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Wide-band and narrow-band approximations for donor–bridge–acceptor systems

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The techniques of wide-band and narrow-band approximations, which have been used in solid state theory, are applied to the theory of donor–bridge–acceptor models which are commonly used to represent molecular switches or wires. The approximations lead to analytical solutions which closely match the numerical calculations. These approximations are based on one of the simplest one-electron models where the interaction is time independent and the bridge band is completely initially empty. The form of the analytical solutions and the stability of the numerical calculations are discussed. © *1996 American Institute of Physics.* [S0021-9606(96)02330-6]

I. INTRODUCTION

For many years, there has been considerable interest in the concept of *molecular electronics*[1] and, because of its technological promise, the field is a rapidly growing one.[2] While some of this interest has been speculative, concrete examples for the construction of molecular switches and molecular wires have been discussed. Recent studies have considered molecular models which can be classified as donor–acceptor models[3–5] or as a donor–bridge–acceptor model.[6] For these, the prime candidates for technologically useful materials are conjugated organic molecules and polymers. This is because the π electrons are not tightly bound and hence facilitate charge transfer from the donor to the acceptor molecule. The examples treated in Refs. 2–5 are mainly constructed from such molecules. In Ref. 3 the model is a donor–acceptor with anthracene being the donor and pyromelliticdianhydride (PMDA) being the acceptor. For the donor–bridge–acceptor model in Ref. 5 the donor is again a state of anthracene, the bridge is a polyene and the acceptor is tetraphenylporphyrine (TPP).

Any donor–bridge–acceptor model suitable for describing molecular switches and wires can regarded as a special case or minor modification of those developed to discuss the dynamics of charge transfer between localised sites in large organic and biological molecules. Particularly influential in the formulation and theoretical investigation of such general models has been the paper by McConnell[7] who assumed certain approximations to reduce the many-state system to an effective two-state (DA) system, the two states being associated with the donor and acceptor, respectively, in each case with an admixture (assumed small) of bridge states. When these two states are coupled by an effective interaction matrix element, there is an oscillatory charge transfer between the states. There is now a considerable literature on this topic (for a review see Ref. 8) and, as well as the straightforward molecular orbital approach, Green's function and scattering theory methods have been introduced.[9–12] In recent years, various authors have applied these methods either directly in the context of molecular wires or else in such a way that their results can easily be adapted for them.[10,13–16] Although we do not use it in this paper, we ought to point out that the Green's function approach has the advantage of being easily adapted to perform averages over varying configurations to allow, for example, for disorder. The importance of this for molecular wires is demonstrated in the paper by Kemp, Mujica, and Ratner.[15]

It is, of course, accepted that the standard two-state model does not apply in all circumstances. For some good discussions of this point, see Refs. 10 and 17 and, especially, the paper by Reimers and Hush.[14] It seems to be the general opinion that the model will be satisfactory when the energies of the donor and acceptor states are well separated from those of the bridge states and when the couplings between the bridge states and the donor and acceptor states are small. Care is needed if these requirements are not met. In the case of molecular electronics, we take the view that efficient and rapid charge transfer is desirable and that this is most likely to occur when the donor, bridge and acceptor states are all in resonance or near resonance. This is just the situation where the usual two-state (DA) model may be rather poor.

Similar considerations arise in surface-ion neutralization and other processes of charge transfer in the solid state which occur when atoms or ions are scattered from metal or semiconductor surfaces. Here, too, for effective charge transfer the energy level of the scattered ion or atom should be in resonance with the surface energy band of the solid. Two

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approximations[18–19] have proved to be useful in theoretical studies of these phenomena and it is the purpose of this paper to show how they can be applied to the donor–bridge–acceptor model.

The two approximations are the narrow-band and wide-band approximations and we shall apply these to the case the bridge energy levels can be regarded as forming an energy band. The narrow-band approximation is made when the range of energies of the bridge states is narrow so that we can approximate every bridge energy by the same single energy. Thus the bridge states can be regarded as degenerate and this considerably simplifies the time-dependent equations which describe the model. A different but equally useful simplification can be made when the band is wide and, in addition, there are a sufficient number of bridge states for the band to be dense so that the interaction terms linking the bridge states to the donor and acceptor states can be considered as a continuous function of the bridge energy. Both of these approximations can be applied when the various states are in resonance, which is an advantage in the present context. We illustrate these ideas with examples for which we believe the standard two-state (DA) theory is invalid. Of course the narrow-band and wide-band approximations used also have a restricted range of validity. If we denote a typical bridge/acceptor or bridge/donor matrix element by I and the width of the band by W, then for the narrow-band approximation we require $W \ll I$ and for the wide-band approximation we need $W \gg I$. All our examples are in one of these two categories. In spite of these restrictions, we believe that our results provide insight into the charge-transfer processes of molecular electronics.

