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A new approach to the method of source-sink potentials for molecular conduction

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We re-derive the tight-binding source-sink potential (SSP) equations for ballistic conduction through conjugated molecular structures in a form that avoids singularities. This enables derivation of new results for families of molecular devices in terms of eigenvectors and eigenvalues of the adjacency matrix of the molecular graph. In particular, we define the transmission of electrons through individual molecular orbitals (MO) and through MO shells. We make explicit the behaviour of the total current and individual MO and shell currents at molecular eigenvalues. A rich variety of behaviour is found. A SSP device has specific insulation or conduction at an eigenvalue of the molecular graph (a root of the characteristic polynomial) according to the multiplicities of that value in the spectra of four defined device polynomials. Conduction near eigenvalues is dominated by the transmission curves of nearby shells. A shell may be inert or active. An inert shell does not conduct at any energy, not even at its own eigenvalue. Conduction may occur at the eigenvalue of an inert shell, but is then carried entirely by other shells. If a shell is active, it carries all conduction at its own eigenvalue. For bipartite molecular graphs (alternant molecules), orbital conduction properties are governed by a pairing theorem. Inertness of shells for families such as chains and rings is predicted by selection rules based on node counting and degeneracy. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4935716>]

I. INTRODUCTION

The subject of unimolecular electrical conduction and devices based on it has a venerable history,^{1–5} and has a vast research literature; a recent review article has an impressive 607 references,⁶ and reviews,^{7,8} journal special issues and discussion volumes^{9–11} and books^{12,13} devoted to the different aspects of the topic continue to appear.

The present paper deals with an attractive approach for qualitative modelling of single-molecule conduction, due to Ernzerhof and his group. The Source-Sink Potential (SSP) model^{14–27} is a simple and convenient methodology for the study of ballistic electronic conduction through molecular devices. The method uses a model device depicted in Fig. 1(a) in which a molecule is attached to a source atom, L, that creates a flux of electrons, and to a sink atom, R, that destroys it. The electron flux through the model device is designed to be identical to that in a cognate device (the lower diagram of Fig. 1) with infinite wires, in which an electron beam with wavevector q_L in the left wire is partly transmitted through the molecule, emerging as a beam of wavevector q_R in the right. In this work, we consider an n -atom molecular π -system based on a carbon skeleton and treat it using the Hückel (tight-binding) formalism. The molecular adjacency matrix is \mathbf{A} , where $A_{pq} = 1$ if $p \neq q$ and p is bonded to q , and $A_{pq} = 0$ otherwise. The connections $L\bar{L}$ and $\bar{R}R$ have resonance parameters $\beta_{L\bar{L}}$ and $\beta_{\bar{R}R}$, respectively. The molecule has resonance parameter β , and coulomb parameter α . In the usual system of units, α is set to zero, and $|\beta|$ is taken as 1.

We have previously utilised the SSP formalism to derive analytical expressions for electronic transmission.^{28–35} In our approach, the solutions for an incoming beam of electrons with energy E are written in terms of five molecular *structural* polynomials, which comprise the real characteristic polynomials,²⁸

$$\begin{aligned} s &= \det(\mathbf{E}\mathbf{1} - \mathbf{A}), \\ t &= \det(\mathbf{E}\mathbf{1} - \mathbf{A})^{[\bar{L}, \bar{L}]}, \\ u &= \det(\mathbf{E}\mathbf{1} - \mathbf{A})^{[\bar{R}, \bar{R}]}, \\ v &= \det(\mathbf{E}\mathbf{1} - \mathbf{A})^{[\bar{L}\bar{R}, \bar{L}\bar{R}]}, \\ j &= (-1)^{\bar{L}+\bar{R}} \det(\mathbf{E}\mathbf{1} - \mathbf{A})^{[\bar{L}, \bar{R}]}, \end{aligned} \quad (1)$$

where the superscripts in braces indicate which rows (left) and columns (right) corresponding to connection atoms \bar{L} and/or \bar{R} are to be struck out from the characteristic matrices. The polynomial, j , with row \bar{L} and column \bar{R} removed from the determinant satisfies the Jacobi-Sylvester relation³⁶

$$j^2 = ut - sv. \quad (2)$$

The expression for the overall transmission²⁸ is

$$T(E) = \mathcal{B}(q_L, q_R) \frac{j^2}{|D|^2}, \quad (3)$$

where E is the energy of the incoming stream of electrons and

$$\mathcal{B}(q_L, q_R) = (2\beta_L \sin q_L)(2\beta_R \sin q_R) \beta_{L\bar{L}}^2 \beta_{\bar{R}R}^2 \quad (4)$$

and

$$\begin{aligned} D(E) &= \beta_L e^{-iq_L} \beta_R e^{-iq_R} s - \beta_R e^{-iq_R} \beta_{L\bar{L}}^2 t \\ &\quad - \beta_L e^{-iq_L} \beta_{\bar{R}R}^2 u + \beta_{L\bar{L}}^2 \beta_{\bar{R}R}^2 v. \end{aligned} \quad (5)$$

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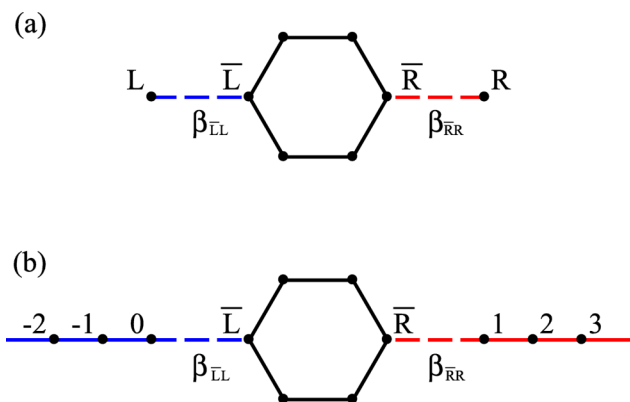


FIG. 1. (a) A SSP molecular device comprising a molecule attached to source and sink atoms L and R via contacts \bar{L} and \bar{R} , respectively. (b) A molecule attached to infinite left- and right-hand wires, showing the numbering scheme adopted for the atoms in the wires.

Wavevectors q_L and q_R are functions of E and satisfy the dispersion relations

$$E = \alpha_L + 2\beta_L \cos q_L = \alpha_R + 2\beta_R \cos q_R. \quad (6)$$

These dispersion relations are appropriate for the infinite wires in Fig. 1(b), assuming Hückel parameters (α_L, β_L) and (α_R, β_R) , for left and right wires, respectively.

The purpose of the current article is to present a reformulation of the SSP approach in Section III and then to use it to give simple derivations of a number of new results.

We first set out the SSP secular equations in the standard atomic-orbital (AO) basis (Subsection III B), and then in the molecular-orbital (MO) basis (Subsection III C). We show that ballistic molecular conduction can be described in complementary ways: as transmission along bonds (graph edges) or through parallel channels based on molecular orbitals. In the latter description, molecular orbitals can be *inert*, having no conduction at any energy (including the orbital eigenvalue), or they can be *active*, and these properties obey selection rules based on degeneracy and nodal character. Sections IV–VIII describe the theoretical framework and give expressions from which orbital transmission can be calculated, and inert/active status decided.

The main new results obtained from the reformulation of the SSP equations are as follows. First, the reformulation itself removes singularities, giving confidence that the results are mathematically well defined at all energies. Second, SSP leads to a direct partition of total transmission into a sum of well-defined orbital contributions, avoiding the need for a *post hoc* projection scheme. Third, the analysis naturally establishes the dichotomy between inert and active orbitals and leads to selection rules to predict the character of a given orbital. Finally, as we discuss briefly in Sec. X, this opens up the way to improved treatment of the role of electron interaction in what is so far a purely Hückel-based model.

Readers interested only in the main chemical conclusions could consider skipping directly to Section IX where illustrative examples are given, along with simple analytical formulas for devices based on paths (linear polyenes) and cycles (annulenes). An extended Sec. X then discusses the qualitative significance of the results derived in the main body of the paper.

II. TECHNICAL NOTES

The algebraic computations reported in this paper were all performed by using Maple 18.³⁷ Computations for the figures were carried out using unbiased ($\alpha_L = \alpha_R = 0$), and symmetric devices ($\beta_L = \beta_R$), with specific values $\beta_L = 1.4\beta$ and $\beta_{\bar{L}L} = \beta_{\bar{R}R} = \beta$.

The equal β approximation used in this paper is ideally adapted to small all-carbon frameworks, but the formalism we develop in terms of structural polynomials exhibited in Eqs. (1) and (3) applies equally to systems for which weighted graphs are appropriate. These include systems displaying π -distortivity,^{38,39} or doped with hetero-atoms which are, of course, important in realistic applications.

Likewise, it may be noted that all applications of the SSP model in the present paper are based on devices with one-dimensional leads attached to single atoms of the molecule. More complicated leads and connection patterns can be accommodated by modification of the contents of the blocks of the device matrix (see Eqs. (25) and (32), later). Examples of SSP treatments of multichannel devices are given in Refs. 27 and 40.

The approach used here is grounded in qualitative molecular-orbital theory; this is a choice based on the belief that such models allow “for a transparent interpretation of molecular conductance in terms of discrete eigenstates.”¹⁹ The use, either explicit or implicit, of orbitals and orbital densities gives an opportunity for using familiar chemical concepts to give insight.^{22,26,41,42} Many researchers in the field use Green’s Function approaches, particularly for calculation, and of course these too have their specific advantages. However, it has been shown that the two approaches, when used with the SSP model approximations, lead to identical expressions for transmission.³³

A remark about notation: we will use labels p, q, \dots for atoms, k, k', \dots for molecular orbitals, and K for shells.

III. A REDERIVATION OF THE SSP EQUATIONS

We begin by considering the normalisation of the wavefunctions for the full device that is replicated by the SSP device of Fig. 1(a), and consists of the molecule with two attached infinite wires (cf. Fig. 1(b)). The numbering scheme for atoms in Fig. 1(b) is designed to simplify the algebra that follows by elimination of the unnecessary phase factors that have plagued previous derivations.^{18,26,28} We first consider the normalisation of the wavefunctions for the infinite wires.

A. Flux normalization

The wavefunctions $\psi^{\text{left}}, \psi^{\text{right}}$ in left- and right-hand wires, respectively, are written in the tight-binding (Hückel) approximation as

$$\begin{aligned} \psi^{\text{left}} &= \sum_{p=-\infty}^0 c_p^{\text{left}} \phi_p, \\ \psi^{\text{right}} &= \sum_{p=1}^{\infty} c_p^{\text{right}} \phi_p, \end{aligned} \quad (7)$$

where the ϕ_p are basis functions on the atoms of left and right wires, and the Hückel Coulomb and resonance parameters are α_L, β_L , and α_R, β_R , respectively. Coefficients for the left and right wires are given by

$$\begin{aligned} c_p^{\text{left}} &= \frac{1}{N_L} (e^{iq_L p} + r e^{-iq_L p}), \\ c_p^{\text{right}} &= \frac{1}{N_R} \tau e^{iq_R p} \end{aligned} \quad (8)$$

for the specified boundary conditions, where the left-hand wavefunction is a combination of a forward-travelling wave (e^{iq_L}) and a backward-travelling component (e^{-iq_L}) with a reflection coefficient, r . The molecule acts as a potential barrier that produces a reflected wave in the left wire and a forward transmitted wave (e^{iq_R}) in the right wire, with a transmission coefficient, τ . This corresponds to a flux of electrons with energy E , satisfying both Eq. (6) and the Hückel Schrödinger equation for infinite wires.

The total electron transmission probability is then

$$T(E) = 1 - |r|^2 = |\tau|^2. \quad (9)$$

The normalisation factors N_L and N_R have been introduced to obtain the requisite unit electron flux. Hence, the current density⁴³ from atom $(p-1)$ to atom p in the left wire, using the standard Hückel formulation, is

$$\begin{aligned} J_{(p-1) \rightarrow p}^{\text{left}} &= \frac{1}{i} \left(\langle \phi_{p-1} | \hat{H} | \phi_p \rangle c_{p-1}^{\text{left}*} c_p^{\text{left}} - \text{c.c.} \right) \\ &= \frac{2\beta_L \sin q_L}{N_L^2} (1 - |r|^2), \end{aligned} \quad (10)$$

where we have used $\langle \phi_{p-1} | \hat{H} | \phi_p \rangle = \beta_L$. This expression is independent of the index p , showing that a constant current flows down the wire. We require this current to be equal to the transmission probability, $T(E)$. Hence, we deduce that the correct flux normalisation is achieved by setting

$$N_L^2 = 2\beta_L \sin q_L \quad (11)$$

and using an analogous derivation for the right-hand wire

$$N_R^2 = 2\beta_R \sin q_R. \quad (12)$$

B. The SSP equations in the atomic orbital basis

The secular equations of the device shown in Fig. 1(b) for atom 0 in the left-hand wire and for atom 1 in the right-hand wire are

$$\begin{aligned} \beta_L c_{-1}^{\text{left}} + (\alpha_L - E) c_0^{\text{left}} + \beta_{LL} c_L &= 0, \\ \beta_{RR} c_R + (\alpha_R - E) c_1^{\text{right}} + \beta_R c_2^{\text{right}} &= 0 \end{aligned} \quad (13)$$

where β_{LL}, β_{RR} are resonance parameters for the connections from the wires to the molecule. We wish to replace the left wire by a single source atom, L, sited at atom 0 and creating a flux of electrons corresponding to the wavefunction ψ^{left} in Eqs. (7) and (8). Similarly, we wish to replace the right wire by a single sink atom, R sited at atom 1 and removing the transmitted flux. This requires the definition of complex potentials, Θ_L, Θ_R , on these source and sink atoms to replace the effects of atoms to the left of atom 0, and to the right of atom 1, respectively.

Hence, we define

$$\begin{aligned} \beta_L c_{-1}^{\text{left}} &= \Theta_L c_0^{\text{left}}, \\ \beta_R c_2^{\text{right}} &= \Theta_R c_1^{\text{right}}. \end{aligned} \quad (14)$$

The potentials can now be derived by using the expressions from Eq. (8) for the orbital coefficients

$$\begin{aligned} \Theta_L &= \beta_L \frac{c_{-1}^{\text{left}}}{c_0^{\text{left}}} = \beta_L \frac{(e^{-iq_L} + r e^{iq_L})}{(1+r)}, \\ \Theta_R &= \beta_R \frac{c_2^{\text{right}}}{c_1^{\text{right}}} = \beta_R e^{iq_R}. \end{aligned} \quad (15)$$

In the standard SSP formalism,^{14,26,28} these potentials are used directly in the SSP secular equations. However, when the reflection coefficient, r , becomes equal to -1 , the potential Θ_L becomes infinite. A more satisfactory approach, avoiding this singularity, is obtained by substituting the explicit form of c_{-1}^{left} into Eq. (13) to give

$$\frac{\beta_L}{N_L} (e^{-iq_L} + r e^{iq_L}) + (\alpha_L - E) c_L + \beta_{LL} c_L = 0 \quad (16)$$

and noting from Eq. (8) that

$$c_L \equiv c_0^{\text{left}} = \frac{1+r}{N_L} \quad (17)$$

we deduce that

$$r = N_L c_L - 1. \quad (18)$$

Substituting for r in Eq. (16), we obtain

$$\begin{aligned} (\beta_L e^{iq_L} + \alpha_L - E) c_L + \beta_{LL} c_L &= \frac{2i\beta_L \sin q_L}{N_L} \\ &= iN_L, \end{aligned} \quad (19)$$

where we have placed the inhomogeneity on the right-hand side. We can carry out the same procedure using c_1^{right} from Eq. (8) in Eq. (13) to give

$$c_R \equiv c_1^{\text{right}} = \frac{\tau}{N_R} e^{iq_R} \quad (20)$$

and hence

$$c_2^{\text{right}} = e^{2iq_R} \frac{\tau}{N_R} = e^{iq_R} c_R. \quad (21)$$

Substitution of this expression into Eq. (13) gives

$$\beta_{RR} c_R + (\alpha_R - E + \beta_R e^{iq_R}) c_R = 0 \quad (22)$$

which does not contain an inhomogeneity.

