summaries of the results are given in Tables V–IX. In the tables, we count "pure" cases of each type. Pure ipso or distinct omni-insulators/conductors are, respectively, ipso or distinct but not strong.

If extrapolation from small numbers can be trusted, omni-conductors and omni-insulators constitute only a small fraction of chemical graphs and general graphs. In chemical graphs, the proportion appears to oscillate around a general decrease with increasing n. Subject to the caveat about small numbers, pure ipso omni-conductors are more numerous than strong omni-conductors, which in turn are more

TABLE V. Distribution of omni-insulators and omni-conductors amongst chemical graphs with $n \leq 16$. $N(n)$ is the total number of chemical graphs, N^i_{ipso} is the number of pure ipso omni-insulators, and N^i_{distinct} is the number of pure distinct omni-insulators. N^c_{ipso} is the number of pure ipso omni-conductors, N^c_{distinct} is the number of pure distinct omni-conductors, and N^c_{strong} is the number of strong (ipso + distinct) omni-conductors. N_{nut} counts the chemical graphs that are also nut graphs.

		Insulators		Conductors			
n	$N(n)$	N^i_{ipso}	N^i_{distinct}	N^c_{ipso}	N^c_{distinct}	N^c_{strong}	N_{nut}
2	1	1	0	0	1	0	0
3	2	0	0	0	0	1	0
4	6	1	1	2	0	1	0
5	10	0	0	1	0	1	0
6	29	6	1	4	0	2	0
7	64	0	1	2	0	5	0
8	194	24	0	15	0	8	0
9	531	0	1	26	0	14	1
10	1733	132	2	88	5	48	0
11	5524	0	2	210	0	85	8
12	19 430	902	3	665	9	342	9
13	69 322	0	6	2034	0	885	27
14	262 044	7669	10	7055	151	3744	23
15	1 016 740	0	22	26 946	73	10 788	414
16	4 101 318	77 056	45	95 539	2311	50 770	389

TABLE VI. Distribution of omni-insulators and omni-conductors amongst general graphs with $n \leq 10$. $N(n)$ is the total number of connected graphs, N^i_{ipso} is the number of pure ipso omni-insulators, and $N^i_{distinct}$ is the number of pure distinct omni-insulators. N^c_{ipso} is the number of pure ipso omni-conductors, $N^c_{distinct}$ is the number of pure distinct omni-conductors, and N^c_{strong} is the number of strong (ipso + distinct) omni-conductors. N_{nut} counts the general graphs that are also ut graphs.

		Insulators		Conductors			
n	$N(n)$	N^i_{ipso}	$N^i_{distinct}$	N^c_{ipso}	$N^c_{distinct}$	N^c_{strong}	N_{nut}
2	1	1	0	0	1	0	0
3	2	0	0	0	0	1	0
4	6	1	1	2	0	1	0
5	21	0	1	4	0	3	0
6	112	7	2	21	0	7	0
7	853	0	7	136	0	38	3
8	11 117	129	20	1352	0	496	13
9	261 080	0	107	32 575	31	10 002	560
10	11 989 762	15 356	938	1 429 875	406	783 562	12 551

TABLE IX. Distribution of omni-insulators and omni-conductors amongst the cubic polyhedra with $n \leq 20$. $N(n)$ is the total number of cubic polyhedra, N^i_{ipso} is the number of pure ipso omni-insulators, N^c_{ipso} is the number of pure ipso omni-conductors, N^c_{strong} is the number of strong omni-conductors, and N_{nut} is the number of cubic polyhedra that are also nut graphs. In the range, there are neither pure distinct omni-insulators nor pure distinct omni-conductors, but the fullerenes provide examples of larger cubic polyhedra that are pure distinct omni-conductors.[33]

n	$N(n)$	N^i_{ipso}	N^c_{ipso}	$N^c_{distinct}$	N_{nut}
4	1	0	0	1	0
6	1	0	1	0	0
8	2	1	0	0	0
10	5	0	1	4	0
12	14	0	9	4	2
14	50	1	8	17	0
16	233	2	80	125	0
18	1249	0	327	708	285
20	7595	7	1343	3925	0

