

Tuning the through-bond interaction in a two-centre problem

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Abstract. Two centres A and B connected by one or more sets of bridging states (pathways) define a graph in the space of states. The Hamiltonian is decimated in this space and the problem is reduced to that of two sites with corrected energies \tilde{E}_A and \tilde{E}_B and an effective interaction \tilde{V}_{AB} . The goal of the method is to make evident how the pathways should be modified in order to tune the resulting coupling. The condition for maximum coupling is $\tilde{E}_A = \tilde{E}_B$ (resonance) and is related to a generalised reflection–inversion symmetry while the coupling minimises if $\tilde{V}_{AB} = 0$ (anti-resonance). This is a non-trivial situation allowed by the topology of the system which occurs when two or more pathways interfere destructively. The effects of resonances and anti-resonances in electron transfer and other applications are discussed.

1. Introduction

Many important problems in physics, chemistry and biology can be discussed in terms of the electron quantum transport from one centre A to another centre B, which may be separated by many bridging atoms [1]. We have been recently involved in two problems which are examples of this. One is the interaction between paramagnetic ions through polyatomic bridges [2] where the through-bond coupling is manifested in the superexchange parameter [3, 4]. The other problem is the Aharonov–Bohm effect in metal rings and cylinders [5]. Here the essential physics is the quantum diffusion of electrons from one contact to the other, travelling by the two branches of the ring, their relative final phases being dependent on the enclosed magnetic flux [6]. Here the coupling between contacts is manifested in the electrical resistance.

Another problem that we have in mind is the biological electron transfer [7] from one centre to another which may be many inter-atomic distances away. A complete view of the phenomena must consider not only the effective adiabatic coupling but also the molecular vibrations. However, the first is manifested in the rate constant of the process, and therefore it is crucial to understand the parameters which control the process.

All these problems admit description in terms of the quantum evolution which allows for a localised excitation $\langle A | \Psi(t) \rangle = 1$ to be found at site B after a time τ , i.e.

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$\langle B | \Psi(t + \tau) \rangle \approx 1$. In all these cases the molecular orbital (MO) theory can be used as an adequate framework in order to describe the electron wavefunction. However, the number of states which are usually involved makes these problems tractable only numerically with a consequent loss in physical understanding and generality.

The purpose of this paper is to show how the natural topology in the space of states, defined by the main interactions, can be exploited. In this space, a decimation method is introduced. It allows easy manipulation of the problem by mapping it into a simple two-state effective Hamiltonian. The most important consequence of this method is that the analysis of the conditions under which the coupling is maximised (resonance) or minimised (anti-resonance) can be performed in a simple way. This result has a wide range of applications since it shows the possibility of tuning the electron transfer by controlling the bridging effects either by modifying the system or by applying external fields.

The main results of this paper are presented as follows. In section 2 we introduce a set of tight-binding model Hamiltonians and we obtain the expression for the associated two-state effective Hamiltonian. An analysis of the sign and the order of magnitude of the two-state effective interaction is presented for both periodic and non-periodic bridges. In section 3 we show how the decimation procedure can be extended to systems with non-negligible overlaps and multiple cross links. In section 4 the symmetry conditions to achieve an effective degeneracy (resonance) between the centres A and B are established. Also the consequences of quantum interferences in multiple bridged systems (anti-resonances) and the effects of a magnetic field are analysed. In section 5 we discuss the dynamics of the electrons using the effective Hamiltonian and we present an application to a model system. We use these results to give insight into the effects of an inelastic interaction on the kinetic parameters. Section 6 summarises the most striking consequences of resonances and anti-resonances and includes a brief discussion of two particular problems whose basic understanding is provided by the arguments of this paper. These are the tuning of the exchange interaction and the conduction of electrons in multiple connected devices (Aharonov–Bohm effects).

2. The model system and its decimation

In order to clarify the physics we start with a model Hamiltonian which contains only the essentials. We reduce the original MO problem to a tight-binding model which neglects the non-orthogonality of the atomic basis set and allows only for nearest-neighbour matrix elements. Let us consider that the two atomic-like orbitals A and B, which we call ‘centres’, are connected by M independent pathways without mutual cross links, such as those shown in figure 1. All these restrictions do not reduce the generality of our results as will be shown in § 3; thus the eigenvalue problem to be solved is

$$(\varepsilon \mathbf{1} - \mathbf{H})\mathbf{u} = 0 \quad (2.1)$$

where \mathbf{u} is the array of site amplitudes of eigenstates with energy ε , $\mathbf{1}$ is the unit matrix and matrix \mathbf{H} corresponds to the operator

$$H = \left[\frac{E_A}{2} |A\rangle\langle A| + \frac{E_B}{2} |B\rangle\langle B| + \sum_{\nu=1}^M \left(V_{A1}^{\nu} |A\rangle\langle 1_{\nu}| + \sum_{n=1}^{N_{\nu}-1} \left(V_{nn+1}^{\nu} |n_{\nu}\rangle\langle n+1_{\nu}| \right. \right. \right. \\ \left. \left. \left. + \frac{E_{n_{\nu}}}{2} |n_{\nu}\rangle\langle n_{\nu}| \right) + \frac{E_{N_{\nu}}}{2} |N_{\nu}\rangle\langle N_{\nu}| + V_{N_{\nu}B} |N_{\nu}\rangle\langle B| \right) \right] + \text{cc.} \quad (2.2)$$