With these modifications to the boundary conditions, we can now find the wavefunction for the model device. The wavefunction

$$\psi_{\text{SSP}} = \sum_{p=1}^n c_p^{\text{AO}} \phi_p + c_L \phi_L + c_R \phi_R \quad (23)$$

is the solution to the SSP equations in the AO formalism. The ϕ_p here are basis functions on the atomic centres, and ϕ_L, ϕ_R are basis functions on source and sink atoms. The $(n+2)$ -dimensional SSP equations for the SSP device

depicted in Fig. 1(a) can now be written in matrix form as

$$\mathbf{P}_{\text{AO}} \begin{pmatrix} \mathbf{c}^{\text{AO}} \\ c_{\text{L}} \\ c_{\text{R}} \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ -iN_{\text{L}} \\ 0 \end{pmatrix}, \quad (24)$$

where the *device matrix* is

$$\mathbf{P}_{\text{AO}} = \begin{pmatrix} \mathbf{E}\mathbf{1} - \mathbf{A} & -\mathbf{b}_{\text{L}} & -\mathbf{b}_{\text{R}} \\ -\tilde{\mathbf{b}}_{\text{L}} & E - \alpha_{\text{L}} - \beta_{\text{L}}e^{iq_{\text{L}}} & 0 \\ -\tilde{\mathbf{b}}_{\text{R}} & 0 & E - \alpha_{\text{R}} - \beta_{\text{R}}e^{iq_{\text{R}}} \end{pmatrix} \quad (25)$$

and where for our single-atom-contact configurations the *connection matrix* elements are

$$\begin{aligned} (\mathbf{b}_{\text{L}})_{\text{p}} &= \delta_{\text{p}\bar{\text{L}}}\beta_{\bar{\text{L}}\text{L}}, \\ (\mathbf{b}_{\text{R}})_{\text{p}} &= \delta_{\text{p}\bar{\text{R}}}\beta_{\bar{\text{R}}\text{R}} \end{aligned} \quad (26)$$

and the source and sink matrix elements are

$$\begin{aligned} E - \alpha_{\text{L}} - \beta_{\text{L}}e^{iq_{\text{L}}} &= \beta_{\text{L}}e^{-iq_{\text{L}}}, \\ E - \alpha_{\text{R}} - \beta_{\text{R}}e^{iq_{\text{R}}} &= \beta_{\text{R}}e^{-iq_{\text{R}}}. \end{aligned} \quad (27)$$

Here, we have used dispersion relations Eq. (6) to remove E from source and sink matrix elements.

The form of Eq. (24) conforms more closely than the previous formulation²⁸ to the widely used Green's function approach,³ in that the electron flux arises from a single inhomogeneity in the source L-element of the vector on the right-hand side of the equation.

C. The SSP equations in the MO basis

This section describes the form of the SSP matrix equations in the MO representation. This alternative form is useful for analysing the behaviour of the solution at the eigenvalues of the isolated molecule. The Hückel MOs

$$\psi_{\text{k}} = \sum_{\text{p}=1}^n \phi_{\text{p}}U_{\text{pk}} \quad (28)$$

diagonalize the secular matrix of the molecule, i.e.,

$$\sum_{\text{q}=1}^n A_{\text{pq}}U_{\text{qk}} = U_{\text{pk}}\epsilon_{\text{k}} \text{ for } \text{p} = 1, 2, \dots, n. \quad (29)$$

We shall assume throughout this paper that since the $n \times n$ -dimensional adjacency matrix \mathbf{A} is real and symmetric, the matrix \mathbf{U} can be considered to be orthogonal. Hence, we can define an augmented $(n+2) \times (n+2)$ -dimensional orthogonal matrix

$$\begin{pmatrix} \mathbf{U} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & 1 & 0 \\ \mathbf{0} & 0 & 1 \end{pmatrix} \quad (30)$$

which can be used to transform AO-based SSP secular equations (13) to give the MO-based version

$$\mathbf{P}_{\text{MO}} \begin{pmatrix} \mathbf{c}^{\text{MO}} \\ c_{\text{L}} \\ c_{\text{R}} \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ -iN_{\text{L}} \\ 0 \end{pmatrix}, \quad (31)$$

where the SSP device matrix in the MO basis is

$$\mathbf{P}_{\text{MO}} = \begin{pmatrix} \mathbf{p} & -\mathbf{u}_{\text{L}} & -\mathbf{u}_{\text{R}} \\ -\tilde{\mathbf{u}}_{\text{L}} & \beta_{\text{L}}e^{-iq_{\text{L}}} & 0 \\ -\tilde{\mathbf{u}}_{\text{R}} & 0 & \beta_{\text{R}}e^{-iq_{\text{R}}} \end{pmatrix} \quad (32)$$

and the diagonal MO-MO block has

$$\mathbf{p}_{\text{kk}'} = \delta_{\text{kk}'}p_{\text{k}} = \delta_{\text{kk}'}(E - \epsilon_{\text{k}}). \quad (33)$$

The connection matrix in the MO basis is more complicated than in the AO form, i.e.,

$$\begin{aligned} (\mathbf{u}_{\text{L}})_{\text{k}} &= (\tilde{\mathbf{U}}\mathbf{b}_{\text{L}})_{\text{k}} = \beta_{\bar{\text{L}}\text{L}}U_{\bar{\text{L}}\text{k}}, \\ (\mathbf{u}_{\text{R}})_{\text{k}} &= (\tilde{\mathbf{U}}\mathbf{b}_{\text{R}})_{\text{k}} = \beta_{\bar{\text{R}}\text{R}}U_{\bar{\text{R}}\text{k}} \end{aligned} \quad (34)$$

and the MO expansion coefficients are related to those in the AO basis by

$$\mathbf{c}^{\text{MO}} = \tilde{\mathbf{U}}\mathbf{c}^{\text{AO}}. \quad (35)$$

The SSP wavefunction, the solution to Eq. (31), is

$$\psi_{\text{SSP}} = \sum_{\text{k}=1}^n c_{\text{k}}^{\text{MO}}\psi_{\text{k}} + c_{\text{L}}\phi_{\text{L}} + c_{\text{R}}\phi_{\text{R}}, \quad (36)$$

where now the ψ_{k} are MOs of the molecule, the coefficients $c_{\text{L}}, c_{\text{R}}$ are identical in Eqs. (23) and (36), and the MO and AO coefficients are related as in Eq. (35).

The two expansions of the wavefunction ψ_{SSP} , i.e., Eqs. (23) and (36), correspond to different models of the conduction process, as illustrated in Fig. 2 for the example of an end-to-end connected allyl chain. In one, the electron hops from AO to AO along edges of the molecular graph; in the other, the MOs act as parallel channels for conduction of electrons.

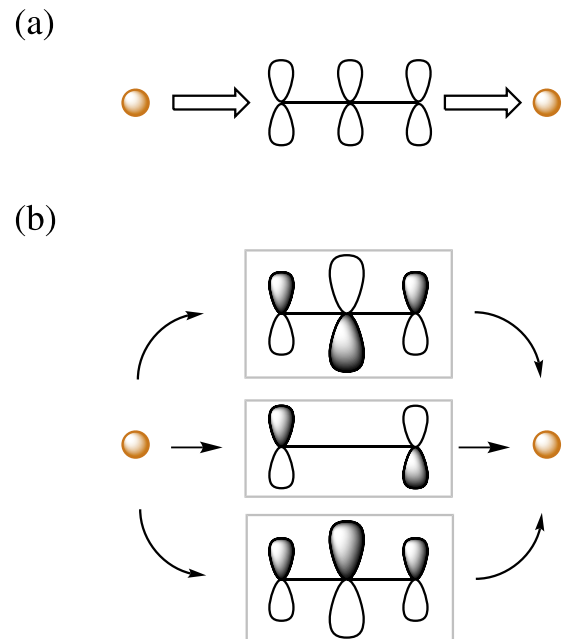


FIG. 2. Alternative schematic representations of ballistic conduction in a source-sink model device: (a) in the AO basis, where conduction between source and sink takes place via bonds between atoms carrying single basis functions, (b) in the MO basis, where the molecular orbitals act as parallel conducting channels between source and sink.

We note that all coefficients c_L , c_R , \mathbf{c}^{MO} , and \mathbf{c}^{AO} are in general complex, but the transformation matrix \mathbf{U} refers to the unperturbed molecule and can always be chosen to be real. It may sometimes be convenient to use complex \mathbf{U} for degenerate eigenvalues, but it is never necessary.

IV. A MATHEMATICAL TOOLKIT

The derivation of the solutions of the SSP equations and their analysis requires a mathematical investigation of the structural polynomials, and quantities related to them. We gather all this information together in the present section in order not to interrupt the flow of the rest of the derivation.

A. Structural polynomials in the MO basis

Our first aim is to express the structural polynomials in terms of the eigenvectors and eigenvalues of the adjacency matrix defined in Eq. (29). Hence,

$$s(E) = \det(\mathbf{E}\mathbf{1} - \mathbf{A}) = \prod_k p_k, \quad (37)$$

where we have used the notation of Eq. (33), and the product runs over the whole molecular spectrum. We shall consider the general structural polynomials

$$\begin{aligned} J_{rs} &= (-1)^{r+s} \det(\mathbf{E}\mathbf{1} - \mathbf{A})^{[r,s]}, \\ v_{pqrs} &= (-1)^{p+q+r+s} \det(\mathbf{E}\mathbf{1} - \mathbf{A})^{[pq,rs]} \end{aligned} \quad (38)$$

which include all the definitions in Eq. (1), viz.,

$$t = J_{\bar{L}\bar{L}}, \quad u = J_{\bar{R}\bar{R}}, \quad J = J_{\bar{L}\bar{R}}, \quad v = v_{\bar{L}\bar{R}\bar{L}\bar{R}}. \quad (39)$$

It can be shown that⁴⁴

$$sv_{pqrs} = \{J_{pr}J_{qs}\}, \quad (40)$$

which has been defined using the notation for the anti-symmetrised product

$$\{X_{pr}X_{qs}\} = X_{pr}X_{qs} - X_{ps}X_{qr}. \quad (41)$$

Eq. (40) is a more general form of the Jacobi-Sylvester relation given in Eq. (2).

It is also convenient to define a notation in which a “hat” symbol indicates a quantity divided by the polynomial s ,

$$\hat{X} = \frac{X}{s}. \quad (42)$$

We shall refer to quantities such as \hat{J}_{rs} as “reduced” structural polynomials. They can be shown to be matrix elements of the inverse of the characteristic matrix by using the well-known Cramer’s rule result

$$\hat{J}_{rs} = (-1)^{r+s} \frac{\det(\mathbf{E}\mathbf{1} - \mathbf{A})^{[r,s]}}{\det(\mathbf{E}\mathbf{1} - \mathbf{A})} = (\mathbf{E}\mathbf{1} - \mathbf{A})_{rs}^{-1}. \quad (43)$$

The spectral representation follows directly as

$$\hat{J}_{rs} = \sum_k \frac{U_{rk}U_{sk}}{E - \epsilon_k}. \quad (44)$$

Defining the quantities

$$\begin{aligned} s_k &= \frac{s}{p_k}, \\ s_{kk'} &= \frac{s}{p_k p_{k'}}, \end{aligned} \quad (45)$$

we see that all the (real) characteristic polynomials of the device, Eq. (1), can be expressed in terms of these factors as

$$\begin{aligned} J_{rs}(E) &= \sum_k U_{rk}U_{sk}s_k, \\ v_{pqrs}(E) &= \sum_{k>k'} \{U_{pk}U_{qk'}\} \{U_{rk}U_{sk'}\} s_{kk'}, \end{aligned} \quad (46)$$

where we have used Eqs. (40) and (43) to deduce the formula for v .

B. Expansion of the reduced structural polynomials

We shall need to expand the solutions of the SSP equations as a series around molecular eigenvalues. We also need to take into account the degeneracy, g , of such eigenvalues. We shall refer to a degenerate space as a “shell,” and use capital roman indices to label such shells. The individual MOs in the shell space, \mathbf{K} , will then be ψ_k for $k \in \mathbf{K}$. (Strictly, g is $g_{\mathbf{K}}$, but the \mathbf{K} dependence will be suppressed when there is no ambiguity.) To understand more fully what happens when the electron energy is at a shell eigenvalue, $\epsilon_{\mathbf{K}}$, we need to explore the behaviour of the reduced structural polynomials near that eigenvalue. For the most general reduced structural polynomial shown in Eq. (38), we have

$$\begin{aligned} \hat{J}_{rs}(E) &= \sum_{k \in \mathbf{K}} \frac{U_{rk}U_{sk}}{E - \epsilon_{\mathbf{K}}} + \sum_{a \notin \mathbf{K}} \frac{U_{ra}U_{sa}}{E - \epsilon_a} \\ &= \sum_k \frac{U_{rk}U_{sk}}{p_{\mathbf{K}}} + \sum_a \frac{U_{ra}U_{sa}}{\epsilon_{\mathbf{K}} - \epsilon_a + p_{\mathbf{K}}}. \end{aligned} \quad (47)$$

In this equation, and in what follows, we use a convention in which the summation indices k, k', \dots , label MOs inside the degenerate shell \mathbf{K} , and indices a, b, \dots , label MOs that are “off-shell,” without explicitly indicating the summation ranges. Within the radius of convergence, each reduced structural polynomial can be expanded in a Laurent series around the point $E = \epsilon_{\mathbf{K}}$. We use $p_{\mathbf{K}} = E - \epsilon_{\mathbf{K}}$ as the expansion parameter. It is easy to deduce that

$$\hat{J}_{rs}(E) = \frac{\hat{J}_{rs,-1}}{p_{\mathbf{K}}} + \hat{J}_{rs,0} + \hat{J}_{rs,1}p_{\mathbf{K}} + \mathcal{O}(p_{\mathbf{K}}^2), \quad (48)$$

where *all* dependence upon E is through powers of $p_{\mathbf{K}}$, and the expansion coefficients are

$$\begin{aligned} \hat{J}_{rs,-1} &= \sum_k U_{rk}U_{sk}, \\ \hat{J}_{rs,0} &= \sum_a \frac{U_{ra}U_{sa}}{(\epsilon_{\mathbf{K}} - \epsilon_a)}, \\ \hat{J}_{rs,1} &= - \sum_a \frac{U_{ra}U_{sa}}{(\epsilon_{\mathbf{K}} - \epsilon_a)^2}. \end{aligned} \quad (49)$$

A similar derivation, using Eq. (40) in the form $\hat{v}_{pqrs} = \{\hat{J}_{pr}\hat{J}_{qs}\}$, produces

$$\begin{aligned} \hat{v}_{pqrs}(E) &= p_{\mathbf{K}}^{-2} \hat{v}_{pqrs,-2} + p_{\mathbf{K}}^{-1} \hat{v}_{pqrs,-1} \\ &\quad + \hat{v}_{pqrs,0} + \hat{v}_{pqrs,1}p_{\mathbf{K}} + \mathcal{O}(p_{\mathbf{K}}^2), \end{aligned} \quad (50)$$

where

$$\begin{aligned}\hat{v}_{\text{pqrs},-2} &= \sum_{k>k'} \{U_{\text{pk}}U_{\text{qk}'}\} \{U_{\text{rk}}U_{\text{sk}'}\}, \\ \hat{v}_{\text{pqrs},-1} &= \sum_{k,a} \frac{\{U_{\text{pk}}U_{\text{qa}}\} \{U_{\text{rk}}U_{\text{sa}}\}}{(\epsilon_K - \epsilon_a)}, \\ \hat{v}_{\text{pqrs},0} &= \sum_{a>b} \frac{\{U_{\text{pa}}U_{\text{qb}}\} \{U_{\text{ra}}U_{\text{sb}}\}}{(\epsilon_K - \epsilon_a)(\epsilon_K - \epsilon_b)} \\ &\quad - \sum_{k,a} \frac{\{U_{\text{pk}}U_{\text{qa}}\} \{U_{\text{rk}}U_{\text{sa}}\}}{(\epsilon_K - \epsilon_a)^2}.\end{aligned}\quad (51)$$

The terms $\hat{J}_{\text{rs},-1}$ (and hence $\hat{t}_{-1}, \hat{u}_{-1}$, and \hat{J}_{-1}) and $\hat{v}_{\text{pqrs},-2}, \hat{v}_{\text{pqrs},-1}$ (and hence $\hat{v}_{-2}, \hat{v}_{-1}$), are all traces over the degenerate shell. It is important to recognise that these are therefore *invariant* to unitary transformations amongst the MOs *within* the shell subspace.