TABLE VII. Distribution of omni-insulators amongst chemical trees with $n \leq 25$. $N(n)$ is the total number of chemical trees with n vertices, N^i_{ipso} is the number of pure ipso omni-insulators, $N^i_{distinct}$ is the number of pure distinct omni-insulators, and η is the nullity of (all) the distinct omni-insulating chemical trees on n vertices.

n	$N(n)$	N^i_{ipso}	$N^i_{distinct}$ (η)	n	$N(n)$	N^i_{ipso}	$N^i_{distinct}$ (η)
2	1	1	0	14	552	96	0
3	1	0	0	15	1132	0	0
4	2	1	1 (2)	16	2410	319	6 (6)
5	2	0	0	17	5098	0	0
6	4	2	0	18	11 020	1135	0
7	6	0	1 (3)	19	23 846	0	13 (7)
8	11	4	0	20	52 233	4150	0
9	18	0	0	21	114 796	0	0
10	37	11	2 (4)	22	254 371	15 690	31 (8)
11	661	0	0	23	565 734	0	0
12	135	30	0	24	1 265 579	60 506	0
13	265	0	3 (5)	25	2 841 632	0	73 (9)

TABLE VIII. Distribution of omni-insulators amongst all trees with $n \leq 10$. $N(n)$ is the total number of trees with n vertices, N^i_{ipso} is the number of pure ipso omni-insulators, $N^i_{distinct}$ is the number of pure distinct omni-insulators, and η is the set of nullities achieved by distinct omni-insulating trees on n vertices, e.g., nullities 8, 6, and 4 for the 7 distinct omni-insulators with 10 vertices.

n	$N(n)$	N^i_{ipso}	$N^i_{distinct}$ (η)
2	1	1	0
3	1	0	0
4	2	1	1 (2)
5	3	0	1 (3)
6	6	2	1 (4)
7	11	0	2 (5,3)
8	23	5	3 (6,4)
9	47	0	4 (7,5)
10	106	39	7 (8,6,4)

numerous than pure distinct omni-conductors. For insulators, strong omni-insulators do not exist (Deduction 5.13), and pure ipso omni-insulators appear to outnumber pure distinct omni-insulators. All nut graphs are strong omni-conductors (Deduction 5.6), but constitute only a small fraction of the total set of strong omni-conductors. Figure 1 shows the smallest chemical nut graph.

Tables V and VI suggest that ipso omni-insulators with odd n are either rare or do not exist. The question is open, but, it is apparent (Deductions 5.7 and 5.9) that all ipso omni-insulators are non-singular, with all vertices of CFV (upper) type (Theorem 4.5). Thus, if ipso omni-insulators with odd n exist, they are non-bipartite (odd bipartite graphs have odd $\eta \geq 1$) and must have at least *two* disjoint odd cycles, since deletion of a vertex leaves a graph with even order but $\eta = 1$, implying a non-bipartite graph. Furthermore, a construction for reducing ipso omni-insulators[38] (Algorithm 36 in that paper) implies that the such smallest graph has no pendant edge.

Tables VII and VIII deal with chemical and general trees. From the results, it appears that there are no ipso (and hence no strong) omni-conducting trees, that there are no ipso omni-insulating trees with odd numbers of vertices, and that K_2 is the only distinct omni-conducting tree. These three observations are all general, as shown by the following arguments. For the first observation, note that every tree has at least one CFV (upper) vertex. Hence by Theorems 4.4 and 4.5, there is at least one ipso-insulating vertex in every tree. For the second, note that an ipso omni-insulator is non-singular, but trees with odd numbers of vertices are all singular. For the third
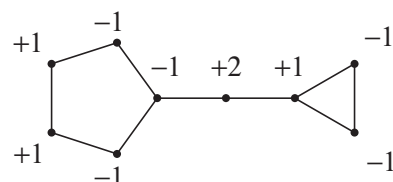

FIG. 1. The smallest nut graph that is also a chemical graph. Relative values of the entries in the unique nullspace eigenvector are shown in the diagram.

observation the chain of reasoning is longer. Distinct omni-conductors are either nut graphs or non-singular. No tree on $n > 1$ vertices is a nut graph. For non-singular distinct omni-conductors, off-diagonal entries in the inverse matrix $\mathbf{A}^{-1}$ are all non-zero (Theorem 4.1). Hence each vertex-deleted sub-graph arising from a putative distinct omni-conducting tree would have to be a nut graph[25] and also a tree, yielding a contradiction unless the starting tree is K_2. Hence, we have the following theorem.