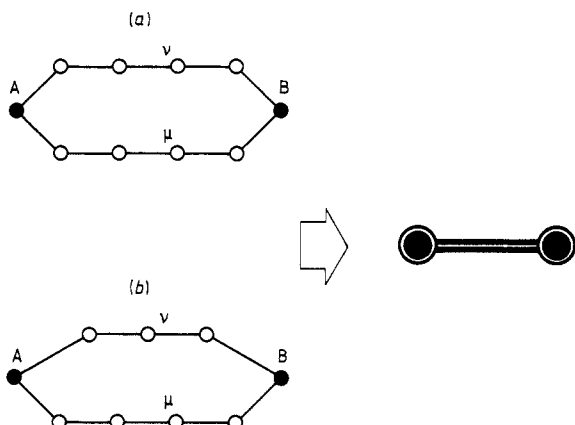


Figure 1. Schematic representation of the decimation procedure for systems without cross links: (a) a system with reflection-inversion symmetry where interactions add constructively (resonant); (b) a system for which interactions may interfere destructively (anti-resonant).

Here the E -values are site energies and V -values are the hopping matrix elements. The pathway ν has N_ν sites.

When one writes (2.1) explicitly for the amplitudes of the pathway μ , it becomes

$$(\varepsilon - E_A)u_A - V_{A1}^\mu u_1^\mu - \sum_{\nu \neq \mu} V_{A1}^\nu u_1^\nu = 0 \quad (2.3a)$$

$$-V_{1A}^\mu u_A + (\varepsilon - E_1^\mu)u_1^\mu - V_{12}^\mu u_2^\mu = 0 \quad (2.3b)$$

$$-V_{21}^\mu u_1^\mu + (\varepsilon - E_2^\mu)u_2^\mu - V_{23}^\mu u_3^\mu = 0. \quad (2.3c)$$

Taking u_1^μ from equation (2.3b) and substituting it in equations (2.3a) and (2.3c) gives us

$$[\varepsilon - (E_A + \Delta_A^\mu)]u_A - \tilde{V}_{A2}^\mu u_2^\mu - \sum_{\nu \neq \mu} V_{A1}^\nu u_1^\nu = 0 \quad (2.4a)$$

$$-\tilde{V}_{2A}^\mu u_A + [\varepsilon - (E_2^\mu + \Delta_2^\mu)]u_2^\mu - V_{23}^\mu u_3^\mu = 0 \quad (2.4b)$$

with

$$\begin{aligned} \Delta_A^\mu &= V_{A1}^\mu [1/(\varepsilon - E_1^\mu)]V_{1A}^\mu \\ \Delta_2^\mu &= V_{21}^\mu [1/(\varepsilon - E_1^\mu)]V_{12}^\mu \\ \tilde{V}_{A2}^\mu &= V_{A1}^\mu [1/(\varepsilon - E_1^\mu)]V_{12}^\mu = \tilde{V}_{2A}^{\mu*}. \end{aligned} \quad (2.5)$$

Note that equations (2.4a) and (2.4b) have the same formal structure as equations (2.3a) and (2.3b) respectively, but now the first site in the bridge is that with index 2, which is connected to A through an effective hopping \tilde{V}_{A2}^μ . Sites A and 2 have self-energy corrections Δ_A^μ and Δ_2^μ , respectively. This procedure can be repeated until the last site

of the bridge is eliminated. The effective interaction and self-energies are obtained with the recursive scheme

$$\begin{aligned}\tilde{V}_{A_{n+1}}^\mu &\leftarrow \tilde{V}_{A_n}^\mu \{1/[\varepsilon - (E_n^\mu + \Delta_n^\mu)]\} V_{nn+1}^\mu \\ \Delta_A^\mu &\leftarrow \tilde{V}_{A_n}^\mu \{1/[\varepsilon - (E_n^\mu + \Delta_n^\mu)]\} \tilde{V}_{nA}^\mu + \Delta_A^\mu \\ \Delta_{n+1}^\mu &\leftarrow V_{n+1n}^\mu \{1/[\varepsilon - (E_n^\mu + \Delta_n^\mu)]\} V_{nn+1}^\mu.\end{aligned}\quad (2.6)$$

Once all the pathways are eliminated, equation (2.1) becomes

$$\begin{pmatrix} \varepsilon - \tilde{E}_A(\varepsilon) & -\tilde{V}_{AB}(\varepsilon) \\ -\tilde{V}_{BA}(\varepsilon) & \varepsilon - \tilde{E}_B(\varepsilon) \end{pmatrix} \begin{pmatrix} u_A \\ u_B \end{pmatrix} = 0 \quad (2.7a)$$

with

$$\tilde{E}_A = E_A + \Delta_A = E_A + \sum_\nu \Delta_A^\nu(\varepsilon) \quad (2.7b)$$

$$\tilde{E}_B = E_B + \Delta_B = E_B + \sum_\nu \Delta_B^\nu(\varepsilon) \quad (2.7c)$$

$$\tilde{V}_{AB} = \sum_\nu \tilde{V}_{AB}^\nu(\varepsilon). \quad (2.7d)$$

The described procedure recognises some antecedents in the calculation of exact spectra [8–10] and localisation properties [10, 11] in various solid state systems. In fact, since no approximation has been done yet, equation (2.7a) is equivalent to equation (2.1) for the determination of the eigenvalues because their secular determinants are proportional. \tilde{E}_A and \tilde{E}_B are quotients of polynomials on ε and the exact eigenvalues can be obtained with an iteration procedure. The only conceptual limitation of equation (2.7) is that it does not allow for the normalisation of the eigenvectors, although the relative amplitudes of u_A and u_B are correctly described.