In later parts of this paper, we will need definitions of structural polynomials dependent only upon “off-shell” orbitals, i.e.,

$$\begin{aligned}s_A(E) &= \prod_a p_a, \\ \hat{J}_{A,\text{rs}}(E) &= \sum_a \frac{U_{\text{ra}}U_{\text{sa}}}{E - \epsilon_a}, \\ \hat{v}_{\text{pqrs},A}(E) &= \sum_{a>b} \frac{\{U_{\text{pa}}U_{\text{qb}}\} \{U_{\text{ra}}U_{\text{sb}}\}}{(E - \epsilon_a)(E - \epsilon_b)},\end{aligned}\quad (52)$$

where “A” denotes *all* eigenvectors associated with eigenvalues $\epsilon_a \neq \epsilon_K$. These definitions are exactly analogous to those in Section IV A. It can be seen from Eqs. (47) and (48) and (50) and (51), that the whole energy-dependence of the structural polynomials can be expressed as

$$\begin{aligned}p_K \hat{J}_{\text{rs}}(E) &= \hat{J}_{\text{rs},-1} + p_K \hat{J}_{A,\text{rs}}(E), \\ p_K^2 \hat{v}_{\text{pqrs}}(E) &= \hat{v}_{\text{pqrs},-2} + p_K \hat{v}_{\text{pqrs},-1} + p_K^2 \hat{v}_{A,\text{pqrs}}(E).\end{aligned}\quad (53)$$

In our earlier papers,^{31,35} we have linked conduction and insulation properties to the interlacing properties of the eigenvalues of a graph. Since

$$s(E) = p_K^g s_A(E), \quad (54)$$

we deduce that the polynomials can be written *exactly* in terms of the degeneracy as

$$\begin{aligned}J_{\text{rs}}(E) &= p_K^{g-1} s_A(E) [\hat{J}_{\text{rs},-1} + p_K \hat{J}_{A,\text{rs}}(E)], \\ \hat{v}_{\text{pqrs}}(E) &= p_K^{g-2} s_A(E) [\hat{v}_{\text{pqrs},-2} + p_K \hat{v}_{\text{pqrs},-1} \\ &\quad + p_K^2 \hat{v}_{A,\text{pqrs}}(E)].\end{aligned}\quad (55)$$

The Laurent expansion about the shell eigenvalue equivalent to these expressions is

$$\begin{aligned}J_{\text{rs}}(E) &= p_K^{g-1} s_A(E) (\hat{J}_{\text{rs},-1} + \hat{J}_{\text{rs},0} p_K \\ &\quad + \hat{J}_{\text{rs},1} p_K^2 + \dots), \\ \hat{v}_{\text{pqrs}}(E) &= p_K^{g-2} s_A(E) (\hat{v}_{\text{pqrs},-2} + \hat{v}_{\text{pqrs},-1} p_K \\ &\quad + \hat{v}_{\text{pqrs},0} p_K^2 + \hat{v}_{\text{pqrs},1} p_K^3 + \dots).\end{aligned}\quad (56)$$

The structural polynomial $t = J_{\bar{L}\bar{L}}$ is the characteristic polynomial for the $(n-1)$ -vertex graph derived by removing vertex \bar{L} from the original molecular graph. We can read

the degeneracy, g_t , for eigenvalue ϵ_K in the spectrum of this vertex-deleted graph directly from the lowest non-vanishing coefficient of the expansion of t in Eq. (56). Hence, if $\hat{t}_{-1} \neq 0$, then $g_t = g - 1$, etc. Similar deductions can be made for the graphs corresponding to polynomials u and v .

This machinery can be applied to the case of electron transmission at $E = \epsilon_K$, to give a simple link to our previous results deduced using interlacing³¹ (see Section VII D).

C. The expansion of $D(E)$

We can use the expansion of the structural polynomials in Eq. (53) together with an expansion of the denominator from Eq. (5) to give

$$\hat{D} = \frac{D}{s} = p_K^{-2} \hat{D}_{-2} + p_K^{-1} \hat{D}_{-1} + \hat{D}_0 + O(p_K), \quad (57)$$

where the expansion terms

$$\begin{aligned}\hat{D}_{-2} &= \beta_{\text{LL}}^2 \beta_{\text{RR}}^2 \hat{v}_{-2}, \\ \hat{D}_{-1} &= \beta_{\text{LL}}^2 \beta_{\text{RR}}^2 \hat{v}_{-1} \\ &\quad - \beta_{\text{L}} e^{-iq_{\text{L}}} \beta_{\text{RR}}^2 \hat{u}_{-1} - \beta_{\text{R}} e^{-iq_{\text{R}}} \beta_{\text{LL}}^2 \hat{t}_{-1}, \\ \hat{D}_0 &= \beta_{\text{L}} e^{-iq_{\text{L}}} \beta_{\text{R}} e^{-iq_{\text{R}}} + \beta_{\text{LL}}^2 \beta_{\text{RR}}^2 \hat{v}_0 \\ &\quad - \beta_{\text{L}} e^{-iq_{\text{L}}} \beta_{\text{RR}}^2 \hat{u}_0 - \beta_{\text{R}} e^{-iq_{\text{R}}} \beta_{\text{LL}}^2 \hat{t}_0\end{aligned}\quad (58)$$

are deduced directly from Eq. (5). Strictly speaking, the values of the wire momenta, q_{L} and q_{R} in Eq. (58), are to be evaluated at the eigenvalue ϵ_K . These momenta should also be expanded in powers of p_K . The leading term in this expansion is $O(1)$, and is just the momentum evaluated at the eigenvalue. The higher terms in p_K do not contribute to any expressions we derive. Of course, the \hat{D}_0 term in Eq. (58) will contain a contribution arising from the expansion of the momenta in \hat{D}_{-1} . These extra terms are unimportant for our purposes, since they vanish in all the cases where \hat{D}_0 is the leading term in the expansion of \hat{D} .

We can also use Eqs. (54) and (57) to write $D(E)$ in the form of Eq. (53) as

$$D(E) = p_K^{g-2} s_A(E) \{ \hat{D}_{-2} + p_K \hat{D}_{-1} + p_K^2 \hat{D}_A(E) \}. \quad (59)$$

This expression can be used to deduce the values of E at which $D(E)$ vanishes. In particular, it is clear that $D(E)$ may have a root at $E = \epsilon_K$, with a multiplicity that depends on which (if any) of the terms \hat{D}_{-2} , or \hat{D}_{-1} is non-zero, and on the degeneracy g . The “off-shell” quantity \hat{D}_A is defined as

$$\begin{aligned}\hat{D}_A &= \beta_{\text{L}} \beta_{\text{R}} e^{-i(q_{\text{L}}+q_{\text{R}})} - \beta_{\text{R}} \beta_{\text{LL}}^2 e^{-iq_{\text{R}}} \hat{t}_A(E) \\ &\quad - \beta_{\text{L}} \beta_{\text{RR}}^2 e^{-iq_{\text{L}}} \hat{u}_A(E) + \beta_{\text{LL}}^2 \beta_{\text{RR}}^2 \hat{v}_A(E).\end{aligned}\quad (60)$$

V. SOLUTIONS OF THE SSP EQUATIONS IN THE AO BASIS

Equation (24) has a unique solution provided the $(n+2)$ -dimensional SSP characteristic matrix, \mathbf{P}_{AO} , on the left-hand side of Eq. (24) has an inverse, i.e., iff

$$\det \mathbf{P}_{\text{AO}} = \det \mathbf{P}_{\text{MO}} = D(E) \neq 0, \quad (61)$$

where $D(E)$ is given by Eq. (5). The matrix may be singular in cases where E matches an eigenvalue of the isolated molecule,

depending on fulfilment of some conditions on the rank of a related matrix (see Section VII C and Eq. (59)).

It is useful, however, first to assume that the inverse exists, and only later to examine separately the cases where it does not. The first line of the AO SSP matrix equation, Eq. (24), can be rearranged to give

$$\mathbf{c}^{\text{AO}} = (\mathbf{E}\mathbf{1} - \mathbf{A})^{-1} (\mathbf{b}_{\text{L}c_{\text{L}}} + \mathbf{b}_{\text{R}c_{\text{R}}}) \quad (62)$$

provided E is not an eigenvalue of \mathbf{A} . In components, this is the two-term formula

$$\begin{aligned} c_{\text{p}}^{\text{AO}} &= (\mathbf{E}\mathbf{1} - \mathbf{A})_{\text{pL}}^{-1} \beta_{\text{LL}} c_{\text{L}} + (\mathbf{E}\mathbf{1} - \mathbf{A})_{\text{pR}}^{-1} \beta_{\text{RR}} c_{\text{R}} \\ &= \hat{J}_{\text{pL}} \beta_{\text{LL}} c_{\text{L}} + \hat{J}_{\text{pR}} \beta_{\text{RR}} c_{\text{R}}. \end{aligned} \quad (63)$$

The source-and-sink equations from Eq. (24) are

$$\begin{aligned} -\tilde{\mathbf{b}}_{\text{L}} \mathbf{c}^{\text{AO}} + \beta_{\text{L}} e^{-iq_{\text{L}}} c_{\text{L}} &= -iN_{\text{L}}, \\ -\tilde{\mathbf{b}}_{\text{R}} \mathbf{c}^{\text{AO}} + \beta_{\text{R}} e^{-iq_{\text{R}}} c_{\text{R}} &= 0. \end{aligned} \quad (64)$$

The secular equations, Eq. (64), can be simplified by substituting for \mathbf{c}^{AO} from Eq. (62), and noting that the products $\tilde{\mathbf{b}}(\mathbf{E}\mathbf{1} - \mathbf{A})^{-1}$ reduce to single entries in the inverse, which can in turn be expressed as ratios of determinants by Cramer's rule, giving

$$\begin{aligned} \hat{F}_{\text{L}c_{\text{L}}} - \beta_{\text{LL}} \beta_{\text{RR}} \hat{J}_{\text{c}_{\text{R}}} &= -iN_{\text{L}}, \\ -\beta_{\text{LL}} \beta_{\text{RR}} \hat{J}_{\text{c}_{\text{L}}} + \hat{F}_{\text{R}c_{\text{R}}} &= 0 \end{aligned} \quad (65)$$

as a 2×2 matrix equation for c_{L} and c_{R} . The new quantities used in Eq. (65) are \hat{F}_{L} and \hat{F}_{R} ,

$$\begin{aligned} \hat{F}_{\text{L}} &= \beta_{\text{L}} e^{-iq_{\text{L}}} - \beta_{\text{LL}}^2 \hat{t}, \\ \hat{F}_{\text{R}} &= \beta_{\text{R}} e^{-iq_{\text{R}}} - \beta_{\text{RR}}^2 \hat{u} \end{aligned} \quad (66)$$

given in terms of the *reduced* structural polynomials defined previously. The solution to Eq. (65) gives the source and sink coefficients in the wavefunction as

$$\begin{aligned} c_{\text{L}} &= -iN_{\text{L}} \frac{\hat{F}_{\text{R}}}{\hat{D}} = -iN_{\text{L}} \frac{F_{\text{R}}}{D}, \\ c_{\text{R}} &= -iN_{\text{L}} \beta_{\text{LL}} \beta_{\text{RR}} \frac{\hat{J}}{\hat{D}} = -iN_{\text{L}} \beta_{\text{LL}} \beta_{\text{RR}} \frac{J}{D}, \end{aligned} \quad (67)$$

where $D = D(E) = s\hat{D}(E)$ is given by Eq. (5).

A. Transmission

We are now in a position to derive the expression Eq. (3) for the total transmission, using Eqs. (20) and (67), as

$$T = |\tau|^2 = (\beta_{\text{LL}} \beta_{\text{RR}} N_{\text{L}} N_{\text{R}})^2 \frac{J^2}{|D|^2} = \mathcal{B}(q_{\text{L}}, q_{\text{R}}) \frac{J^2}{|D|^2} \quad (68)$$

which is, of course, identical to that derived previously.²⁸

The current from the source to the left contact in the molecule is

$$\begin{aligned} J_{\text{L} \rightarrow \bar{\text{L}}}^{\text{AO}} &= \frac{1}{i} (\langle \phi_{\text{L}} | \hat{H} | \phi_{\bar{\text{L}}} \rangle c_{\text{L}}^* c_{\bar{\text{L}}}^{\text{AO}} - c.c.) \\ &= -i\beta_{\text{LL}} (c_{\text{L}}^* c_{\bar{\text{L}}}^{\text{AO}} - c.c.) \end{aligned} \quad (69)$$

and since from Eq. (63)

$$c_{\bar{\text{L}}}^{\text{AO}} = \beta_{\text{LL}} \hat{t} c_{\text{L}} + \beta_{\text{RR}} \hat{u} c_{\text{R}}, \quad (70)$$

it follows that

$$\begin{aligned} (c_{\bar{\text{L}}}^* c_{\bar{\text{L}}}^{\text{AO}} - c.c.) &= (\beta_{\text{LL}} \hat{t} |c_{\text{L}}|^2 + \beta_{\text{RR}} \hat{u} c_{\text{L}}^* c_{\text{R}} - c.c.) \\ &= \hat{J}_{\text{RR}} (c_{\text{L}}^* c_{\text{R}} - c_{\text{L}} c_{\text{R}}^*). \end{aligned} \quad (71)$$

Substitution of Eq. (71) into Eq. (69) gives

$$\begin{aligned} J_{\text{L} \rightarrow \bar{\text{L}}}^{\text{AO}} &= -i\beta_{\text{LL}}^2 \beta_{\text{RR}}^2 \frac{N_{\text{L}}^2 J^2}{|D|^2 s} (F_{\text{R}}^* - F_{\text{R}}) \\ &= -i\beta_{\text{R}} \beta_{\text{LL}}^2 \beta_{\text{RR}}^2 N_{\text{L}}^2 \frac{J^2}{|D|^2} (e^{iq_{\text{R}}} - e^{-iq_{\text{R}}}) \\ &= \mathcal{B}(q_{\text{L}}, q_{\text{R}}) \frac{J^2}{|D|^2} \end{aligned} \quad (72)$$

which is the same expression as that given for the gross transmission $T(E)$ in Eqs. (3) and previously,²⁸ as it must be, since there is a single edge connection between $\bar{\text{L}}$ and L through which all current must pass. It is easy to derive the analogous expression for the current in the right-hand link, and to show that likewise

$$J_{\bar{\text{R}} \rightarrow \text{R}}^{\text{AO}}(E) = J_{\text{L} \rightarrow \bar{\text{L}}}^{\text{AO}}(E) = T(E). \quad (73)$$

We now wish to partition these expressions for total current.

B. Bond currents

We shall refer to the currents between atoms within the molecule as *bond* or *edge* currents. They are

$$\begin{aligned} J_{\text{p} \rightarrow \text{q}}^{\text{AO}} &= \frac{1}{i} (\langle \phi_{\text{p}} | \hat{H} | \phi_{\text{q}} \rangle c_{\text{p}}^{\text{AO}*} c_{\text{q}}^{\text{AO}} - c.c.) \\ &= -i\beta_{\text{pq}} (c_{\text{p}}^{\text{AO}*} c_{\text{q}}^{\text{AO}} - c.c.). \end{aligned} \quad (74)$$

Using Eqs. (63) and (67), we can deduce that

$$\begin{aligned} J_{\text{p} \rightarrow \text{q}}^{\text{AO}} &= \mathcal{B}(q_{\text{L}}, q_{\text{R}}) \beta_{\text{pq}} \frac{J}{|D|^2} \frac{\{J_{\text{pL}} J_{\text{qR}}\}}{s} \\ &= \mathcal{B}(q_{\text{L}}, q_{\text{R}}) \beta_{\text{pq}} \frac{J}{|D|^2} \nu_{\text{pqLR}}, \end{aligned} \quad (75)$$

where the final equality uses definition Eq. (40).

The bond current, $J_{\text{p} \rightarrow \text{q}}^{\text{AO}}$, vanishes when $c_{\text{L}} = c_{\text{R}} = 0$. This is implied by Eqs. (63) and (74). We shall use this fact in our discussion of behaviour of transmission quantities at molecular eigenvalues.