Theorem 6.1

(i)   *No tree is an ipso omni-conductor;*
(ii) *no tree with an odd number of vertices is an ipso omni-insulator; and*
(iii) *the only tree that is a distinct omni-conductor is K_2.*

In the range $2 \leq n \leq 25$ distinct omni-insulating chemical trees are rare, appearing only at $n = 3k + 4$, and interestingly these examples also have $\eta = k + 2$. We will see below that there is a structural explanation for this observation, in terms of vertex fusion of S_3 graphs (stars with 3 peripheral vertices), which in turn suggests an explanation for the counts for general trees and a conjecture for all chemical graphs. Amongst chemical trees, the trend appears to be towards a smaller fraction of pure distinct omni-conductors with increasing n.

Benzenoid graphs give results that do not need a table: Kekulean (non-singular) benzenoids are all ipso omni-insulators (all vertices of a non-singular bipartite graph are CFV upper). In the range $1 \leq h \leq 12$, where h is the number of hexagonal faces, no Kekulean benzenoids belong to any other class of omni-conductors or omni-insulators, and no non-Kekulean benzenoids have any omni-conducting or omni-insulating properties.

Cubic polyhedral graphs (candidates for carbon cages) (Table IX) show a bias to strong omni-conduction: for example, of the 7595 cubic polyhedra with $n = 20$ vertices, 3925 are strong omni-conductors. Interestingly, these graphs appear to include neither distinct omni-insulators nor pure distinct omni-conductors. Restriction to the fullerene subclass of cubic polyhedra gives an even greater pre-dominance of strong omni-conductors.[33] The data for the small cases in Table IX might be taken to suggest that no cubic polyhedra are pure distinct omni-conductors, but this is disproved by the counterexample of fullerenes on, e.g., $n = 54$ vertices.[33]

B. Some families of omni-conductors

Observations from constructions suggest several general families of omni-conductors: all complete graphs K_n with $n > 2$ are strong omni-conductors, as are all nut graphs, all cycles C_{4N+1} and C_{4N+3}, bi-cycles formed by fusion of an odd cycle and an aromatic $(4N + 2)$ cycle, bowtie graphs consisting of two odd cycles linked by a chain of any length, and all $[p]$prisms with odd $p \neq 0 \mod 3$ (see Figure 2).

Pure ipso omni-conductors include anti-aromatic cycles C_{4N}, bi-cycles formed by fusion of odd cycles C_p and C_q with $p - q \neq 0 \mod 4$, and $[p]$prisms for all odd p and all $p = 0 \mod 6$.
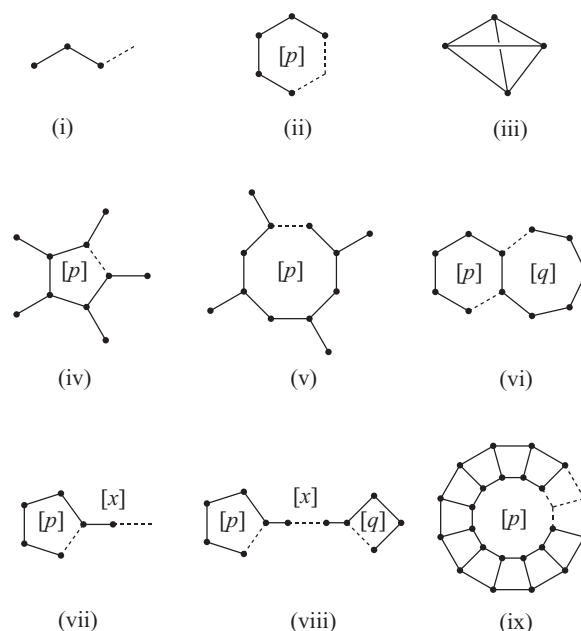