Before going further, let us discuss the meaning of equations (2.7b)–(2.7d). The first point to note is that we can obtain these values from a Brillouin–Wigner perturbation series [12, 13], which has the general form

$$\sum_{j,k,l,\dots,n \neq i, \neq f} V_{ij}^\nu \frac{1}{\varepsilon - E_j^\nu} V_{jk}^\nu \frac{1}{\varepsilon - E_k^\nu} V_{kl}^\nu \frac{1}{\varepsilon - E_l^\nu} \dots \frac{1}{\varepsilon - E_n^\nu} V_{nf}^\nu. \quad (2.8)$$

In particular, Δ_A^ν is the sum of *all* the journeys which starting from A return to A without having passed through site B. The reciprocal situation is valid for Δ_B^ν . Since the term in equation (2.8) is just the irreducible term of the expansion of the Green function $\langle i | (\varepsilon \mathbf{1} - \mathbf{H})^{-1} | f \rangle$, it is not difficult to check that

$$\Delta_A(\varepsilon) = \sum_\nu V_{A1}^\nu \langle 1 | (\varepsilon \mathbf{1} - \mathbf{H}^\nu)^{-1} | 1 \rangle V_{1A}^\nu = \sum_\nu V_{A1}^\nu \left(\sum_\beta \frac{a_{1\beta}^{\nu*} a_{1\beta}^\nu}{\varepsilon - E_\beta^\nu} \right) V_{1A}^\nu \quad (2.9)$$

where \mathbf{H}^ν is the restriction to pathway ν of \mathbf{H} , i.e. the molecular bridge Hamiltonian with the energies E_β^ν and eigenstate amplitudes $a_{i\beta}^\nu$.

The second point to note concerns the effective interaction which corresponds to the sum of all those journeys which having started from A have stopped once they reach point B, i.e.

$$\begin{aligned}\tilde{V}_{AB}(\varepsilon) &= \sum_{\nu} V_{A1}^{\nu} \langle 1 | (\varepsilon \mathbf{1} - \mathbf{H}^{\nu})^{-1} | N_{\nu} \rangle V_{N_{\nu}B}^{\nu} \\ &= \sum_{\nu} V_{A1}^{\nu} \left(\sum_{\beta} \frac{a_{1\beta}^{\nu*} a_{N_{\nu}\beta}^{\nu}}{\varepsilon - E_{\beta}^{\nu}} \right) V_{N_{\nu}B}^{\nu}.\end{aligned}\quad (2.10)$$

In order to solve (2.7a) it is convenient to make some approximations. For that purpose it is observed that, in the absence of site B, the exact eigenvalue associated with site A should be

$$\begin{aligned}\tilde{E}_A &= E_A + \Delta_A(\tilde{E}_A) = E_A + \Delta_A(E_A) + (\partial\Delta_A/\partial\varepsilon)(\varepsilon - E_A) + \dots \\ &\simeq E_A + \Delta_A(E_A).\end{aligned}\quad (2.11)$$

Therefore, for a situation in which the bridging molecules do not have eigenvalues near E_A and hence $\Delta_A(\varepsilon)$ does not have singularities in the neighbourhood of E_A , we get a very good approximation by retaining only the first two terms. An identical analysis is valid to evaluate $\Delta_B(\varepsilon)$ and we obtain

$$\tilde{E}_B \simeq E_B + \sum_{\nu} \Delta_B^{\nu}(E_B).\quad (2.12)$$

Also the effective interaction can be evaluated by performing an expansion around $E_0 = (\tilde{E}_A + \tilde{E}_B)/2$:

$$\begin{aligned}\tilde{V}_{AB}(\varepsilon) &= \tilde{V}_{AB}(E_0) + (\partial\tilde{V}_{AB}/\partial\varepsilon)|_{\varepsilon=E_0}(\varepsilon - E_0) + \dots \\ &\simeq \tilde{V}_{AB}(E_0).\end{aligned}\quad (2.13)$$