II. THE MODEL

The standard theoretical model for a *molecular switch* consists of a donor (D) connected by a bridge (B) to an acceptor (A). We assume that it is sufficient to consider only a single state, with energy E_{D} and wave function ψ_{D}, associated with the donor. Similarly, we consider only a single state, with energy E_{A} and wave function ψ_{A}, for the acceptor. For the bridge states we use $\{\psi_j^{\mathrm{B}}, E_j^{\mathrm{B}}, j=1 \cdot N\}$, and the number of states N can vary considerably from one bridge to another, sometimes being quite small and sometimes large. In either case, we regard these as forming the bridge band.

All of these states are one-electron states since we are restricting ourselves to the case of a single electron, originally on the donor and the problem is to determine the probability of its transfer to the acceptor. To do this we need the system's time-dependent one-electron wave function which has the form

$$\Psi(t)=c_{\mathrm{D}}(t)\psi_{\mathrm{D}}+\sum_{j=1}^{N} c_j(t)\psi_j^{\mathrm{B}}+c_{\mathrm{A}}(t)\psi_{\mathrm{A}}. \tag{1}$$

The base states, $\psi_D, \psi_j^{\mathrm{B}}, \psi_A$ are independent of time so that the time dependence of the wave function is carried by the coefficients c_{D}, c_j, and c_{A}. The differential equations determining them are obtained by substituting Eq. (1) into the time-dependent Schrödinger equation. If we assume that the base-state wave functions are real and form an orthonormal set, these equations are

$$i\dot{c}_{\mathrm{D}}=E_{\mathrm{D}}c_{\mathrm{D}}+\sum_j v_j^{\mathrm{D}}c_j+v^{\mathrm{AD}}c_{\mathrm{A}}, \tag{2a}$$

$$i\dot{c}_j=E_jc_j+v_j^{\mathrm{D}}c_{\mathrm{D}}+v_j^{\mathrm{A}}c_{\mathrm{A}}, \tag{2b}$$

$$i\dot{c}_{\mathrm{A}}=E_{\mathrm{A}}c_{\mathrm{A}}+\sum_j v_j^{\mathrm{A}}c_j+v^{\mathrm{AD}}c_{\mathrm{D}}. \tag{2c}$$

In these equations the v_j^{D}, etc., are the matrix elements of the Hamiltonian H between the various base states and these will be real because of our assumption that the base states are real. In particular, the matrix elements linking the bridge states to the donor and acceptor states are

$$v_j^{\mathrm{D}}=\langle\psi_{\mathrm{D}}|H|\psi_j^{\mathrm{B}}\rangle \tag{3}$$

and

$$v_j^{\mathrm{A}}=\langle\psi_{\mathrm{A}}|H|\psi_j^{\mathrm{B}}\rangle, \tag{4}$$

while the direct interaction between the donor and acceptor has the matrix element

$$v^{\mathrm{AD}}=\langle\psi_{\mathrm{A}}|H|\psi_{\mathrm{B}}\rangle. \tag{5}$$

For many cases v^{AD} will be zero and the transfer of the electron from the donor to the acceptor will have to proceed indirectly via the bridge states as intermediates. The linear set of Eqs. (2a)–(2c) have to be solved subject to the boundary condition that initially the electron is on the donor so that

$$c_{\mathrm{D}}=1, \quad c_j=0, \quad c_{\mathrm{A}}=0. \tag{6}$$

At a later time t, the probabilities P_{D} that the electron remains on the donor, P_{B} that the electron is in a bridge state, and P_{A} that the electron has transferred to the acceptor are

$$P_{\mathrm{D}}=|c_{\mathrm{D}}(t)|^2, \quad P_{\mathrm{B}}=\sum_j |c_j(t)|^2, \quad P_{\mathrm{A}}=|c_{\mathrm{A}}(t)|^2. \tag{7}$$

In deriving these equations, we have assumed that the bridge band is entirely empty initially so that all the bridge states are available as intermediates from the beginning. If this is not the case, the treatment is somewhat more complicated and we reserve it for a future paper.

III. PARAMETER VALUES FOR AN INITIALLY EMPTY BRIDGE BAND

At this point we anticipate the next section by discussing some parameter values. It is necessary to do so at this stage because one combination of parameters is zero for an initially empty bridge band and this fact strongly influences the development of the equations.

The most usual description of a bridge band is one where there is a set of m localized orbitals, usually the valence orbitals of the atoms forming the bridge, and these orbitals are combined together to form m bridge states. With our assumption that the all of the orbitals in the bridge band are available as intermediates, it follows that we must have

$m=N$. Denoting the localized orbitals by $\{\omega_r,\ r=1,\ldots,N\}$, then for each bridge state we have an expansion of the form

$$\psi_j^{\mathrm{B}}=\sum_{r=1}^{N} b_{jr}\omega_r . \tag{8}$$

The assumption that the orbitals are localized implies that we may model the ω_r as orthonormal functions and the orthonormality of the bridge wave functions ψ_j^{B} leads to a result of the form

$$\mathbf{B}^T\mathbf{B}=\mathbf{B}\mathbf{B}^T=\mathbf{I}, \tag{9}$$

where $\mathbf{B}$ is a square matrix whose columns are b_{jr} $(j=1,\ldots,N)$. If we assume further that the donor interacts significantly only with a single orbital r and the acceptor interacts significantly only with a single, different, orbital s then we have, from Eqs. (3) and (4),

$$v_j^{\mathrm{D}}=b_{jr}\langle\psi_{\mathrm{D}}|H|\omega_r\rangle=b_{jr}V_r^{\mathrm{D}}, \tag{10}$$

$$v_j^{\mathrm{A}}=b_{js}\langle\psi_{\mathrm{A}}|H|\omega_s\rangle=b_{js}V_s^{\mathrm{A}}. \tag{11}$$

An example of this would be a bridge consisting of a long chain molecule, with the donor and acceptor situated at opposite ends. Thus, the donor would interact with ω_r on the end atom at its end of the bridge and the acceptor with ω_s on the end atom at the opposite end.