The bond currents satisfy a sum rule. Hence, using the first line of Eq. (74) and the p -th secular equation from Eq. (24),

$$\begin{aligned} \sum_{\text{q}} J_{\text{p} \rightarrow \text{q}}^{\text{AO}}(E) &= \delta_{\text{pL}} \frac{\beta_{\text{LL}}}{i} (c_{\text{p}}^{\text{AO}} c_{\text{L}}^* - c_{\text{p}}^{\text{AO}*} c_{\text{L}}) \\ &\quad + \delta_{\text{pR}} \frac{\beta_{\text{RR}}}{i} (c_{\text{p}}^{\text{AO}} c_{\text{R}}^* - c_{\text{p}}^{\text{AO}*} c_{\text{R}}) \end{aligned} \quad (76)$$

and substitution of Eq. (63) in Eq. (76) gives

$$\sum_{\text{q}} J_{\text{p} \rightarrow \text{q}}^{\text{AO}}(E) = \frac{\beta_{\text{LL}} \beta_{\text{RR}}}{i} (c_{\text{L}}^* c_{\text{R}} - c_{\text{R}}^* c_{\text{L}}) (\delta_{\text{pL}} \hat{J}_{\text{pR}} - \delta_{\text{pR}} \hat{J}_{\text{pL}}). \quad (77)$$

After substitution of Eq. (67), we obtain the final result

$$\sum_{\text{q}} J_{\text{p} \rightarrow \text{q}}^{\text{AO}}(E) = T(E) (\delta_{\text{pL}} - \delta_{\text{pR}}). \quad (78)$$

Eq. (78) says that the sum of currents out of *any* vertex is zero. The term $\delta_{p\bar{L}}$ on the right-hand side of Eq. (78) arises because the vertex \bar{L} has a current *in* from the source L to balance its outward currents. A similar remark can be made for the vertex \bar{R} .

C. A physical corollary for *ipso* devices

An important result follows from Eq. (75). It is clear from the structure of the equation that

$$J_{p \rightarrow q}^{\text{AO}} = 0 \text{ when } \bar{L} = \bar{R}, \quad (79)$$

i.e., in the case of an *ipso* connection there are no internal molecular currents. Conduction can only take place for *ipso* devices, if at all, through the directly connected links $L\bar{L}$ and $\bar{L}R$.

The physical interpretation of this mathematical fact is also clear. In an *ipso* device, the net flow into the rest of the molecule from the single contact atom $\bar{L} = \bar{R}$ is $J_{L \rightarrow \bar{L}}^{\text{AO}}(E) = J_{\bar{L} \rightarrow R}^{\text{AO}}(E) = T(E)$, so any putative flow of current within the molecule would consist of a set of self-cancelling closed circulations of arbitrary direction. It makes physical sense that these should have zero amplitude.

VI. GENERAL SOLUTIONS OF THE SSP EQUATIONS IN THE MO BASIS

For solution of the SSP equations in the MO basis, we first study the equations for energies away from molecular eigenvalues.

A. Solutions away from eigenvalues

The solution of the SSP equations, assuming that E is not an eigenvalue, proceeds in the same way as for the AO case. For the SSP coefficients, c_k^{MO} , we find, from Eq. (31) with $E \neq \epsilon_K$ and hence $p_K \neq 0$,

$$c_k^{\text{MO}} = p_K^{-1} (c_L \beta_{\bar{L}L} U_{\bar{L}k} + c_R \beta_{\bar{R}R} U_{\bar{R}k}). \quad (80)$$

The equations for c_L and c_R are of course identical in MO and AO representations. However, the interpretations of the solutions in both cases are different.

A new possibility arises from Eq. (80), of obtaining an expression for the current from ϕ_L into a given MO ψ_k , via

$$J_{L \rightarrow k}^{\text{MO}} = \frac{1}{i} [\langle \phi_L | \hat{H} | \psi_k \rangle c_L^* c_k^{\text{MO}} - \text{c.c.}] \quad (81)$$

and, since

$$\langle \phi_L | \hat{H} | \psi_k \rangle = \beta_{\bar{L}L} U_{\bar{L}k}, \quad (82)$$

it follows that

$$\begin{aligned} J_{L \rightarrow k}^{\text{MO}} &= -i \beta_{\bar{L}L} \beta_{\bar{R}R} \frac{U_{\bar{L}k} U_{\bar{R}k}}{p_K} (c_L^* c_R - c_L c_R^*) \\ &= \mathcal{B}(q_L, q_R) U_{\bar{L}k} U_{\bar{R}k} s_k \frac{J}{|D|^2}. \end{aligned} \quad (83)$$

Using Eq. (46) we can see that there is a simple sum rule

$$\sum_k J_{L \rightarrow k}^{\text{MO}}(E) = T(E) \quad (84)$$

as we would expect, and of course the sum over *all* orbitals ψ_k of contributions $J_{L \rightarrow k}^{\text{MO}}$ recovers the total current. The n molecular orbitals in the molecule provide n channels over which the total current is distributed (cf. Fig. 2).

If the spectrum of the molecular graph has degeneracies, the choice of orthonormal MOs within each eigenspace (shell) is arbitrary, and it is sensible to sum currents over degenerate sets to give

$$J_{L \rightarrow K}^{\text{MO}} = \mathcal{B}(q_L, q_R) \hat{j}_{-1} \frac{\hat{J}}{|\hat{D}|^2}, \quad (85)$$

where we have divided numerator and denominator by s^2 , and used the shell invariant $\hat{j}_{-1} = \hat{j}_{\bar{L}\bar{R}, -1}$ defined in Eq. (49). The shell current is a fraction of the total current, given formally by

$$J_{L \rightarrow K}^{\text{MO}} = \frac{\hat{j}_{-1}}{\hat{j}} T. \quad (86)$$

This “fraction” may be positive or negative, and indeed may be greater than 1.

We can follow a similar derivation for the current from ψ_k to the sink atom, R. This gives a simple conservation law,

$$J_{k \rightarrow R}^{\text{MO}}(E) = J_{L \rightarrow k}^{\text{MO}}(E) \quad (87)$$

as there can be no current *between* MOs, since

$$\langle \phi_k | \hat{H} | \psi_{k'} \rangle = 0$$

when $k \neq k'$.

B. Active and inert orbitals and shells

A final feature revealed by Eq. (83) is that some MOs may be insulating at *all* electron energies, i.e., they can be *inert*. This property occurs when either or both of $U_{\bar{L}k}$ or $U_{\bar{R}k}$ are zero for the particular choice of device connections and MO. Hence, it is a joint property of the molecule (construction of the eigenspaces) and the device (placement of the connections relative to possible nodes in the eigenvectors). Orbitals that are not inert are *active*.

Inert orbitals or shells are merely bystanders in the conduction of the molecular device. Rules for prediction of the occurrence of inert shells can be deduced from case-by-case analysis, as we will see in Secs. VII D and VII E.

VII. SOLUTIONS OF THE SSP EQUATIONS IN THE MO BASIS AT MOLECULAR EIGENVALUES

We now study the nature of solutions of the SSP equations at a particular eigenvalue ϵ_K which we shall assume to have degeneracy, $g = g_K \geq 1$.

A. Shell partitioning of the SSP equations

We can partition the SSP equations into three parts: “on-shell” (g equations with block label K), “off-shell” ($n - g$ equations with block label A), and “source-sink” (two equations). The SSP matrix in Eq. (32) is then given more

explicitly by

$$\mathbf{P}_{\text{MO}} = \begin{pmatrix} p_{\text{K}}\mathbf{1} & 0 & -\mathbf{u}_{\text{KL}} & -\mathbf{u}_{\text{KR}} \\ 0 & \mathbf{p}_{\text{A}} & -\mathbf{u}_{\text{AL}} & -\mathbf{u}_{\text{AR}} \\ -\tilde{\mathbf{u}}_{\text{KL}} & -\tilde{\mathbf{u}}_{\text{AL}} & \beta_{\text{L}}e^{-iq_{\text{L}}} & 0 \\ -\tilde{\mathbf{u}}_{\text{KR}} & -\tilde{\mathbf{u}}_{\text{AR}} & 0 & \beta_{\text{R}}e^{-iq_{\text{R}}} \end{pmatrix} \quad (88)$$

so that the SSP equations become

$$\mathbf{P}_{\text{MO}} \begin{pmatrix} \mathbf{c}_{\text{K}}^{\text{MO}} \\ \mathbf{c}_{\text{A}}^{\text{MO}} \\ c_{\text{L}} \\ c_{\text{R}} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ -iN_{\text{L}} \\ 0 \end{pmatrix}. \quad (89)$$

We note that as $E \rightarrow \epsilon_{\text{K}}$, then $(\mathbf{p}_{\text{A}})_{\text{ab}} \rightarrow \delta_{\text{ab}}(\epsilon_{\text{K}} - \epsilon_{\text{a}}) \neq 0$. As we know that $p_{\text{a}} \neq 0$, we may safely write for the off-shell block

$$c_{\text{a}}^{\text{MO}} = p_{\text{a}}^{-1} (c_{\text{L}}\beta_{\text{LL}}U_{\text{L}\text{a}} + c_{\text{R}}\beta_{\text{RR}}U_{\text{R}\text{a}}). \quad (90)$$

This step cannot be used to solve the equations for the shell orbitals because p_{K} vanishes at the shell eigenvalue.

However, the SSP equations derived from the matrix in Eq. (88) can now be used in exactly the same way as in the previous derivation (cf. Eqs. (62)-(65)), by substituting Eq. (90) into L and R equations in Eq. (88) to produce a set of $(g+2)$ SSP equations with the ‘‘off-shell’’ components folded into the L,R block, and the degenerate shell handled explicitly. The result is

$$\mathbf{P}'_{\text{MO}} = \begin{pmatrix} p_{\text{K}}\mathbf{1} & -\mathbf{u}_{\text{KL}} & -\mathbf{u}_{\text{KR}} \\ -\tilde{\mathbf{u}}_{\text{KL}} & \hat{F}_{\text{AL}} & -\beta_{\text{LL}}\beta_{\text{RR}}\hat{J}_{\text{A}} \\ -\tilde{\mathbf{u}}_{\text{KR}} & -\beta_{\text{LL}}\beta_{\text{RR}}\hat{J}_{\text{A}} & \hat{F}_{\text{AR}} \end{pmatrix} \quad (91)$$

for the device matrix and

$$\mathbf{P}'_{\text{MO}} \begin{pmatrix} \mathbf{c}_{\text{K}}^{\text{MO}} \\ c_{\text{L}} \\ c_{\text{R}} \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ -iN_{\text{L}} \\ 0 \end{pmatrix} \quad (92)$$

for the SSP equation. The 2×2 source-sink terms are defined by analogy with Eq. (66), viz.,

$$\begin{aligned} \hat{F}_{\text{AL}}(E) &= \beta_{\text{L}}e^{iq_{\text{L}}} - \beta_{\text{LL}}^2 \hat{t}_{\text{A}}, \\ \hat{F}_{\text{AR}}(E) &= \beta_{\text{R}}e^{iq_{\text{R}}} - \beta_{\text{RR}}^2 \hat{u}_{\text{A}}. \end{aligned} \quad (93)$$

The ‘‘off-shell’’ polynomials appearing in Eq. (93) were defined in Eq. (52).

B. The shell connection matrix, rank, and the echelon representation

A key to understanding Eq. (93) is the $(g \times 2)$ -dimensional *shell connection matrix* between the source-sink and degenerate shell, K, blocks

$$\mathbf{B}_{\text{K}}^{\text{con}} = (\mathbf{u}_{\text{KL}} \quad \mathbf{u}_{\text{KR}}) = \begin{pmatrix} \beta_{\text{LL}}U_{\text{L}1} & \beta_{\text{RR}}U_{\text{R}1} \\ \beta_{\text{LL}}U_{\text{L}2} & \beta_{\text{RR}}U_{\text{R}2} \\ \vdots & \vdots \\ \beta_{\text{LL}}U_{\text{L}g} & \beta_{\text{RR}}U_{\text{R}g} \end{pmatrix}. \quad (94)$$

As the first diagonal block of Eq. (91) is proportional to the unit matrix, we are free to make any suitable orthogonal transformation amongst the orbitals within the shell, K. In particular, we can use a sequence of 2×2 rotations to bring the matrix $\mathbf{B}_{\text{K}}^{\text{con}}$ to *row echelon* form

$$\mathbf{B}_{\text{K}}^{\text{con}} = \begin{pmatrix} a & b \\ 0 & d \\ 0 & 0 \\ \vdots & \vdots \end{pmatrix}, \quad (95)$$

where $a = \beta_{\text{LL}}U'_{\text{L}1}$, $b = \beta_{\text{RR}}U'_{\text{R}1}$, and $d = \beta_{\text{LL}}U'_{\text{R}2}$ are expressed in terms of the only non-zero $\bar{\text{L}}$ and $\bar{\text{R}}$ components of the orbitals after the operation of the sequence of orthogonal transformations leading to this *echelon* representation of the degenerate shell. The echelon representation is different, in principle, for each possible device, i.e., for each possible choice of $\bar{\text{L}}, \bar{\text{R}}$.

We can use the fact that the coefficients $\hat{t}_{-1}, \hat{u}_{-1}, \hat{j}_{-1}$, and \hat{v}_{-2} defined in Eqs. (49) and (51) are *invariant* to orthogonal transformations amongst the shell orbitals to obtain simple expressions for the coefficients a, b , and d . These are

$$\begin{aligned} a^2 &= \beta_{\text{LL}}^2 \hat{t}_{-1}, \\ b^2 + d^2 &= \beta_{\text{RR}}^2 \hat{u}_{-1}, \\ ab &= \beta_{\text{LL}}\beta_{\text{RR}}\hat{j}_{-1}, \\ a^2d^2 &= \beta_{\text{LL}}^2\beta_{\text{RR}}^2 \hat{v}_{-2}. \end{aligned} \quad (96)$$

Necessary and sufficient conditions for the shell connection matrix to have rank 1 are now obvious, i.e., that *either* $d = 0$ *or* $a = 0$. In each case, it follows that

$$\hat{v}_{-2} = 0 \iff \{U_{\text{L}k}U_{\text{R}k'}\} = 0 \forall k, k' \in \text{K}. \quad (97)$$

The necessary and sufficient conditions for the connection matrix to be of rank 0 are that $a = b = d = 0$, which imply that $\hat{t}_{-1} = \hat{u}_{-1} = \hat{v}_{-2} = 0$, and hence that

$$U_{\text{L}k} = U_{\text{R}k} = 0, \text{ for } k = 1, \dots, g \quad (98)$$

in which case the quantities $\hat{j}_{-1}, \hat{v}_{-1}$ also vanish.

The rank, r_{K} , of the transformed $\mathbf{B}_{\text{K}}^{\text{con}}$ matrix must be $r_{\text{K}} \leq \min(g, 2)$, and hence

$$p_{\text{K}}c_{\text{k}} = 0 \text{ for } k = r_{\text{K}} + 1, \dots, g. \quad (99)$$

These $g - r_{\text{K}}$ equations have solution $c_{\text{k}}^{\text{MO}} = 0$ when $E \neq \epsilon_{\text{K}}$. When the energy is equal to the eigenvalue, ϵ_{K} , we have a case where the SSP matrix in Eq. (88) has no inverse, and the solution in the $(g - r_{\text{K}})$ -dimensional manifold is undetermined. We can use *continuity*, however, to argue that it makes no physical sense for an insulating orbital suddenly to become conducting at its own eigenvalue. We can, therefore, take $c_{\text{k}}^{\text{MO}} = 0$ for all values of E . Hence, as shown in Subsection VII D, we need consider only solutions of the SSP equations in the $(r_{\text{K}} + 2)$ -dimensional manifold determined by the first r molecular orbitals and the source and sink atoms.

C. Shell and bond currents in the echelon representation

The shell current, $J_{L \rightarrow K}^{\text{MO}}$, from the source L to shell K in the echelon representation goes entirely through the first orbital. From Eq. (83), we have

$$\begin{aligned} J_{L \rightarrow K}^{\text{MO}}(E) &= \mathcal{B}(q_L, q_R) U'_{L1} U'_{R1} \frac{\hat{J}}{|\hat{D}|^2} \\ &= \mathcal{B}(q_L, q_R) \hat{J}_{-1} \frac{\hat{J}}{|\hat{D}|^2} = J_{L \rightarrow K}(E). \end{aligned} \quad (100)$$

We shall also examine the behaviour of currents along bonds (graph edges) by looking at the quantity $J_{p \rightarrow q}^{\text{AO}}(\epsilon_K)$ (cf. Eq. (75)) in the “hatted” form,

$$J_{p \rightarrow q}^{\text{AO}} = \mathcal{B}(q_L, q_R) \beta_{pq} \frac{\hat{J}}{|\hat{D}|^2} \hat{v}_{pq\bar{L}\bar{R}}. \quad (101)$$

To explore the behaviour of the bond currents at the shell eigenvalue, we have to expand the antisymmetric quantity in Eq. (101) using Eq. (53). The expansion of \hat{v} contains the coefficients defined in Eq. (51). Note that the quantity $\hat{v}_{pq\bar{L}\bar{R}, -2}$ contains factors $\{U_{Lk} U_{Rk'}\}$. The leading term in the expansion of $J_{p \rightarrow q}^{\text{AO}}$, therefore, is determined by the rank of the connection matrix, $\mathbf{B}_K^{\text{con}}$. Ranks 2, 1, and 0 give, in principle, leading terms $\hat{v}_{pq\bar{L}\bar{R}, -2}$, $\hat{v}_{pq\bar{L}\bar{R}, -1}$, and $\hat{v}_{pq\bar{L}\bar{R}, -0}$, respectively.