The first term is enough to give an approximation compatible with that of Δ . This readily allows us to estimate the coupling with a pocket-held calculator as well as to discuss the fundamental physics involved. If a better approximation is desired, the corrected energies can be evaluated by a few iterations of equations (2.11) and (2.12). Simultaneously a good estimation of the slopes $\partial\Delta_A/\partial\varepsilon$ and $\partial\Delta_B/\partial\varepsilon$ can be performed. Conserving the linear terms in ε in the expression for $\Delta(\varepsilon)$ but only the term independent of ε in \tilde{V}_{AB} , equation (2.7) gives a result identical with that of an ε -independent site energy with a further correction in the hopping parameter:

$$\tilde{V}_{AB} = \tilde{V}_{AB}(E_0) / \sqrt{(1 - (\partial\Delta_A/\partial\varepsilon)|_{\varepsilon=E_0})(1 - (\partial\Delta_B/\partial\varepsilon)|_{\varepsilon=E_0})}.\quad (2.14)$$

This new value accounts for the 'reaction' of the site energy when the hopping tends to 'push' the levels apart. With these corrections a high degree of accuracy is obtained in the computation of the eigenvalues E^+ and E^- associated with the symmetric and anti-symmetric combinations of centres $|A\rangle$ and $|B\rangle$.

We end this section by discussing some properties of the effective interaction through a given path. The key point is to observe that this portion of the system is topologically one

dimensional, and for this situation the old result in [14] holds for each path contribution to equation (2.10), which becomes

$$\tilde{V}_{AB}^{\nu}(\varepsilon) = V_{A1}^{\nu} \left(\prod_{i=1}^{N_{\nu}-1} V_{i+1}^{\nu} \right) \left/ \prod_{\alpha=1}^{N_{\nu}} (\varepsilon - E_{\alpha}^{\nu}) \right. V_{N_{\nu}B}^{\nu}. \quad (2.15)$$

Equation (2.15) makes it evident that the bonding hopping elements contribute with a sign $(-1)^{N_{\nu}+1}$ while the energy denominators contribute with a sign $(-1)^{N_{\text{un}}}$, where N_{un} is the number of unoccupied states in the bridge. This gives for the hopping an overall sign of $(-1)^{N_{\text{oc}}+1}$ where N_{oc} is the number of occupied states. This result gives a formal proof of the ideas in [15] about the symmetry of the ground orbital and is consistent with more recent numerical simulations [16, 17].

A further analysis of the amplitude of the Green function developed in [18] for a chain of asymptotically large length, which may be either periodic or random, allows us to evaluate the magnitude of the interaction as

$$\tilde{V}_{AB}(\varepsilon) = (V_{A1} V_{NB} / \langle V \rangle_g) [\exp[-N/\lambda(\varepsilon)] \quad (N \rightarrow \infty) \quad (2.16)$$

where $\langle V \rangle_g$ is the geometrical average of the inter-site hoppings in the bridge, and the attenuation length λ in the exponent is given by the dispersion relation

$$\frac{1}{\lambda(\varepsilon)} = \int \ln \left| \frac{\varepsilon - \varepsilon'}{\langle V \rangle_g} \right| dN(\varepsilon'). \quad (2.17)$$

with $N(\varepsilon)$ being the distribution of states of the chain. The integral (2.17) can be evaluated explicitly for bridges which have a periodic structure and allows us to obtain an attenuation length which is useful even for short bridges. For long aperiodic chains, some bounds for λ can be established [19] in terms of the parameters which characterise the randomness.

3. The general decimation procedure

The models discussed previously were selected to have a very simple topology. In this section we show how the described procedure can be extended. The key point is to truncate the range of overlaps and hopping elements so that local states can be divided in sets with an ordinal sequence where only consecutive sets are linked. Then, the Hamiltonian and overlap matrices in Roothaan's equation

$$(\varepsilon \mathbf{S} - \mathbf{H})\mathbf{u} = 0 \quad (3.1)$$

have M paths connecting states A and B which are tridiagonal in blocks. Now the recursive formulae have the same expression as equation (2.6) with the replacements

$$(\varepsilon - E_i^{\nu})^{-1} \rightarrow (\varepsilon \mathbf{S}_i^{\nu} - \mathbf{H}_i^{\nu})^{-1} \quad (3.2)$$

where \mathbf{H}_i^{ν} and \mathbf{S}_i^{ν} are $n \times n$ matrices corresponding to the restriction of the Hamiltonian and overlap to the set i of path ν . The new hoppings are

$$-\mathbf{V}_{i+1}^{\nu} \rightarrow (\varepsilon \mathbf{S}_{i+1}^{\nu} - \mathbf{H}_{i+1}^{\nu}) \quad (3.3)$$

where again \mathbf{V}_{i+1}^{ν} and \mathbf{S}_{i+1}^{ν} are $n \times m$ matrices which link the sets i and $i+1$ having n and m states, respectively. Note that, if there is no direct overlap between A and B centres,

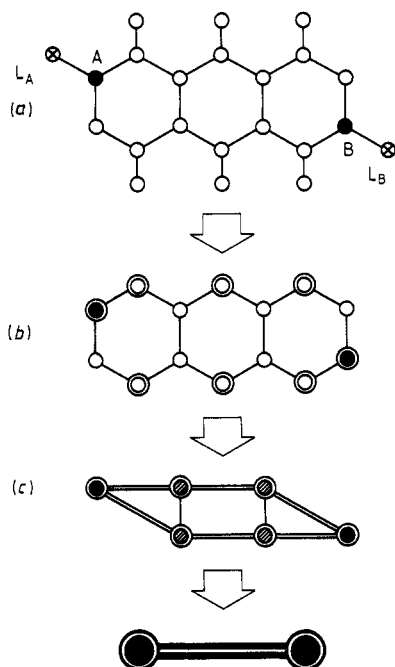


Figure 2. Schematic representation of the steps in the decimation of a complex system: (a) decimation of dangling ends; (b) decimation of linear portions; (c) matrix decimation of cross linked backbone.

the reduced two-state problem will not involve overlaps since all the non-orthogonality effects are automatically included in \tilde{E}_A , \tilde{E}_B and \tilde{V}_{AB} .