FIG. 2. Families of chemical graphs with interesting conduction and insulation behaviour. Those illustrated are: (i) paths ($n = p$, $m = p - 1$, $p \geq 2$); (ii) cycles ($n = m = p$, $p \geq 3$); (iii) complete graphs ($n = p$, $m = p(p - 1)/2$, $p \geq 2$); (iv) radialenes ($n = p$; $m = 2p$, $p \geq 3$); (v) semi-radialenes ($n = m = 3p/2$, $p \geq 4$); (vi) bi-cycles ($n = p + q - 2$, $m = p + q - 1$, $p, q \geq 3$); (vii) tadpoles ($n = m = p + x$, $p \geq 3$, $x \geq 1$); (viii) bowties ($n = p + q + x$, $m = n + 1$, $p, q \geq 3$, $x \geq 0$); and (ix) prisms ($n = 2p$, $m = 3p$, $p \geq 3$).

The preceding observations can be proved using theorems given earlier (e.g., Theorem 4.5). For example, the complete graph K_n ($n > 1$) has all vertices of CFV (middle) type, and hence the graph is an ipso omni-conductor. Also, for $n > 2$, two deletions lead to a smaller complete graph, K_{n-2}, and we therefore have case 3c(iiA)/7 of Table III, with $g = 0$ and $j^2 = ut - sv = E + 1$, and hence a strong omni-conductor.

C. Some families of omni-insulators

Construction of families of graphs leads to a number of observations about omni-insulators that can be proved from the theorems in Secs. IV A and IV B. For example, ipso omni-insulators are common.

Examples of families of ipso omni-insulators include even paths P_{2N}, aromatic cycles C_{4N+2}, all radialenes, tadpoles with an aromatic cycle and an even number of vertices in the tail, bi-cycles formed by fusion of two even rings, bowties with two aromatic rings and an even number of vertices in the intervening chain, $[p]$prisms with p even and $\neq 0 \mod 6$ (Figure 2). As for the omni-conductors, all the above observations about insulators can be proved straightforwardly.

Families of distinct omni-insulators are also found amongst the chemical graphs: for example, all semi-radialenes with more than 6 vertices, belong to this class, as do the subset of chemical trees mentioned in Sec. VI A. A common substructure appears in these and other examples. A construction that often but not invariably leads from a parent chemical graph to a chemical graph that is a distinct omni-insulator is "starification." In this construction each vertex of
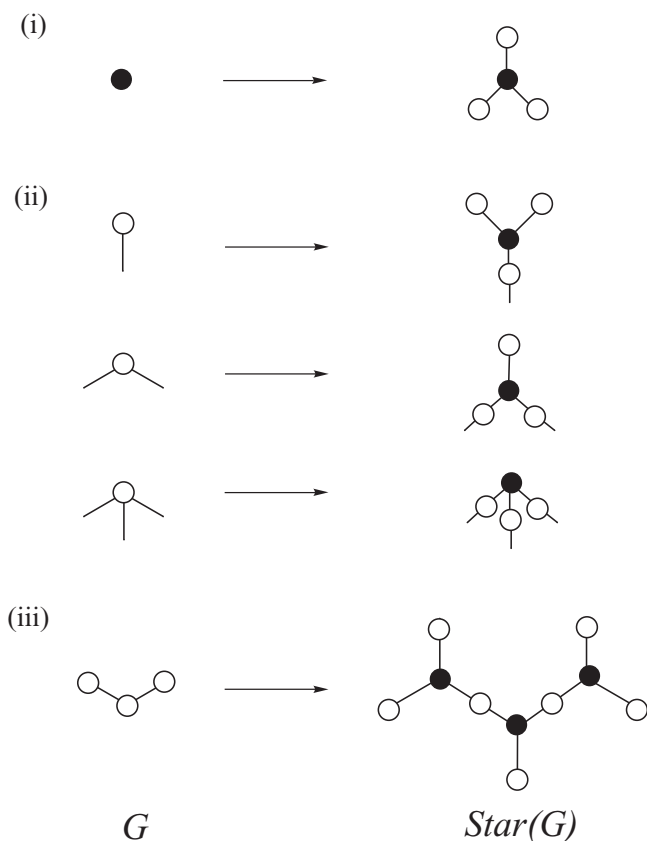
FIG. 3. The star construction. Starting from a parent G, (i) each vertex is replaced by a star graph S_3; (ii) stars that are neighbours along an original edge of G are fused at a peripheral vertex, leaving $(3-d)$ pendent vertices per star replacing the original vertex of degree d.