D. The eleven canonical molecular conduction cases for a shell with eigenvalue ϵ_K

We now make a connection with our previous work^{31,35} which uses graph theoretical concepts. The molecule can be represented by an n -vertex graph, G , and the eigenvalues of the adjacency matrix (or equivalently the roots of the characteristic polynomial) for G can be written in non-increasing order as $\{\epsilon_1 \geq \epsilon_2 \geq \dots \epsilon_n\}$.

We consider three vertex-deleted graphs, $G - \bar{L}$, $G - \bar{R}$, $G - \bar{L} - \bar{R}$, which are related to the molecular device. We label the eigenvalues of these graphs, respectively, as $\{\epsilon_1^{(t)} \geq \epsilon_2^{(t)} \geq \dots \epsilon_{n-1}^{(t)}\}$, $\{\epsilon_1^{(u)} \geq \epsilon_2^{(u)} \geq \dots \epsilon_{n-1}^{(u)}\}$, and $\{\epsilon_1^{(v)} \geq \epsilon_2^{(v)} \geq \dots \epsilon_{n-2}^{(v)}\}$.

The Cauchy interlacing theorem⁴⁵ implies that

$$\begin{aligned} \epsilon_k &\geq \epsilon_k^{(t)} \geq \epsilon_{k+1}, \quad k = 1, \dots, n-1, \\ \epsilon_k &\geq \epsilon_k^{(u)} \geq \epsilon_{k+1}, \quad k = 1, \dots, n-1, \\ \epsilon_k^{(t)} &\geq \epsilon_k^{(v)} \geq \epsilon_{k+1}^{(t)}, \quad k = 1, \dots, n-2, \\ \epsilon_k^{(u)} &\geq \epsilon_k^{(v)} \geq \epsilon_{k+1}^{(u)}, \quad k = 1, \dots, n-2. \end{aligned} \quad (102)$$

Hence, for a root of the characteristic polynomial of G , of multiplicity, $g \geq 1$, the multiplicities of the roots of the other characteristic polynomials must obey

$$\begin{aligned} \max(0, g-1) &\leq g_t \leq g+1, \\ \max(0, g-1) &\leq g_u \leq g+1, \\ \max(0, g-2) &\leq g_v \leq g+2. \end{aligned} \quad (103)$$

We have previously used the interlacing theorem to show that transmission at the Fermi level in molecular devices can be classified under a set of *eleven* cases characterised by the nullities (numbers of zero eigenvalues) g, g_t, g_u , and g_v of the four graphs we have described.^{31,35} The interlacing theorem

TABLE I. Patterns of conduction for *non-ipsa* molecular devices, showing the total transmission, $T(\epsilon_K)$, the bond currents $J_{p \rightarrow q}^{\text{AO}}(\epsilon_K)$ calculated at the shell eigenvalue ϵ_K , and the shell current $J_{L \rightarrow K}^{\text{MO}}(E)$ at any energy. The non-zero quantities $T_a = \mathcal{B}(q_L, q_R) \hat{J}_0^2 / |\hat{D}_0|^2$, $T_b = \mathcal{B}(q_L, q_R) \beta_{pq} \hat{J}_0 \hat{v}_{pq\bar{L}\bar{R}, 0} / |\hat{D}_0|^2$, $T_c = \mathcal{B}(q_L, q_R) \hat{J}_{-1}^2 / |\hat{D}_{-1}|^2$, and $T_d = \mathcal{B}(q_L, q_R) \beta_{pq} \hat{J}_{-1} \hat{v}_{pq\bar{L}\bar{R}, -1} / |\hat{D}_{-1}|^2$ are evaluated using Eq. (58), subject to conditions implied by g_t, g_u , and g_v in the particular case.

r_K	Case	g_t	g_u	g_v	g_j	$T(\epsilon_K)$	$J_{p \rightarrow q}^{\text{AO}}(\epsilon_K)$	$J_{L \rightarrow K}^{\text{MO}}(E)$
0	1	$g+1$	$g+1$	$g+2$	$\geq g+1$	0	0	0
	2	$g+1$	$g+1$	g	g	T_a	T_b	0
	3	$g+1$	g	$g+1$	$\geq g+1$	0	0	0
	4	$g+1$	g	g	g	T_a	T_b	0
	6	g	g	$g+1$	g	T_a	T_b	0
	7.1	g	g	g	g	T_a	T_b	0
	7.2	g	g	g	$\geq g+1$	0	0	0
1	5	$g+1$	$g-1$	g	$\geq g$	0	0	0
	8	g	$g-1$	$g-1$	$\geq g$	0	0	0
	9	$g-1$	$g-1$	g	$g-1$	T_c	T_d	$\neq 0$
	10	$g-1$	$g-1$	$g-1$	$g-1$	T_c	T_d	$\neq 0$
2	11.1	$g-1$	$g-1$	$g-2$	$g-1$	0	0	$\neq 0$
	11.2	$g-1$	$g-1$	$g-2$	$\geq g$	0	0	0

alone does not give access to full information about g_j but the table included here does so, enabling some new sub-cases to be distinguished. The cases were previously stated in terms of the Fermi energy, but the analysis can be extended to the whole eigenvalue spectrum of G .⁴⁶

We re-examine these eleven canonical cases in detail in the Appendix according to the rank of the connection matrix, $\mathbf{B}_K^{\text{con}}$, where it is shown that the eight possibilities for the construction of $\mathbf{B}_K^{\text{con}}$ in the echelon representation map onto the eleven cases for conduction determined by interlacing. The results of this process are given in Table I, showing *total* transmission, T , and bond currents $J_{p \rightarrow q}^{\text{AO}}$, both evaluated at the shell eigenvalue, ϵ_K , and the shell current, $J_{L \rightarrow K}$, for any energy. The property of inertness or activity of the shell can be read off from the final column of the table. An entry “ $\neq 0$ ” means that the shell is active, and “0” means that it is inert. Overall conduction or insulation of the device is given by the entry in column 7 of the table.

The rank-0 cases in Table I possess the very important property that for all these cases the shell is insulating at *all* energies, i.e., is inert. As far as conduction is concerned, it is as if the shell were not present. Any conduction at the eigenvalue predicted in that rank-0 case must, therefore, be carried through “off-shell” orbitals. This is very different from the normal behaviour, where an “active” shell carries all the transmission at its own shell eigenvalue.

The property of inertness is not particularly unusual nor is it restricted to degenerate shells. Indeed, Table I shows that all cases bar three (9, 10, and 11.1) of the possible eigenvalue combinations imply an inert shell.

The classification of case by rank r_K matches exactly the classification by *Varieties* in the mathematical treatment of Fermi-level conduction published elsewhere.⁴⁷ We note that rank zero corresponds to Variety 3, rank one to Variety 2, and rank two to Variety 1. Devices that fall under cases 11.1 and 11.2 are based on uniform-core graphs described in Ref. 47.

Two further remarks can be made about the applicability of this extended table, compared to that of Table I in Refs. 31 and 35 which were limited to describing behaviour at the Fermi level for devices based on general and bipartite graphs, respectively. The first is about the interpretation of the present table for the case when all quantities are evaluated at a value, E , that is not an eigenvalue of G , i.e., when $g = 0$. The formally allowed cases in Table I are then those with $\min\{g_t - g, g_u - g, g_v - g\} \geq 0$, i.e., the cases of rank $r_K = 0$. In such cases, the generic statements about overall transmission (column 7) and bond currents (column 8) hold, provided all the quantities are evaluated by taking the structural polynomials at E . The shell current, $J_{L \rightarrow K}^{\text{MO}}(E)$ (column 9), has no meaning in this case.

The second remark is about the use of the extended table for devices based on bipartite graphs. When the table referred only to $\epsilon_K = 0$, it was possible to use the special property that the nullity and order of a bipartite graph have the same parity to reduce the number of cases from 11 to 5 (or from 13 to 6 in the finer classification used in the present paper). When ϵ_K is a general eigenvalue, the link between nullity and order is broken; deletion of a vertex of a bipartite graph may leave the degeneracy of a given eigenvalue unchanged, (or increased or decreased by one), and hence, any of the cases in Table I may apply.

E. Conduction in *ipso* devices

Devices where the external links are connected to the *same* internal atom are termed *ipso* devices. In this case it is easy to see that we can take $t = u = j$, and $v \equiv 0$, and it is clear that the connection matrix can have rank 0 or 1 only. In our treatment we consider that the parameters β_L, β_{LL} , and β_R, β_{RR} have the same values as for *non-ipso* devices. The expansion of \hat{D} becomes

$$\begin{aligned} \hat{D}_{-2} &= 0, \\ \hat{D}_{-1} &= -(\beta_L e^{-iq_L} \beta_{RR}^2 + \beta_R e^{-iq_R} \beta_{LL}^2) \hat{t}_{-1}, \\ \hat{D}_0 &= \beta_L e^{-iq_L} \beta_R e^{-iq_R} - (\beta_L e^{-iq_L} \beta_{RR}^2 \\ &\quad + \beta_R e^{-iq_R} \beta_{LL}^2) \hat{t}_0 \end{aligned} \quad (104)$$

\hat{D}_{-2} vanishes because $v \equiv 0$.

There are only three possible cases (cf. Table II) depending on the allowed g_t values for the graph with vertex \bar{L} removed. There is no restriction on the value of g .

TABLE II. Patterns of conduction for *ipso* molecular devices, showing the total transmission $T(\epsilon_K)$, the bond currents $J_{p \rightarrow q}^{\text{AO}}(\epsilon_K)$ calculated at the shell eigenvalue ϵ_K , and the shell current $J_{L \rightarrow K}^{\text{MO}}(E)$ at *any* energy. The non-zero quantities $T_a = \mathcal{B}(q_L, q_R) \hat{t}_0^2 / |\hat{D}_0|^2$ and $T_b = \mathcal{B}(q_L, q_R) \hat{t}_{-1}^2 / |\hat{D}_{-1}|^2$ are evaluated using Eq. (104) for the particular case.

r_K	Case	g_t	$T(\epsilon_K)$	$J_{p \rightarrow q}^{\text{AO}}(\epsilon_K)$	$J_{L \rightarrow K}^{\text{MO}}(E)$
0	I1	$g + 1$	0	0	0
	I2	g	T_a	0	0
1	I3	$g - 1$	T_b	0	$\neq 0$

The cases exhibit all possible combinations of device conduction/insulation and shell character.

Case I1 ($g_t = g + 1$)

This case has a rank-0 connection matrix because $\hat{t}_{-1} = \hat{t}_0 = 0$. The numerator in c_R is $O(p_K)$, whereas \hat{D}_0 is the leading term in the denominator. Hence $c_R = 0$ at the eigenvalue; there is device insulation and the shell is inert.

Case I2 ($g_t = g$)

This case also has rank 0 because $\hat{t}_{-1} = 0$. As $\hat{t}_0 \neq 0$, and \hat{D}_0 is the leading term in the denominator, there is device conduction at the eigenvalue. However, the shell is inert, so conduction at this eigenvalue is carried entirely by orbitals from other shells.

Case I3 ($g_t = g - 1$)

This case has a rank-1 connection matrix, and is the equivalent of the *non-ipso* case I1. We have $\hat{t}_{-1} \neq 0$, and so $\hat{D}_{-1} \neq 0$. The numerator and denominator have the same order in p_K , and device conduction occurs at the eigenvalue. The shell is active and carries all the current at the shell eigenvalue.

F. A difference between conduction of *ipso*- and *non-ipso* devices

The remaining feature of *ipso* devices is that the expressions for currents and total transmission depend upon the behaviour of a single structural polynomial. For this reason, the transmission $T(E)$ has zeros every time that $\hat{t}(E)$ vanishes. It is easy to see from the definition, Eq. (43), that $\hat{t}(E)$ is a piecewise continuous curve with asymptotes at the molecular eigenvalues, and that the gradient is always negative. It follows that there will be a zero of $\hat{t}(E)$ between each molecular eigenvalue (cf. Fig. 9). Consequently, *ipso* transmission curves typically look very different from the curves for *non-ipso* devices based on the same molecule, cf. Section IX.

VIII. CONDUCTION IN MOLECULES WITH BIPARTITE GRAPHS

An alternant molecule has a bipartite molecular graph containing two disjoint sets of nodes (atoms) and in which edges (bonds) connect only members of the two sets. We shall call these two sets \mathcal{S}_o and \mathcal{S}_* . If we number the members of the sets contiguously, then we can write the adjacency matrix in the form

$$\mathbf{A} = \begin{pmatrix} 0 & \mathbf{B} \\ \tilde{\mathbf{B}} & 0 \end{pmatrix}, \quad (105)$$

where we have placed the n_o un-starred vertices in the first, and the n_* starred vertices in the second block, and we assume that $n_o \leq n_*$. The dimension of the matrix \mathbf{B} is, therefore, $n_o \times n_*$.

A simple two-component SSP approach to conductivity in bipartite molecules has been developed^{26,48} for the case $E = 0$. In this section, we derive rules that apply to such molecules at general values of E .

A. The Coulson-Rushbrooke theorem

For convenience, we present a compact derivation of this well-known⁴⁹ theorem in a formalism that is useful for our study of conduction.

We can solve the eigenvector problem for the positive semi-definite matrix $\tilde{\mathbf{B}}\mathbf{B}$ of dimension $n_o \times n_o$ and of rank $r \leq n_o$, in the form

$$\begin{aligned} \tilde{\mathbf{B}}\mathbf{B}\mathbf{V}_k &= \mathbf{V}_k\sigma_k^2 \text{ for } k = 1, \dots, r, \\ \tilde{\mathbf{B}}\mathbf{B}\mathbf{V}_k &= 0 \text{ for } k = r + 1, \dots, n_o, \end{aligned} \quad (106)$$

where the $n_o \times n_o$ matrix, \mathbf{V} , formed from the n_o columns \mathbf{V}_k is an orthogonal transformation with $n_o - r$ null-space eigenvectors. We can also consider the n_* -dimensional eigenvalue problem

$$\begin{aligned} \tilde{\mathbf{B}}\mathbf{B}\mathbf{W}_k &= \mathbf{W}_k\sigma_k^2 \text{ for } k = 1, \dots, r, \\ \tilde{\mathbf{B}}\mathbf{B}\mathbf{W}_k &= 0 \text{ for } k = r + 1, \dots, n_*, \end{aligned} \quad (107)$$

which has r identical positive eigenvalues, a null-space of dimension $n_* - r$, and the matrix \mathbf{W} is orthogonal. We can write the *singular value decomposition* of \mathbf{B} as

$$\mathbf{B}\mathbf{W} = \mathbf{V}\mathbf{\Sigma}$$

or

$$\tilde{\mathbf{B}}\mathbf{V} = \tilde{\mathbf{W}}\mathbf{\Sigma}, \quad (108)$$

where the $n_o \times n_*$ matrix, $\mathbf{\Sigma}$ is in principle rectangular, with a diagonal containing the *positive* numbers $\sigma_1 \geq \sigma_2 \geq \dots \geq \sigma_r > 0$.

We can now construct an $(n_o + n_*)$ -dimensional orthogonal transformation

$$\begin{pmatrix} \mathbf{V} & 0 \\ 0 & \mathbf{W} \end{pmatrix} \quad (109)$$

that when applied to adjacency matrix Eq. (105) gives rise, for each of the r terms having $\sigma_k > 0$, to a series of 2×2 interacting blocks of the form

$$\begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}. \quad (110)$$

These blocks are each diagonalised by the same 2-dimensional orthogonal transformation

$$\begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix}. \quad (111)$$

The appropriate combination of Eqs. (109) and (111) solves the original eigenvalue problem by providing r paired solutions $\psi_k, \psi_{\bar{k}}$ having eigenvalues $+\sigma_k$ and $-\sigma_k$, respectively, and constructed from columns of the orthogonal matrices \mathbf{V} and \mathbf{W} . They are

$$\begin{aligned} \psi_k &= \frac{1}{\sqrt{2}} \left(\sum_{p \in \mathcal{S}_o} V_{pk} \phi_p + \sum_{p \in \mathcal{S}^*} W_{pk} \phi_p \right), \\ \psi_{\bar{k}} &= \frac{1}{\sqrt{2}} \left(\sum_{p \in \mathcal{S}_o} V_{pk} \phi_p - \sum_{p \in \mathcal{S}^*} W_{pk} \phi_p \right) \end{aligned} \quad (112)$$

for $k = 1, \dots, r$, and the nullspace is

$$\begin{aligned} \psi_k &= \sum_{p \in \mathcal{S}_o} V_{pk} \phi_p \text{ for } k = r + 1, \dots, n_o, \\ \psi_{\bar{k}^*} &= \sum_{p \in \mathcal{S}^*} W_{pk} \phi_p \text{ for } k^* = r + 1, \dots, n_*. \end{aligned} \quad (113)$$

Hence, there are $2r$ eigenvalues in pairs related to each other by a change of sign, and a nullspace of dimension $n_o + n_* - 2r$. This is the content of the Coulson-Rushbrooke pairing theorem.⁵⁰⁻⁵² We now derive an extension for conduction properties.