In some cases, as shown in figure 2, it could be convenient to mix matrix and scalar decimations. In these cases a possible sequence is

- (i) to decimate all the dangling fragments of the bridge as well as the terminal ligands L_A and L_B (the consequence of this step is the renormalisation of the site energies),
- (ii) to decimate all the linear portions of the bridging system and
- (iii) to treat the remaining sites with the matrix procedure, a step which sometimes allows further reduction.

In figure 2 the inversion symmetry of the bridging system allows us to decouple it into two independent chains.

4. Resonances and anti-resonances

Once the effective Hamiltonian parameters involved in equation (2.7a) are obtained with the approximations in equations (2.11)–(2.13), the natural parameter to measure the magnitude of the coupling is

$$\eta = |\tilde{V}_{AB}| / |\tilde{E}_A - \tilde{E}_B|. \quad (4.1)$$

The coupling is strong if $\eta \gg 1$ and in particular it would diverge when

$$\tilde{E}_A = \tilde{E}_B. \quad (4.2)$$

This is what we call the resonant condition, in which the splitting among the final levels

is $2\tilde{V}_{AB}$. It is interesting to remark that strong coupling is not assured by the condition $\tilde{V}_{AB} \geq V_{nn+1}$. This situation could occur, for example, when there is an eigenstate in the bridging molecule with energy E_α near E_0 . From the analysis of the leading terms in equations (2.9) and (2.10) with the condition $|E_\alpha - E_0| \ll |E_\beta - E_0| \forall \beta \neq \alpha$, we get

$$\eta = |V_{A1} a_{1\alpha}^{v*} a_{N\alpha}^v V_{NB}| / |V_{A1} a_{1\alpha}^v|^2 - |V_{NB} a_{N\alpha}^v|^2. \quad (4.3)$$

In this case, the generalised symmetry required for resonance is

$$|V_{A1} a_{1\alpha}^v| = |V_{NB} a_{N\alpha}^v|. \quad (4.4)$$

Dimers in which the centres A and B are related by reflection or inversion symmetry are cases which satisfy equation (4.4) trivially. The non-obvious consequence of this equation is that an asymmetry on the V -values may be compensated by the bridging molecule through a reciprocal asymmetry in the amplitudes at its edges. In linear bridging molecules, the weak-coupling condition, $\eta \ll 1$, is a manifestation of the lack of generalised symmetry.

A new possibility arises when there is more than one pathway. This is because different contributions to the effective hopping may have opposite signs allowing mutual cancellations:

$$\tilde{V}_{AB} = 0. \quad (4.5)$$

Since in this situation the coupling vanishes even when the symmetry may allow for a resonance, we call equation (4.5) the anti-resonant condition. This implies that the excitation in A propagates through all the bridges but interferes destructively when arriving at site B. In order to evaluate the possibility of an anti-resonant situation for molecules with multiple cross links or non-nearest neighbour hoppings the predominant backbone should be identified. The destructive interference depends on the resulting topology. In our model, it requires that the numbers of occupied states in the bridges have different parities. This is the situation depicted in figure 1(b). The exact anti-resonant condition given by equation (4.5) has in practice a low probability of occurrence, but the destructive interference effects must be taken into account in engineering the bridging systems. Interactions do not always sum constructively.

The anti-resonant situation can also be achieved by the application of either electrostatic or magnetic fields and shows the Aharonov–Bohm effects. The effect of an electrostatic field is quite obvious in the geometry of figure 1 if we consider that the field produces a potential difference between the branches. Since their respective energy levels are shifted, the effective hoppings are also modified. If the energy shifts are large enough to modify the occupation of the states, the sign of the interaction changes, and the interference condition varies from destructive to constructive or vice versa.

The effect of the magnetic field is somewhat more subtle. Here we note that the presence of a magnetic vector potential \mathbf{A} gives a different phase to each hopping element. Thus, for a case with two pathways, the effective hopping between contacts A and B becomes

$$\tilde{V}_{AB} = \tilde{V}_{AB}^v \exp(i2\pi\varphi_{AB}^v/\varphi_0) + \tilde{V}_{AB}^\mu \exp(i2\pi\varphi_{AB}^\mu/\varphi_0) \quad (4.6)$$

where $\varphi_0 = h/e$, and the phases are calculated as path integrals along each pathway: $\varphi_{AB}^v = \int_A^B \mathbf{A} \cdot d\mathbf{S}_v$ and $\varphi_{AB}^\mu = \int_A^B \mathbf{A} \cdot d\mathbf{S}_\mu$. They are related to the total magnetic flux threading the system: $\varphi = \varphi_{AB}^v - \varphi_{AB}^\mu$. The system has fixed amplitudes for the inter-

action through each pathway (branch), but the total hopping will oscillate with φ . For $\varphi = (n + \frac{1}{2})\varphi_0$ the effective coupling changes the sign of the interference, verifying that

$$|\tilde{V}_{AB}(\varphi)|^2 = (\tilde{V}_{AB}^\nu)^2 + (\tilde{V}_{AB}^\mu)^2 + 2\tilde{V}_{AB}^\nu \tilde{V}_{AB}^\mu \cos(2\pi\varphi/\varphi_0). \quad (4.7)$$