a parent graph G is replaced by a three-pointed star S_3, and pairs of stars corresponding to edges of G are fused by superposition of a terminal vertex of each (see Figure 3). Given that S_3 has three peripheral vertices, as the starting graph is chemical (i.e., connected and with maximum degree ≤ 3) with n vertices and m edges, the derived graph $Star(G)$ has $4n - m$ vertices and $3n$ edges of which $3n - 2m$ are leaves, connecting central vertices of stars to vertices of degree 1. If G has adjacency eigenvalues $\{\mu_i\}$, the graph $Star(G)$ has $2n$ eigenvalues given by $\pm\sqrt{3 + \mu_i}$, with all other eigenvalues zero. Precisely in the case that G is cubic and bipartite, $Star(G)$ has two zero eigenvalues arising from $\mu_n = -3$ of G. Hence, the total number of zero eigenvalues of $Star(G)$ is $2n - m + 2$ for cubic bipartite G and $2n - m$ for all chemical graphs.

Application of the starification operation to all chemical graphs with $2 < n < 14$ indicates that "nearly all" $Star(G)$ for chemical parents G are distinct omni-insulators. The "exceptions" ($Star(G)$ that are not distinct omni-insulators) are comparatively rare: for parents with $n = 2, \dots 14$, there are only 0, 0, 1, 1, 4, 4, 14, 23, 73, 166, 533, 1504, 5061, ... exceptions (to be compared with the much larger total numbers of chemical graphs listed in Table VII). Features common to the exceptions are under investigation. For example, some but not all cubic graphs G lead to exceptions, whereas all chemical trees G on n vertices lead to distinct omni-insulators $Star(G)$ with $3n + 1$ vertices.

It is intriguing to ask exactly "why" the omni-insulating chemical trees have their characteristic property, and "why" in general insulation should be associated with high nullity. A hint comes from observations on calculated transmission in so-called cross-conjugated systems:[11,39,40] a connection across a cross-conjugated junction in model systems leads to strong reduction in transmission[40] at energies that are associated with the eigenvalues of the intervening side chain.[39] Within the graph-theoretical version of the SSP model,[13] this corresponds to a theorem that can be derived straightforwardly from our previous work on composite systems.[17]

Theorem 6.2. *Let three fragments A, B, and C be connected via a single three-coordinate vertex D to form a Y-shaped junction. The vertices adjacent to D in A, B, C are w_A, w_B, and w_C, respectively. If a device is constructed with $\bar{L}$ in A and $\bar{R}$ in B, the opacity polynomial of the device, $j^2 = ut - sv$, is*

$$j^2(ABC) = j^2(A)j^2(B)\phi^2(C),$$

where $j^2(A)$ is the opacity polynomial for a device consisting of A alone with connections $\bar{L}$ and w_A, $j^2(B)$ is the opacity polynomial for a device consisting of B with connections w_B and $\bar{R}$, and $\phi(C)$ is the characteristic polynomial of the graph C.

Proof is by combination of Theorems 6 and 7 from our earlier paper.[17] Our omniconducting trees include multiple copies of such Y-junctions, and the denominator of the transmission $T(E)$ will therefore contain zeroes at $E = 0$ arising from the many leaves on these particular trees, as will the characteristic polynomial of the tree itself. This is suggestive of a more general connection between between nullity, cross-conjugation, and omni-insulation.

VII. CONCLUSIONS

It has been shown here that the graph theoretical SSP model leads naturally to the definition of omni-conductors and omni-insulators, that membership of the various categories is crucially dependent on graph nullity (number of non-bonding orbitals) and is governed by a number of general theorems, and that many families of chemically relevant molecular graphs omni-conduct. For example, many bicyclic π-systems, and almost all fullerenes,[33] are strong omniconductors.

It will be interesting to see the extent to which these properties are retained in more sophisticated models of molecular conduction.

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