B. Structural polynomials for bipartite graphs

For bipartite graphs (alternant molecules), we can obtain structural polynomials from the above formulae for the eigenvectors and eigenvalues, together with the spectral expansions given earlier. Hence, after some algebra,

$$\begin{aligned} \hat{i} &= E \sum_{k=1}^r \frac{V_{\bar{L}k}^2}{E^2 - \sigma_k^2} + \frac{1}{E} \sum_{k=r+1}^{n_o} V_{\bar{L}k}^2 \text{ for } \bar{L} \in \mathcal{S}_o, \\ \hat{i} &= E \sum_{k=1}^r \frac{W_{\bar{L}k}^2}{E^2 - \sigma_k^2} + \frac{1}{E} \sum_{k=r+1}^{n_*} W_{\bar{L}k}^2 \text{ for } \bar{L} \in \mathcal{S}^*. \end{aligned} \quad (114)$$

The formulae for \hat{u} are easily obtained by analogy. It is seen that

$$\begin{aligned} \hat{i}(-E) &= -\hat{i}(E), \\ \hat{u}(-E) &= -\hat{u}(E), \end{aligned} \quad (115)$$

so that both functions are *odd*, as expected from parity arguments. The equations for \hat{j} are more complicated, as there are two cases, depending on whether indices \bar{L}, \bar{R} belong to the same or different sets. When $\bar{L} \in \mathcal{S}_o$ and $\bar{R} \in \mathcal{S}_o$,

$$\hat{j} = E \sum_{k=1}^r \frac{V_{\bar{L}k} V_{\bar{R}k}}{E^2 - \sigma_k^2} + \frac{1}{E} \sum_{k=r+1}^{n_o} V_{\bar{L}k} V_{\bar{R}k} \quad (116)$$

which is an odd function of E . When $\bar{L} \in \mathcal{S}_o$ and $\bar{R} \in \mathcal{S}^*$,

$$\hat{j} = \sum_{k=1}^r \sigma_k \frac{V_{\bar{L}k} W_{\bar{R}k}}{E^2 - \sigma_k^2} \quad (117)$$

which is even. From the formula $\hat{v} = \hat{u}\hat{i} - \hat{j}^2$, it is clear that $\hat{v}(E) = \hat{v}(-E)$, regardless of the nature of \bar{L} and \bar{R} .

C. Conduction properties of alternant molecules

We now consider the transmission properties of molecules with bipartite graphs for unbiased devices, i.e., those for which $\alpha_L = \alpha_R = 0$, under the transformation $E \rightarrow -E$. This transformation affects the momenta (cf. Eq. (6)) through $q_L \rightarrow \pi - q_L$ and $q_R \rightarrow \pi - q_R$. It follows that $\exp(-iq_L) \rightarrow -\exp(iq_L)$, and $\sin q_L \rightarrow -\sin q_L$. The terms in q_R behave in an identical manner. From the discussion of the transformation properties of these quantities, it is obvious from Eq. (5) that

$$D(-E) = D(E)^* \quad (118)$$

and hence

$$T(-E) = T(E) \quad (119)$$

so that the total transmission is symmetric about $E = 0$ for unbiased devices.

We can also look at the symmetry properties of the MO currents by writing Eq. (83) in terms of the hatted polynomials,

$$J_{L \rightarrow k}^{\text{MO}}(E) = \mathcal{B}(q_L, q_R) \frac{U_{\bar{L}k} U_{\bar{R}k}}{E - \epsilon_k} \frac{\hat{j}(E)}{|\hat{D}(E)|^2}. \quad (120)$$

Putting this equation into the context of the current section: for the paired orbitals, $\psi_k, \psi_{\bar{k}}$, we recognise that the eigenvectors for the paired MOs satisfy

$$\begin{aligned} U_{pk} &= U_{p\bar{k}} \text{ for } p \in \mathcal{S}_o, \\ U_{pk} &= -U_{p\bar{k}} \text{ for } p \in \mathcal{S}_*, \end{aligned} \quad (121)$$

and

$$J_{L \rightarrow k}^{\text{MO}}(E) = J_{L \rightarrow \bar{k}}^{\text{MO}}(-E). \quad (122)$$

The paired orbitals have currents that are reflections of each other about the line $E = 0$. It is also obvious that Eq. (122) for $g \geq 2$ extends also to shells, so that

$$J_{L \rightarrow K}^{\text{MO}}(E) = J_{L \rightarrow \bar{K}}^{\text{MO}}(-E). \quad (123)$$

It can be shown that bond currents in bi-partite molecules also display the same symmetry,

$$J_{p \rightarrow q}^{\text{AO}}(E) = J_{p \rightarrow \bar{q}}^{\text{AO}}(-E). \quad (124)$$

D. Conduction at the Fermi level

We now turn to the conduction properties of the shell at $\epsilon_k = 0$. The conduction properties can be discussed in a very simple manner using the eigenspaces listed in Eqs. (112) and (113), and the connection matrix in Eqs. (31) and (34).

For molecular graphs that possess a nullspace, we have a single shell with $\epsilon_K = 0$ and degeneracy $g = n_o + n_* - 2r$. There are two possibilities.

1. Contact atoms in different sets, e.g., $\bar{L} \in \mathcal{S}_o$ and $\bar{R} \in \mathcal{S}_*$.

In this case, the structure of the *null-space* connection vector is

$$\mathbf{u}_L = \beta_{\bar{L}\bar{L}} \begin{pmatrix} V_{\bar{L}r+1} \\ \vdots \\ V_{\bar{L}n_o} \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \mathbf{u}_R = \beta_{\bar{R}\bar{R}} \begin{pmatrix} 0 \\ \vdots \\ 0 \\ W_{\bar{R}r+1} \\ \vdots \\ W_{\bar{R}n_*} \end{pmatrix}. \quad (125)$$

The formula for MO currents, Eq. (83), shows that current is proportional to a product of \bar{L} and \bar{R} MO coefficients from the connection vectors. The structure of the vectors in Eq. (125) implies that this product is identically zero. The shell carries no current and is inert regardless of the rank of the connection matrix.

2. Contact atoms in the same set, e.g., $\bar{L} \in \mathcal{S}_o$ and $\bar{R} \in \mathcal{S}_o$.

In this case, the structure of the *null-space* connection vector is

$$\mathbf{u}_L = \beta_{\bar{L}\bar{L}} \begin{pmatrix} V_{\bar{L}r+1} \\ \vdots \\ V_{\bar{L}n_o} \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \mathbf{u}_R = \beta_{\bar{R}\bar{R}} \begin{pmatrix} V_{\bar{R}r+1} \\ \vdots \\ V_{\bar{R}n_o} \\ 0 \\ \vdots \\ 0 \end{pmatrix}. \quad (126)$$

The $n_* - r$ molecular orbitals from the starred space are all *inert*, but the MOs from the un-starred space are not necessarily inert. The shell may therefore still be active, depending on the case to which the shell belongs (cf. Table I).

For cases where $E = 0$ is *not* an eigenvalue, the present reasoning makes a connection with a ‘‘symmetry rule’’ (actually a graph-theoretical rule) for *non-ipsa* conduction at the Fermi level for closed-shell alternant molecules.^{42,53} It was observed that the predicted Fermi-level conduction of a molecule with bipartite molecular graph and a non-zero HOMO-LUMO gap (specifically a Kekulean benzenoid) is large when both HOMO and LUMO have entries of large magnitude on both connection vertices (our \bar{L} and \bar{R}) and the product of entries is of opposite sign for HOMO and LUMO. By the pairing theorem, this latter requirement implies that the connection vertices are in different partite sets.

This rule has a straightforward interpretation in terms of shell contributions. HOMO and LUMO shells of a bipartite graph have mirror conduction curves, so are either both active or both inert. For active shells, both shell conduction curves will be close to local maxima in the vicinity of the Fermi level. If the connection vertices are in opposite sets, the curves will contribute equal amounts to the total conduction at the Fermi level. (Other active shells will typically also contribute. Such contributions may be positive or negative.) If the connection vertices belong to the same partite set, however, we have nullity signature $g = 0$, $g_r = g_u = 1$, $g_v = 2$ and insulation at the Fermi level.³¹

IX. SOME ILLUSTRATIVE EXAMPLES

We illustrate our description of molecular conduction with a proof that every molecular graph has at least one active shell, then some analytical examples for chains and rings, and finally some more general molecular examples.

A. Molecular conduction of LOMO and HUMO shells

Every π system with a connected molecular graph G has a non-degenerate lowest-lying π level. Mathematically, the eigenvector corresponding to the largest positive eigenvalue of G , ϵ_{max} , i.e., the lowest occupied π molecular orbital (LOMO), has specific implications for the conduction properties. This maximum eigenvalue is known as the Perron eigenvalue; it has multiplicity one for a connected graph, and the associated eigenvector has a non-zero entry of the same sign on every

vertex.⁵⁴ Deletion of any vertex in a connected graph leads to a decrease in the maximum eigenvalue; deletion of a second vertex will lead to a further decrease or may leave the maximum eigenvalue unchanged (only if removal of the first vertex had disconnected the graph).

Hence, the LOMO always constitutes an active shell, belonging to case 10. A proof based on interlacing is straightforward. Whilst the Perron eigenvalue of graph G has degeneracy $g = 1$, degeneracies g_l and g_u are both 0, as the maximum eigenvalue falls on vertex deletion. Whether the graph $G - \bar{L} - \bar{R}$ is disconnected or not, the maximum eigenvalue of this graph is strictly less than ϵ_{\max} , and so $g_v = 0$, and we have case 10, which is active (cf. Table I).

The LOMO typically contributes some conduction at all energies that are not eigenvalues, and so will have a (small) contribution at the Fermi level if G is non-singular. If G is connected and bipartite, then it has a unique eigenvalue ϵ_{\min} , and the conduction properties of the corresponding “anti-Perron” eigenvector (the HUMO) also follow case 10, and in particular will have a conduction peak near the eigenvalue. For a nonsingular molecular graph, this will reinforce the contribution of the LOMO at the Fermi level.

B. Conduction in chains

We gave explicit analytical formulae for the total transmission in chains and rings, based on full electron delocalisation, in our earlier work.²⁸ Here, we concentrate on the conditions for inert orbitals and shells.

The molecular graph of the general linear polyene C_nH_{2n+2} is the path on n vertices, P_n . All eigenvalues of P_n are non-degenerate, and so the set of cases for exploration is 1 to 10 (connection matrix of rank 1 or 0), and shells are active if they belong to cases 9 or 10. Both of these cases occur.

An orbital is inert whenever \bar{L} or \bar{R} , or both, is at a node. The k th vector ($k = 1, \dots, n$) has entry

$$U_{pk} = \sqrt{2/(n+1)} \sin(pk\pi/(n+1)) \quad (127)$$

on vertex p , such that $p = 1, \dots, n$. Hence, there are nodes at $kp = \mathcal{P}(n+1)$, where \mathcal{P} is a non-zero integer and shell k is inert, therefore, if $k\bar{L} = \mathcal{P}(n+1)$ and/or $k\bar{R} = \mathcal{P}(n+1)$. For example, all odd chains connected via their central vertex ($p = (n+1)/2$) have inert orbitals at all even k (implying $\mathcal{P} = k$).

Given that both k and p are less than $n+1$, a small general observation follows for even chains: if $n+1$ is prime, the chain has no inert shells, since kp cannot contain $n+1$ as a factor. Hence, chains with $n = 2, 4, 6, 10, 12, 16, \dots$ have no inert shells.

C. Conduction in rings

A device based on a C_nH_n ring has connections $\bar{L} = 1$, $\bar{R} - \bar{L} = p$ ($0 \leq p \leq n-1$). The spectrum of the cycle is

$$\epsilon_k = 2 \cos(2\pi k/n)$$

with $k = 0, 1, \dots, \lfloor n/2 \rfloor$ and degeneracies $g = 1$ for $k = 0$ (Perron) and $k = n/2$ (anti-Perron, for even n only), but $g = 2$ for all other values of k . The shells with $\epsilon_k = +2$ (and -2 for even n) are active, by the arguments given above for the Perron eigenvalue.

Deletion of any vertex of the cycle C_n yields the path P_{n-1} , and so $g_l = g_u = 1$ for all shells with $g = 2$. Therefore, all *ipso* devices based on the cycle are of type I3 (Table I) and all shells are active. For *non-ipso* devices, the possible cases for inertness/activity are limited to 9, 10, 11.1, and 11.2 of Table I, and hence all shells are active except those that fall under case 11.2 ($g_v = 0$, $g_j \geq 2$). Detection of inert shells can be done in several ways. One route is via the connection matrix. For a degenerate shell of the cycle, the matrix $\mathbf{B}_K^{\text{con}}$ is

$$\begin{aligned} \mathbf{B}_K^{\text{con}} &= \begin{pmatrix} \beta_{\bar{L}\bar{L}} U_{\bar{L}1} & \beta_{\bar{R}\bar{R}} U_{\bar{R}1} \\ \beta_{\bar{L}\bar{L}} U_{\bar{L}2} & \beta_{\bar{R}\bar{R}} U_{\bar{R}2} \end{pmatrix} \\ &= \begin{pmatrix} \sqrt{\frac{2}{n}} \beta_{\bar{L}\bar{L}} \cos\left(\frac{2\pi k\bar{L}}{n}\right) & \sqrt{\frac{2}{n}} \beta_{\bar{R}\bar{R}} \cos\left(\frac{2\pi k\bar{R}}{n}\right) \\ \sqrt{\frac{2}{n}} \beta_{\bar{L}\bar{L}} \sin\left(\frac{2\pi k\bar{L}}{n}\right) & \sqrt{\frac{2}{n}} \beta_{\bar{R}\bar{R}} \sin\left(\frac{2\pi k\bar{R}}{n}\right) \end{pmatrix} \end{aligned} \quad (128)$$

in the sine/cosine representation of the eigenspace and with $k = 1, \dots, \lfloor n/2 \rfloor$.

For case 11.2, we must have $\hat{v}_{-2} \neq 0$ and $\hat{j}_{-1} = 0$ (to give $g_v = g - 2$ and $g_j = g - 1$). Now, with our definition of $\bar{R} - \bar{L} = p$, by Eq. (46),

$$\begin{aligned} \hat{v}_{-2} &= \frac{4\beta_{\bar{L}\bar{L}}^2 \beta_{\bar{R}\bar{R}}^2}{n^2} \sin^2(2\pi kp/n), \\ \hat{j}_{-1} &= \frac{2\beta_{\bar{L}\bar{L}} \beta_{\bar{R}\bar{R}}}{n} \cos(2\pi kp/n). \end{aligned} \quad (129)$$

The expression for \hat{j}_{-1} vanishes for $4kp = (2q+1)n$, with integer q . This condition is sufficient to ensure that $\hat{v}_{-2} \neq 0$, and hence that we are in case 11.2.

Clearly, if n is *odd*, $4kp$ cannot be the product of two odd integers, and so *no* shells of an odd cycle are inert.

Equally, if n is of the form $4N+2$, $2kp$ cannot be the product of two odd integers, and so *no* shells of a $(4N+2)$ cycle are inert.

The remaining case is where n is of the form $4N$. Devices based on C_{4N} cycles have inert shells whenever the shell index k and the pathlength p between connection vertices obey $kp = (2q+1)N$. For example, C_8 has inert shells with $k = 1, 3$ for $p = 2$, but $k = 2$ for $p = 1$ and $p = 3$. Likewise, C_{20} has inert shells at $k = 5$ for $p = 1, 3, 5, 7, 9$ and at $k = 1, 3, 5, 7, 9$ for $p = 5$.