If $|\tilde{V}_{AB}^\nu| = |\tilde{V}_{AB}^\mu|$, the exact anti-resonant situation can be achieved.

5. Resonances and the rate of electron transfer

In the study of the time-dependent quantum transfer probability $P_{AB}(t)$, it is important to evaluate how the maximum value P_{\max} and the characteristic time τ_q at which quantum interference becomes important depend on the parameters of the system. This time, in terms of the exact eigenvalues of the system E_+ and E_- , the result is

$$\tau_q = \hbar/|E_+ - E_-|. \quad (5.1)$$

We are going to discuss the consequences of the bridging conditions in three model systems using the decimation scheme developed in section 2. Within the effective Hamiltonian approximation (equation (2.11)–(2.13)), (5.1) becomes

$$\tau_q = \hbar/\sqrt{(\tilde{E}_A - \tilde{E}_B)^2 + 4|\tilde{V}_{AB}|^2} \quad (5.2)$$

and defining

$$P_{\max} = 4\eta^2/(4\eta^2 + 1) = 4\tilde{V}_{AB}^2\tau_q^2/\hbar^2 \quad (5.3)$$

the time-dependent transfer probability results:

$$P_{AB}(t) \simeq P_{\max} \sin^2(t/2\tau_q). \quad (5.4)$$

A comparison of these simple expressions with the exact results will show how the effective Hamiltonian approximation works. Simultaneously, it will allow us to discuss simply the rate constant in the non-adiabatic limit.

5.1. Model examples

We start by considering as example a the system represented in figure 1(a) in which $N_\nu = N_\mu = 4$. For simplicity we have selected all hoppings $V_{ii+1} = -V$, and site energies $E_A = E_B = 4V$, $E_i^\nu = E_j^\mu = 0$. The symmetry of the problem shows that the coupling is resonant. The corrected energies are $\tilde{E}_A = E_A + 2\Delta = \tilde{E}_B = E_0 = 4.53659V$, with

$$\Delta = V^2/\{E - V^2/[E - V^2/(E - V^2/E)]\} = 0.2679V.$$

Note that the continued fraction is a convergent function of the bridge length [11], of the form

$$[\Delta(N) - \Delta(N+1)] \sim \Delta(\infty) \exp(-N/2\lambda) \quad (5.5)$$

with λ calculated for an infinite bridge, in which case equation (2.17) becomes

$$1/\lambda(E_0) = \cosh^{-1}(E_0/2V) = 1.44\dots \quad (5.6)$$

For the hopping parameter we have

$$\tilde{V}_{AB} = 2V^2 G_{1N}(E_0) = (-V)^{N+2} / \prod_{\alpha} (E_0 - E_{\alpha}) = 5.5 \times 10^{-3}V$$

with eigenvalues given by $E_{\alpha} = 2V \cos(\alpha\pi/N + 1)$ ($\alpha = 1, 2, \dots, N$). Although $N = 4$

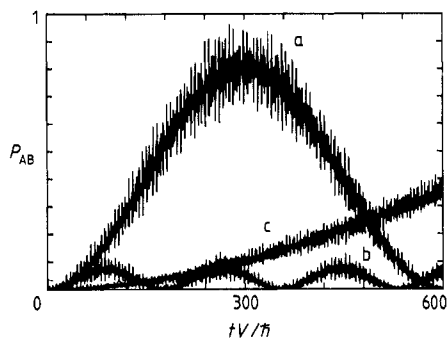


Figure 3. Exact time dependence of the quantum transfer probability P_{AB} for resonant (curve a), non-resonant (curve b) and nearly anti-resonant (curve c) systems. The chosen parameters produce a similar magnitude for the effective hopping through each pathway in all cases.

represents a small chain length, we see that equation (2.16) still gives a good estimation for the effective hopping:

$$\tilde{V}_{AB} = 2V \exp(-N/\lambda) = 5.8 \times 10^{-3}V.$$

In the resonant case we expect that, if the two-state approximation were good, most charge placed at site A at $t = 0$ should be found at site B at time $t = \pi\hbar/2\tilde{V}_{AB}$. The exact evolution calculated from the complete Hamiltonian is shown in figure 3(a). Note that the main oscillation of the form of equation (5.4) is not affected very much by the small high-frequency oscillations that are superimposed. Even when there is a defect from the maximum transfer probability, we can consider the two-state approach as a good enough approximation.