There is a particular implication for conduction at the Fermi level through devices based on $4N$ cycles. Note that even/odd values of p correspond to devices with \bar{L} and \bar{R} in the same/opposite partite sets. Therefore, the shell at $\epsilon = 0$ ($k = 2N$) is active (case 9) when \bar{L} and \bar{R} are in the same partite set, and inert (case 11.2) when they are in opposite sets. The cycles C_{4N+2} are also bipartite, but do not have $\epsilon = 0$ as an eigenvalue.

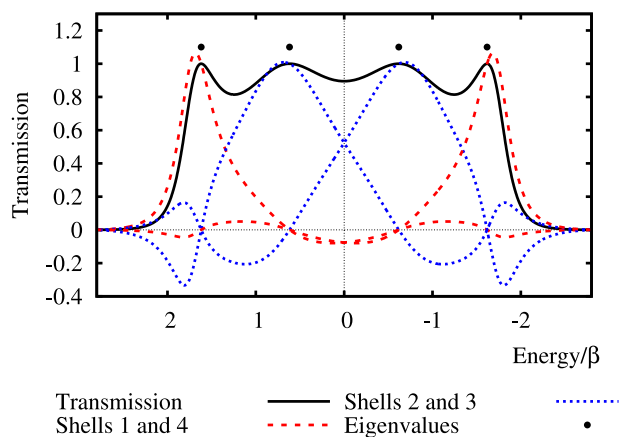


FIG. 3. Total electron transmission and currents through individual MOs in butadiene. The terminal atoms are the two connections in the device.

D. Butadiene in a device connected via terminal atoms

The shell currents are shown in Fig. 3 for a device comprising a chain of four conjugated atoms (butadiene) with the source and sink connected to the terminal atoms. This is a simple example in which each orbital is non-degenerate and exhibits case 10 behaviour. All the orbitals are active. It is evident from Eq. (45) that $J_{L \rightarrow k}^{MO}(\epsilon_{k'}) = 0, \forall \epsilon_{k'} \neq \epsilon_k$, because $s_k(\epsilon_{k'}) = 0$. All intensities go through a single active shell when E is equal to the shell eigenvalue. The off-shell MO currents vanish at each eigenvalue other than their own. The molecular graph is bipartite, so the global transmission curve is symmetric about $E = 0$. Pairs of eigenvalues related by a change of sign have MO currents that are related by reflection about the line $E = 0$. Individual MO currents have regions where they can be negative or greater than 1, but the total transmission always satisfies $0 \leq T \leq 1$, as it must, in the SSP analytical model.

Bond currents are uninteresting in this case because there is only one path through the molecule, and each bond carries a bond current equal to $T(E)$.

E. Anthracene with a symmetrical *non-ipso* device

The shell currents for a device comprising anthracene with connections to atoms 4 and 11 (cf. Fig. 4) are shown in Fig. 5. Anthracene has D_{2h} point group symmetry, and this device was chosen because \bar{L} and \bar{R} connection atoms lie in a mirror plane, σ , perpendicular to the plane of the molecule. The orbital energies and the conduction cases at those eigenvalues

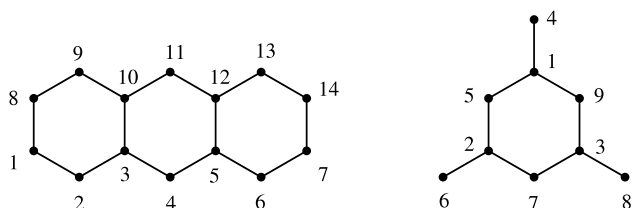


FIG. 4. The graphs of the molecules described in Sections IX E–IX G (left) and IX H (right), showing the labelling schemes for the atoms.

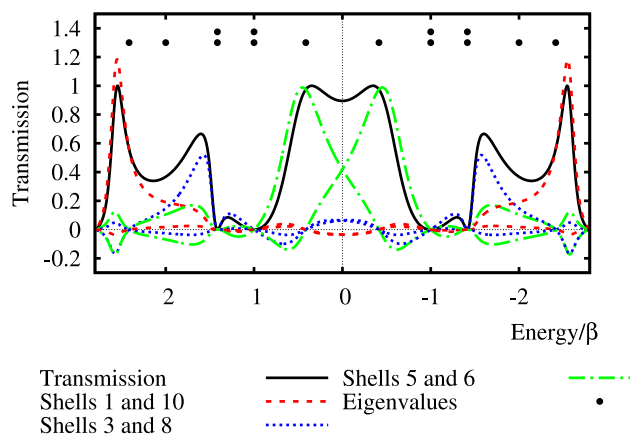


FIG. 5. Anthracene shell currents and transmission for a symmetrical *non-ipso* device connected to atoms 4 and 11, as shown in Fig. 4.

are shown in Table III. Each of the doubly degenerate shells contains a pair of orbitals belonging to different irreducible representations of D_{2h} , so that these degeneracies do not arise from point group symmetry, and are in that sense “accidental.” The irreducible representations that are antisymmetric with respect to the σ mirror plane are B_{1g} and B_{3u} , whilst A_g and B_{2u} are symmetric.

Anthracene has a bipartite molecular graph, so the transmission curves and the eigenvalues again exhibit symmetry about $E = 0$. Shells that are antisymmetric to the mirror plane (shells 2 and 4 and their respective paired partners, 9 and 7) are of rank 0 and inert, as the nodal plane passes through the connection atoms. Conduction occurs at each singly degenerate eigenvalue, and insulation is found at all others. The shells with eigenvalues at $\pm\sqrt{2}$ are case 11.1, so there is no molecular conduction at this eigenvalue, but these shells carry current at other energies. Shells at eigenvalues ± 1 , are, however, case 1, so the shells are inert and the molecule is insulating at this eigenvalue.

Bond currents for this device are displayed in Fig. 6. The current from atom 1 to atom 8 is the current in the leftmost vertical bond (cf. Fig. 4), whilst the current from atom 3 to atom 10 is the current in the inner left-hand vertical bond. Corresponding currents in the right hand rings are obtained by symmetry. The four currents add together to give the total transmission, $T(E)$, carried by the four unique routes from source to sink. Component bond currents are not always

TABLE III. Conduction cases and shell symmetries at the molecular eigenvalues (in units of β) of anthracene for the devices described in Secs. IX E–IX G. Shells 2 and 4, and their paired partners are inert for all three devices.

Shells	Shell symmetries	Eigenvalues	Cases		
			IX E	IX F	IX G
1 and 10	A_g	$\pm(1+\sqrt{2})$	10	10	13
2 and 9	B_{3u}	± 2	6	8	12
3 and 8	$A_g + B_{2u}$	$\pm\sqrt{2}$	11.1	10	13
4 and 7	$B_{1g} + B_{3u}$	± 1	1	5	11
5 and 6	B_{2u}	$\pm(-1+\sqrt{2})$	10	10	13

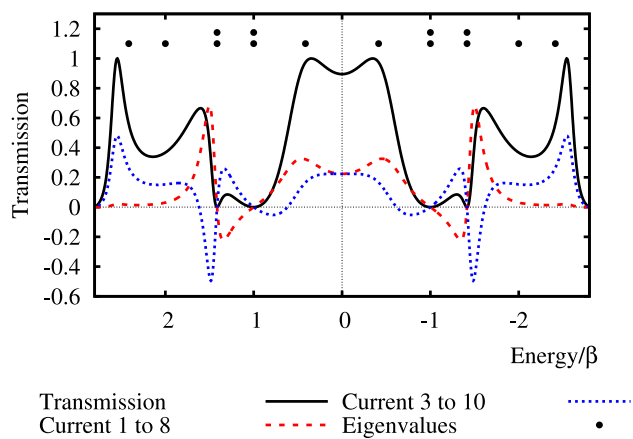


FIG. 6. Anthracene bond currents and transmission for a symmetrical *non-ipso* device connected to atoms 4 and 11, and with atoms numbered as shown in Fig. 4.

of the same sign. This is noticeable at energies near the eigenvalues for shells 3 and 4 (and their paired partners), i.e., near eigenvalues where $T(\epsilon_K)$ vanishes.

F. Anthracene with an unsymmetrical *non-ipso* device

This device is connected such that \bar{R} is in the apical position at the bottom of the left-hand ring (atom 2), and \bar{L} is in the upper apical position in the middle ring (atom 4). The device is not symmetrical, yet it benefits from the underlying symmetry of the molecule, as it has \bar{L} situated in the nodal plane of those orbitals that are anti-symmetrical with regard to the mirror plane through atoms 4 and 11 (cf. Fig. 4). The coefficient $U_{\bar{L}k}$ is identically zero for such anti-symmetric orbitals. This accounts for the fact that shells 2 and 9 are case 8, and shells 4 and 7 are case 5. Shell currents are shown in Fig. 7. The bond currents display the effects of asymmetry of the device, and currents across the mid-section of the molecule are all different, as shown in Fig. 8.

A satisfying feature of the calculated transmission curves is that conduction at the Fermi level is dominated by the nearby frontier orbitals. This is a justification of the

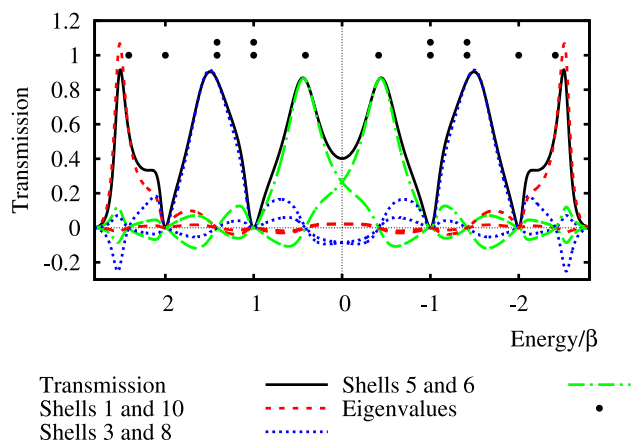


FIG. 7. Anthracene shell currents and transmission for an unsymmetrical *non-ipso* device connected to atoms 2 and 11, as shown in Fig. 4.

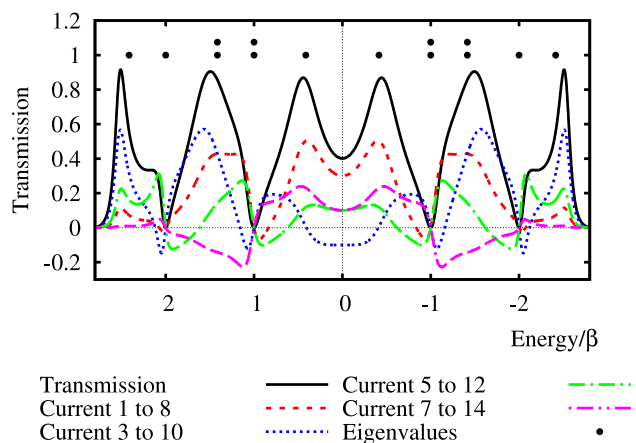


FIG. 8. Anthracene bond currents and transmission for an unsymmetrical *non-ipso* device connected to atoms 2 and 11, and with atoms numbered as shown in Fig. 4.

perturbation treatment of $T(0)$ (for all *non-ipso* devices based on bipartite molecular graphs), as used in other theories of orbital contributions.^{16,42,53}

G. Anthracene with a symmetrical *ipso* device

In the anthracene *ipso* device with source and sink both connected to atom 4 (cf. Fig. 4), the MOs antisymmetric with respect to the central mirror plane once again form a set of inert shells because the connection matrix elements vanish. Most shells have the same conducting properties as for the *non-ipso* devices previously discussed; the exceptions are the singly degenerate shells at $E = \pm\sqrt{2}$, which here are conducting. The molecule has no internal bond currents (cf. Section V C), but the MOs conduct through the external links $\bar{L}\bar{L}$ and $\bar{R}\bar{R}$. The transmission curve shows *additional* zero conduction at energies other than eigenvalues where it happens that the single structural polynomial $j = t = u$ vanishes. This is shown in Fig. 9, which gives the reduced structural polynomial $\hat{i}(E)$ as well as the shell currents and the total transmission. The analysis of the conduction cases at the molecular eigenvalues for the anthracene *ipso* device is shown in Table III.

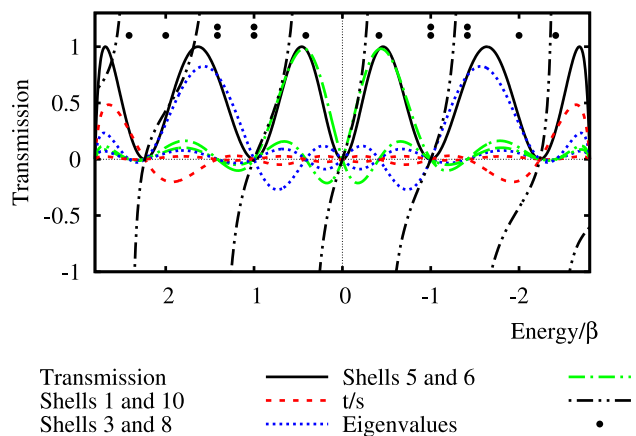


FIG. 9. Anthracene shell currents and transmission for a symmetrical *ipso* device connected to atom 4, as shown in Fig. 4. The structural polynomial $\hat{i} = t/s$ is also shown.

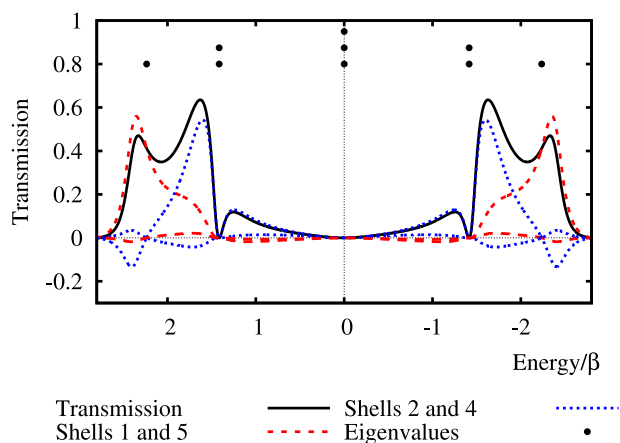


FIG. 10. The shell currents for a device connected to atoms 1 and 8 of the molecule depicted on the right in Fig. 4.

H. An alternant molecule with a space of non-bonding orbitals

The right-hand molecule shown in Fig. 4 has 9 atoms with $n_* = 3$, and $n_o = 6$. The device treated in this example has connections via atoms 1 and 8. The (3×6) -dimensional matrix \mathbf{B} in Eq. (105) has rank 3, and there are three nullspace vectors, concentrated on the unstarred set of atoms. Shells 1 and 5 are case 10, whilst shells 2 and 4 are case 11.2. It can be seen from Fig. 10 that the triply degenerate nullspace (shell 3) is inert. This shell is an example of case 5, which is also insulating. The inert character of the null shell arises from the special eigenvector structure for a bipartite molecule, as outlined in Section VIII.

X. CONCLUSIONS

We have presented a new analysis of the SSP model, which is the simplest approach to ballistic molecular conduction. The strengths (and the limitations) of the model stem from its graph-theoretical form. We exploited the connection with spectral graph theory to find a new and chemically informative way to think about ballistic conduction in terms of orbital contributions. To do this, we first presented a re-derivation of the SSP equations in a manner that gives easier access to quantities of interest and elucidates behaviour in special circumstances.

Current through molecules can be discussed in terms of transmission through a series of bonds, i.e., bond currents. These bond currents can go with or against the main direction of current flow, and strong cancellation occurs frequently near energies at which there is overall insulation. There is not always an obvious interpretation of these currents.¹⁷ In the bond current picture, intramolecular interference effects are inevitable.²

Current through molecules can also be discussed in terms of parallel channels corresponding to molecular orbitals and shells of molecular orbitals. These currents can be negative, but typically behave in a more stable fashion than do bond currents, and at every energy they add up to the total transmission, $T(E)$.

Transmission has been partitioned into orbital contributions in other computational schemes, using projection

techniques.^{55–58} The scheme followed here gives shell contributions naturally and uniquely within the tight-binding approach.

Shell currents turn out to have some interesting general properties governing their contributions to transmission across the range of accessible energies. It has been shown previously that total transmission at eigenvalues can be classified in terms of 11 cases derived by use of the interlacing theorem. The new SSP equations give a finer classification, splitting two cases to give a total of 13 possibilities for behaviour in terms of insulation and conduction both at and between eigenvalues.

Shell currents are classified in terms of the same set of cases, which reveal specific behaviour at eigenvalues and a global property of activity/inertness. It turns out that some shells are *inert*. That is to say, they are insulating at all values of E . Shells that conduct at some energy E are *active*.

This inertness/activity property has a simple interpretation in terms of nodal character. This is nicely expressed in terms of the notation of core and core forbidden vertex sets,⁵⁹ which is usually used for the nullspace of a graph, but has a natural extension for any shell.⁴⁶ In this extended sense, the vertices in the core set for a given shell are those with a non-zero sum of amplitudes of entries when summed over the shell. In chemical terms, they have non-zero partial π charges for occupation of the shell. Vertices outside the core are *core-forbidden vertices* (CFV): they are nodal points in all possible representations of the degenerate set of orbitals. A shell is inert in a given device if one (or both) of the connection atoms \bar{L} and \bar{R} corresponds to vertices in the *core forbidden* set for that shell.

CFV can in some cases be identified by symmetry arguments. If vertex r is a CFV for the eigenspace \mathbf{K} , the eigenvector entry U_{rk} vanishes and the local adjacency condition $\sum_{s \sim r} U_{sk} = 0$ applies for all $k \in \mathbf{K}$. If r is at a special point of the point group, the vanishing of U_{rk} may be enforced by the symmetry spanned by the eigenspace (the set of degenerate orbitals). For example, if r lies in a mirror plane and all vectors in the eigenspace are antisymmetric with respect to reflection in that plane, r must be a CFV for shell \mathbf{K} . Thus, for example, the central vertex of an odd path is always CFV for even k (cf. Section IX B). More typical is the situation for a doubly degenerate shell where it will often be possible to choose one symmetric and one anti-symmetric vector with respect to a given plane, and r is therefore not a CFV. This is the case for all degenerate shells of the cycle.

The language of CFVs also gives an alternative view of the effects of side-chains on conduction, more usually expressed in terms of quantum interference.^{15,60–63} In this analysis, quantisation conditions for side-chains force a node at the junction with the backbone, i.e., a CFV that kills conduction.³⁰ Nodal positions are robust to improvements in the level of theory if they are determined by symmetry; if they result from a cancellation within the Hückel model, they may shift, but the qualitative prediction of zero shell conduction may still be an indicator of a low contribution to conduction.

Only three cases (9, 10, and 11.1) out of the 13 represent active shells. A practical application of this classification scheme is that transmission near the Fermi energy is dominated by frontier-shell contributions. If any of these shells are inert, the conductivity of the molecule will be greatly decreased.

Finally, as the reader may have guessed, the viewpoint based on orbital rather than bond current contributions will be especially useful when further refinements of the SSP model are considered. Molecular-orbital contributions to transmission could be derived by similar methods for more complex, multi-channel devices such as those treated in the extended SSP model by Dumont.⁴⁰ They will be at their most useful when considering the proper inclusion of electron repulsion.

In its basic form, SSP is an “empty-molecule” picture; the ballistic electron passes through the molecule or stack of molecular orbitals without interacting with any electrons that may already be present in the molecule. Adaptation to a more physically realistic theory²⁵ in which electron repulsion and Pauli effects are explicitly included is clearly much easier if current is partitioned into shell contributions. Conductivity of a molecule will then be dominated by contributions from low-lying unoccupied shells, and their inertness or activity will be crucial.

APPENDIX: DETAILED ANALYSIS OF THE 11 CANONICAL CASES

We shall assume that the rank of the SSP equations, (cf. Eqs. (91) and (92)), in the echelon representation is 2. The general solution in the linearly independent space to the SSP equations for any energy, $E \neq \epsilon_K$, in this case is given by

$$\begin{pmatrix} c_1^{\text{MO}} \\ c_2^{\text{MO}} \\ c_L \\ c_R \end{pmatrix} = -\frac{iN_L}{\hat{\Delta}} \begin{pmatrix} -ad^2 + p_K(a\hat{F}_{\text{AR}} + b\beta_{\text{LL}}\beta_{\text{RR}}\hat{J}_A) \\ d(ab + p_K\beta_{\text{LL}}\beta_{\text{RR}}\hat{J}_A) \\ p_K(-b^2 - d^2 + p_K\hat{F}_{\text{AR}}) \\ p_K(ab + p_K\beta_{\text{LL}}\beta_{\text{RR}}\hat{J}_A) \end{pmatrix}, \quad (\text{A1})$$

where

$$\begin{aligned} \hat{\Delta}(E) = & a^2d^2 - p_K[a^2\hat{F}_{\text{AR}} + (b^2 + d^2)\hat{F}_{\text{AL}} \\ & + 2ab\beta_{\text{LL}}\beta_{\text{RR}}\hat{J}_A] \\ & + p_K^2(\hat{F}_{\text{AR}}\hat{F}_{\text{AL}} - \beta_{\text{LL}}^2\beta_{\text{RR}}^2\hat{J}_A^2). \end{aligned} \quad (\text{A2})$$

When $p_K \neq 0$, the solutions given for c_L and c_R in Eq. (A1) reduce to those already shown in Section VI, as they must, and it can be shown that c_L, c_R are identical to those in Eq. (67). The expressions for c_1^{MO} and c_2^{MO} are not those derived previously, since they refer particularly to orbitals in the echelon representation.

We shall consider the eight possibilities arising from Eq. (95), depending upon whether the constants, a, b , and d are zero or non-zero. Equations (A1) and (A2) are in a form which is robust enough to cover each of the eight cases, so long as $p_K \neq 0$.

We have shown that it is possible to use Eq. (67) for a derivation of SSP solutions at an eigenvalue. We now need to take these solutions for quantities such as c_R and T , and then take the limit $E \rightarrow \epsilon_K$.

The leading term in the expansion (cf. Eqs. (57) and (58)) of \hat{D} is determined entirely by the rank of the connection matrix, $\mathbf{B}_K^{\text{con}}$. Hence, rank 2 gives \hat{D}_{-2} as the leading term. Ranks 1 and 0 have \hat{D}_{-1} and \hat{D}_{-0} as leading terms, respectively.

We now consider the different ranks in turn.

1. Devices with rank-2 connection matrices

We note that this is only possible when $g \geq 2$. In such a case, a rank-2 connection matrix can be achieved in just two different ways out of the eight possibilities for the choice of a, b , and d .

- (i) $a \neq 0, b \neq 0, d \neq 0$

In this case, it is evident from Eq. (96) that $\hat{t}_{-1} \neq 0$, $\hat{u}_{-1} \neq 0, \hat{v}_{-2} \neq 0$, and $\hat{j}_{-1} \neq 0$, so that $g_t = g_u = g_j = g - 1$, and $g_v = g - 2$. This corresponds to case 11 of our previous work.^{31,35} Solution of the linear equations at $p_K = 0$ gives a unique SSP vector

$$\begin{pmatrix} c_1^{\text{MO}} \\ c_2^{\text{MO}} \\ c_L \\ c_R \end{pmatrix} = \frac{iN_L}{a} \begin{pmatrix} 1 \\ -b/d \\ 0 \\ 0 \end{pmatrix}. \quad (\text{A3})$$

The vanishing of c_L and c_R implies that $r = -1$, and $\tau = 0$, and hence $T(\epsilon_K) = 0$. This particular value of the reflection factor (cf. Eq. (18)) is an explicit example of the singularity sometimes present in the original version of the SSP formalism.^{18,28} This case is labelled 11.1 in Table I.

We can also see, from Eq. (100), that the shell is *active*, i.e., the current through shell K at general values of E is non-zero for case 11.1, because of the non-vanishing \bar{L} - and \bar{R} -components of the first echelon orbital.

The bond currents, $J_{p \rightarrow q}^{\text{AO}}$, vanish at ϵ_K because $c_L = c_R = 0$, as noted in Section V B.

- (ii) $a \neq 0, b = 0, d \neq 0$

We also have $\hat{t}_{-1} \neq 0, \hat{u}_{-1} \neq 0$, and $\hat{v}_{-2} \neq 0$, so that $g_t = g_u = g - 1$, and $g_v = g - 2$. This also conforms with the specification of case 11.^{31,35} The unique solution to the SSP equations at $p_K = 0$ is

$$\begin{pmatrix} c_1^{\text{MO}} \\ c_2^{\text{MO}} \\ c_L \\ c_R \end{pmatrix} = \frac{iN_L}{a} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad (\text{A4})$$

and implies that $T(\epsilon_K) = 0$, as before.

The sole change between this and the previous type occurs because $\hat{j}_{-1} = ab = 0$, which means that $g_j \geq g$, and hence the shell is *inert*. We distinguish this as case 11.2.

The bond currents also all vanish, as $c_L = c_R = 0$.

2. Devices with rank-1 connection matrices

There is no restriction on degeneracy for a rank-1 connection matrix, the necessary and sufficient condition for which is that $\hat{v}_{-2} = 0$. This can occur in five ways out of the eight possibilities for the choices of a, b , and c . These are

- (iii) $a = 0, b \neq 0, d \neq 0$

This does not lead to a real example, since an additional 2×2 rotation of the first two orbitals would lead to possibility (v).

(iv) $a = 0, b = 0, d \neq 0$

Thus, $\hat{t}_{-1} = \hat{j}_{-1} = \hat{v}_{-2} = 0$, and $\hat{u}_{-1} \neq 0$. This implies that $g_t \geq g$, $g_u = g - 1$, $g_j \geq g$, and $g_v \geq g - 1$, so that this corresponds to cases 5 and 8.

The solution to the SSP equations is

$$\begin{pmatrix} c_2^{\text{MO}} \\ c_L \\ c_R \end{pmatrix} = -\frac{iN_L}{\hat{F}_{\text{AL}}} \begin{pmatrix} \beta_{\text{LL}}\beta_{\text{RR}}\hat{J}_A/d \\ -1 \\ 0 \end{pmatrix}, \quad (\text{A5})$$

where we have left out the undetermined coefficient, c_1^{MO} , which can be considered to be zero by continuity with the solution at $p_K \neq 0$. We note also that $c_R = 0$ implies that $T(\epsilon_K) = 0$. The condition $\hat{v}_{-2} = 0$ implies, from Eq. (97), that the bond currents also vanish. The condition $\hat{j}_{-1} = 0$ implies that the shell must be *inert*.

(v) $a = 0, b \neq 0, d = 0$

Again $g_t \geq g$, $g_u = g - 1$, $g_j \geq g$, and $g_v \geq g - 1$, which is another example of cases 5 and 8. The (non-unique) solution for the SSP vector

$$\begin{pmatrix} c_1^{\text{MO}} \\ c_L \\ c_R \end{pmatrix} = -\frac{iN_L}{\hat{F}_{\text{AL}}} \begin{pmatrix} -\beta_{\text{LL}}\beta_{\text{RR}}\hat{J}_A/b \\ 1 \\ 0 \end{pmatrix}, \quad (\text{A6})$$

where the arbitrary c_2^{MO} component has been left out of the equations. Analysis of the conduction properties is identical to (iv).

(vi) $a \neq 0, b = 0, d = 0$

This requires $g_t = g - 1$, $g_u \geq g$, $g_j \geq g$, and $g_v \geq g - 1$, which is another example of cases 5 and 8 in which the rôles of g_t and g_u have been swapped. The solution is

$$\begin{pmatrix} c_1^{\text{MO}} \\ c_L \\ c_R \end{pmatrix} = \frac{iN_L}{a} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad (\text{A7})$$

with c_2^{MO} again arbitrary, and conduction properties as described in (iv).

(vii) $a \neq 0, b \neq 0, d = 0$

The values of the constants imply that $\hat{t}_{-1} \neq 0$, $\hat{u}_{-1} \neq 0$, and $\hat{v}_{-2} = 0$, but $\hat{j}_{-1} \neq 0$, so that $g_t = g_u = g_j = g - 1$, and $g_v \geq g - 1$. Hence, this corresponds to cases 9 and 10. The SSP solution is

$$\begin{pmatrix} c_1^{\text{MO}} \\ c_L \\ c_R \end{pmatrix} = \frac{iN_L}{\hat{D}_{-1}} \begin{pmatrix} a\hat{F}_{\text{AR}} + b\beta_{\text{LL}}\beta_{\text{RR}}\hat{J}_A \\ -b^2 \\ ab \end{pmatrix}, \quad (\text{A8})$$

where

$$\hat{D}_{-1} = a^2\hat{F}_{\text{AR}} + 2ab\beta_{\text{LL}}\beta_{\text{RR}}\hat{J}_A + b^2\hat{F}_{\text{AL}}.$$

The coefficient c_2^{MO} is not determined by the equations, but no current can be carried by this MO as $d = 0$. The values of c_L and c_R are, however, uniquely determined, and the total transmission is

$$T(\epsilon_K) = \mathcal{B}(q_L, q_R) \frac{\hat{J}_{-1}^2}{|\hat{D}_{-1}|^2}. \quad (\text{A9})$$

At least some bond currents will be non-zero, and the shell is *active*.

It is clear from their entries in Table I that cases 5 and 8 share the feature that $\hat{j}_{-1} = 0$, which implies that both lead to inert shells. This same feature ensures that the j -factor in the numerator of the expression for c_R is $O(1)$ in the series expansion in powers of p_K . The denominator is clearly $O(p_K^{-1})$ for both cases because of the presence of non-zero terms in \hat{D}_{-1} in Eq. (58). It follows that $c_R = 0$, and hence $T(\epsilon_K) = 0$.

Cases 9 and 10 have a non-zero value of \hat{j}_{-1} . This leads to an *active* shell, and $T(\epsilon_K) \neq 0$.

It is not possible to distinguish between cases 5 and 8, or between 9 and 10, on the basis of the quantities a , b , and c , and indeed because of the similarity of behaviour of these pairs, it does not seem necessary to do so.

3. Devices with rank-0 connection matrices

This is the last of the eight choices of the quantities a , b , and c .

(viii) $a = 0, b = 0, d = 0$

The quantities $\hat{t}_{-1} = \hat{u}_{-1} = \hat{j}_{-1} = 0$. This implies that $g_t \geq g$, $g_u \geq g$, $g_j \geq g$, and $g_v \geq g$. The vanishing of \hat{t}_{-1} and \hat{u}_{-1} means that all \bar{L} and \bar{R} components of the shell wavefunctions vanish, and hence $\hat{v}_{-1} = 0$. The SSP solution is

$$\begin{pmatrix} c_L \\ c_R \end{pmatrix} = \frac{iN_L}{\hat{F}_{\text{AL}}\hat{F}_{\text{AR}} - \beta_{\text{LL}}^2\beta_{\text{RR}}^2\hat{J}_A^2} \begin{pmatrix} \hat{F}_{\text{AR}} \\ \beta_{\text{LL}}\beta_{\text{RR}}\hat{J}_A \end{pmatrix} \quad (\text{A10})$$

with c_L and c_R uniquely determined, and both MO coefficients, c_1^{MO} and c_2^{MO} arbitrary, but set to zero using continuity.

The various cases in Table I cannot be distinguished on the basis of the behaviour of the orbitals of the echelon representation. We can conclude immediately, however, that the shell is inert in all of these cases because $\hat{j}_{-1} = 0$.

Table I indicates that four of the cases conduct at the eigenvalue. It is obvious that such conduction can only occur through other shells. All of these cases have values of g_t , g_u , and g_v that are greater than or equal to g , so that each of the ‘‘hatted’’ structural polynomials has an expansion with a leading term in p_K of $O(1)$ or greater. It follows directly that the leading term in the expansion of \hat{D} is \hat{D}_0 . (cf. Eq. (58).) The decision as to whether or not the various cases conduct at the eigenvalue hinges on the expansion of \hat{j} . We will make a few remarks about each case.

Case 1 ($g_t = g + 1, g_u = g + 1, g_v = g + 2$)

The leading terms in the \hat{u} , \hat{t} and \hat{v} expansions are \hat{t}_1 , \hat{u}_1 and \hat{v}_2 , respectively. Since the 0th term in the j -expansion, when $\hat{j}_{-1} = 0$, can be expressed as

$$\hat{j}_0^2 = \hat{u}_0\hat{t}_0 - \hat{v}_0 + \hat{t}_{-1}\hat{u}_1 + \hat{t}_1\hat{u}_{-1} \quad (\text{A11})$$

the leading term in \hat{j} is \hat{j}_1 . The numerator in the expression for c_R is $O(p_K)$ whilst \hat{D} is $O(1)$. We conclude that $T(\epsilon_K) = 0$.