As a second example (example b) it is interesting to examine what happens when the system is displaced from the resonant condition. This occurs if sites A and B in figure 1(a) are displaced slightly to the left so that $V_{A1}^v = V_{A1}^u = -0.98V$ and $V_{4B}^v = V_{4B}^u = -1.02V$. In this case, both \tilde{E}_0 and \tilde{V}_{AB} do not differ essentially from the previous values, but now $\tilde{E}_A = E_A + 2 \times 0.98^2\Delta$ and $\tilde{E}_B = E_B + 2 \times 1.02^2\Delta$. Thus, the coupling parameter is $\eta = 0.13$ which implies poor coupling. From the analysis of equation (5.3) we predict a $4\eta^2$ -value of about 0.07 for the maximum probability of transfer. This result, easily predicted within our model, agrees with the exact situation in figure 3(b). It is worthwhile to remark that a 2% variation in the hopping parameters at the contact sites implied a reduction in the characteristic time by a factor of $\frac{2}{3}$. To a crude approximation, it can be considered that this is a way in which the vibrations (phonons) of the molecule should alter the coupling. This in turn introduces an irreversible process in the one-body Hamiltonian which breaks the quantum coherence of the tunnelling process.

In both the above examples a and b, the characteristic times evaluated with the effective Hamiltonian approximation have errors of around 10%. These errors become lower than 1% if the refined hopping in equation (2.14) is used. This could be below the error of estimation of the MO parameters. Note also that the two-state approximation predicts at short times a dependence of P_{AB} of the form

$$P_{AB}(t) = \tilde{V}_{AB}^2 t^2 / \hbar^2 \quad (5.7)$$

for both the resonant and the non-resonant situations. This is in agreement with the exact solutions for examples a and b shown in figure 3 which coincide at short-time regimes.

As a final example (example c) we consider an anti-resonant situation. This is illustrated by the system in figure 1(b), where all the parameters are the same as in the resonant case except for the shorter chain, where we selected $V_{A1}^v = V_{4B}^v = -0.4V$ to represent the longer bond length.

Considering that the self-energy does not depend much on the bridge length, we estimate the energy shift as

$$\tilde{E}_A \simeq E_A + 0.4^2 \Delta = 4.3108V.$$

Since the two bridges have different parities for the number of occupied states, \tilde{V}_{AB} is near the anti-resonant condition

$$\tilde{V}_{AB} = V^2 G_{14}^v(E_0) + 0.4^2 V^2 G_{14}^v(E_0) = 1.2 \times 10^{-3} V.$$

Thus the characteristic time for the maximum transfer is 5.6 times that of the resonant case. Again the exact dependence on time, shown in figure 3(c), is in good agreement with the results of the two-state approximation.

5.2 The rate of transfer

Up to this point we have been concerned with the time evolution of an electron described by both exact and effective one-electron Hamiltonians. However, we have pointed out that additional interactions not included in this Hamiltonian will destroy the phase coherence of the evolution after a characteristic time τ_{in} . Examples of these 'inelastic' interactions are electron-electron, electron-phonon, spin-flip and other interactions, depending on the problem. This gives a probability $\exp(-t/\tau_{in}) dt/\tau_{in}$ that the first inelastic collision occurs in the interval $(t, t + dt)$. We may interpret τ_{in} as the mean time at which the first collision occurs. After this a new quantum evolution starts until a second collision occurs at the mean time $2\tau_{in}$ and so on. This defines a classical Markovian process. Following the conceptual scheme which has been very useful in the understanding of quantum transport [20], it is possible to define a rate for this process as the mean probability of transfer in a single collision divided by its characteristic time:

$$k_{AB} = \frac{1}{\tau_{in}} \int_0^\infty P_{AB}(t) \exp\left(-\frac{t}{\tau_{in}}\right) \frac{dt}{\tau_{in}} \simeq \frac{P_{max}}{2\tau_{in}} \frac{\tau_{in}^2}{\tau_{in}^2 + \tau_q^2} \quad (5.8)$$

where we have used equation (5.4) in the evaluation of the integral. From this equation we observe that the effective Hamiltonian parameters determine an upper bound for the rate of transfer. In fact, the rate has its maximum value $P_{max}/4\tau_q$ at $\tau_{in} = \tau_q$.

In the regime $\tau_q \ll \tau_{in}$, equation (5.8) becomes

$$k_{AB} = (2\pi/\hbar) \tilde{V}_{AB}^2 [(1/\pi\hbar) (\tau_q^2/\tau_{in})]. \quad (5.9)$$

Observe that, in the weak-coupling ($\eta \ll 1$) regime, \tilde{V}_{AB} and τ_q are independent variables. Some cases of biological interest in which electron transfer seems to occur under these conditions are believed to be phonon assisted [21]. Consequently, τ_{in} should be temperature dependent and $(1/\pi\hbar)(\tau_q^2/\tau_{in})$ can be identified with a generalised Franck-Condon factor which is an increasing function of temperature. An increase in this factor or in the effective hopping reflects in an increase in the rate constant. This is in agreement with more complete evaluations of the rate constant [22, 23].

Related transport phenomena in disordered solids occur in the variable-hopping-range regime. In this case, electrons tunnel between well separated impurity 'sites' with

energy close to the Fermi energy. The most difficult of these hops determines the behaviour of the conductance which is proportional to $|\tilde{V}_{AB}|^2$. This argument was recently used to predict universal fluctuations as a function of electric [24] and magnetic fields [24], and to determine the sign of the magnetoconductance [25, 26]. The essential point is that these fields modify the interference between the different pathways connecting the relevant sites according to (4.6) and (4.7).

In cases where $\tau_q \gg \tau_{in}$ the rate becomes

$$k_{AB} = \tilde{V}_{AB}^2 \tau_{in} / \hbar^2. \quad (5.10)$$

This regime controls the spin diffusion in a lattice at high temperatures. In this case, \tilde{V}_{AB} must be formally identified with the exchange constant J_{AB} in the Heisenberg Hamiltonian. Here, $\tau_{in} = a\hbar/\tilde{V}_{AB}$, with $a < \frac{1}{2}$, comes from a 'many-body' effect [27].

6. Discussion

We have presented a systematic procedure to reduce some apparently complicated problems to effective two-state ones. Several interesting consequences can be summarised.

(i) For a topologically one-dimensional bridging molecule the sign of the interaction depends on the parity of the number of occupied states.

(ii) The coupling is maximised (resonance) if the condition of generalised inversion-reflection symmetry is satisfied.

(iii) Small modifications of the centre-bridge hoppings as well as of the terminal ligands destroy the resonant condition.

(iv) The coupling is minimised (anti-resonance) if the effective hopping is zero. This is a consequence of the topology of the system which allows contributions from different bridges to cancel each other.

(v) By controlling some of these variables it is possible to tune the coupling. This may be obtained either by changing the bridge so as to modify some of the hopping parameters and/or the site energies or by applying external fields.

As an application of these ideas we may mention the interpretation of magnetostructural correlations. The use of the decimation scheme in the one-bridge problem shows that the effective hopping is proportional to the product $V_{A1}V_{NB}$. With this in mind and using the approach in [3, 4] to estimate the superexchange parameter, we can correlate this value with some structural parameters. In particular, the case of two copper(II) centres connected by an asymmetrical carboxylate bridge was studied by one of us [2]. Experiments show that strong differences in the exchange constant J are correlated with changes in the distance which determines V_{A1} , i.e. the coupling of one copper atom with the bridge. These magnetostructural correlations will be reported elsewhere [28].

A closely connected problem is the design of bimetallic systems exhibiting predictable magnetic properties. One of the recent experimental advances [29] in this direction was the synthesis of ferromagnetic heterobimetallic dimers. This can be understood by noting that an increase in $|\tilde{E}_A - \tilde{E}_B|$ lowers the coupling and hence the kinetic (antiferromagnetic) contribution to J_{AB} , without affecting the ferromagnetic contribution which arises from the through-bond and through-space overlap. Similar phenomena were seen in homobimetallic dimers by modifying the terminal ligands L_A and L_B , which

play the role of ‘adjusting screws’ in the interaction. A novel prediction from our work is that the kinetic contribution can also be minimised by engineering a bridge molecule so as to approach the anti-resonant condition.

A striking manifestation of anti-resonances in solid state systems are the Aharonov–Bohm-like oscillations in the conductance of mesoscopic metal and semiconducting rings. Perfect leads are branched at centres A and B which are connected by two pathways enclosing a magnetic flux φ . At temperatures low enough that $\tau_q < \tau_{in}$ a quantum evolution is expected for the electron with the Fermi energy $\varepsilon_F = E_0$. It is important to note that this is different from the closed systems discussed until now because these effects [6] imply an open system, i.e. a system which allows the electrons to move in and out of the sample. The connections of points A and B to the external world (reservoirs) through the leads provide continuum energy spectra which are expressed as extra complex contributions to \tilde{E}_A and \tilde{E}_B (2.12). This causes the electron evolution from A to B to be non-local but to depend on the connections of these sites to the leads. Therefore, a good description of the transport in such a system must be achieved [30] using the transmission probability coefficients evaluated at the Fermi energy which depends on both the effective Hamiltonian parameters (2.7) and the boundary conditions representing the connection with the external world. A complete analysis of that problem is beyond the scope of this work and is the subject of a separate publication [31]. However, we wish to stress the following observations related to the main results discussed here. As the Fermi energy is moved, a maximum (resonance) in the transmission probability (and hence in the conductance) is observed whenever the condition (4.2) is satisfied. A minimum (anti-resonance) in the transport coefficient appears when the condition (4.5) is reached. Also, at least in the strong-disorder regime (λ less than path length) the oscillations of the magnetoconductance can be explained in simple terms. In that regime, the interaction with the external world is weak and the conductance, just like (5.9), is proportional to $|\tilde{V}_{AB}(\varphi)|^2$. If the parities of the numbers of occupied states are the same for both branches, the interference is constructive and it is weakened by a magnetic field according to (4.7). In the opposite situation, if these parities are different, the magnetic field is able to reduce the destructive interference. In both cases, the characteristic period of the magnetoconductance oscillations is Aharonov–Bohm-like ($\varphi_0 = h/e$). We point out that, in the weak-disorder regime, the interaction with the external world is essential to account [31] for the observed $\varphi_0/2$ period.

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