In our study of a narrow-band bridge, it turns out that the v_j parameters occur in the combinations

$$v_{\mathrm{BD}}=\sum_j (v_j^{\mathrm{D}})^2, \quad v_{\mathrm{BDA}}=\sum_j (v_j^{\mathrm{D}}v_j^{\mathrm{A}}),$$

$$v_{\mathrm{BA}}=\sum_j (v_j^{\mathrm{A}})^2, \tag{12}$$

and it is the second of these, v_{BDA}, which is most significant in determining the donor–acceptor charge transfer. Note, that all of the terms in v_{BD} and v_{BA} are positive and so they accumulate. However, this is not necessarily the case with v_{BDA} because, for some values of j, v_j^{D}, and v_j^{A} can have the same sign while for other values they may differ in sign. Thus there is the possibility of cancellation. Unfortunately, this is what occurs here since, using Eqs. (10) and (11), it follows that

$$v_{\mathrm{BDA}}=V_r^{\mathrm{D}}V_s^{\mathrm{A}}\sum_{j=1}^{N} b_{jr}b_{js}. \tag{13}$$

However, from Eq. (9) we have that, for $N>1$,

$$\sum_{j=1}^{N} b_{jr}b_{js}=0 \quad (r\neq s), \tag{14}$$

so that $v_{\mathrm{BDA}}=0$. On the other hand, except in very unusual circumstances, v_{BD} and v_{BA} will be nonzero.

This result that $v_{\mathrm{BDA}}=0$ is crucial in the analysis of charge transfer through a narrow-band bridge, and it is important to note, that it relies on all the bridge orbitals being initially unoccupied. If the bridge band is partially occupied at the beginning, so that not all of the channels are open for the electron, the dominant features of the solution of Eq. (2) can be very different.

When the wide-band approximation is used, the same combination of parameters arise but they have to be treated in a different way. To make progress, we must impose the further assumption that the number of bridge states is large and that the energy levels are dense within the band. If this is the case then, as is done in the band theory of solids, we can treat the orbital energies as if they were a variable E, say, with $E_L<E<E_U$, corresponding to E lying between the lower and upper band energies. The interaction parameters, also, will become functions of E when j is allowed to vary between $j=1$ and $j=N$ so that the matrix elements in Eqs. (3) and (4) become continuous functions of E and can be regarded as interaction densities. We write $\rho_{\mathrm{D}}(E)$, which can be regarded as an interaction density for the donor–bridge interactions, to replace the $|v_j^{\mathrm{D}}|^2$, $\rho_{\mathrm{A}}(E)$, the interaction density for the acceptor–bridge interactions, to replace the $|v_j^{\mathrm{A}}|^2$ and $\rho_{\mathrm{AD}}(E)$, an overlap interaction density for donor–bridge–acceptor interactions, to replace the $v_j^{\mathrm{D}}v_j^{\mathrm{A}}$.

A convenient analysis of any interaction density $\rho(E)$ can be obtained by using a Fourier series representation. Choosing the zero of energy to be at the center of the band and denoting the width of the band by $W=4\beta$, we have $E_U=-2\beta$ and $E_L=2\beta$ so that

$$\rho(E)=\frac{A_0}{4\beta}+\frac{1}{2\beta}\sum_{n=1}^{\infty}\left[A_n\cos\left(\frac{\pi nE}{2\beta}\right)+B_n\sin\left(\frac{\pi nE}{2\beta}\right)\right], \tag{15}$$

where the explicit dependence of the Fourier coefficients on 2β is emphasized since, to invoke the wide-band approximation in Sec. IV we shall take the limit as 2β becomes large. Note, that so far we have not done this and Eq. (15) is dependent only on the number of states being sufficiently large that we can treat the energies as a continuous rather than a discrete variables.

The constant term in Eq. (15), for each of the densities is proportional to the constants v_{BA}, v_{BD}, and v_{BDA}, respectively, so that except in unusual circumstances, this term survives for $\rho_{\mathrm{A}}(E)$ and $\rho_{\mathrm{D}}(E)$. However, with an initially empty bridge band, the constant term for $\rho_{\mathrm{AD}}(E)$ is zero.

IV. SYSTEMS WITH TIME-INDEPENDENT MATRIX ELEMENTS

Equations (2) are much easier to solve when the interactions between donor, bridge and acceptor do not vary with time so that the matrix elements are time independent. We make this assumption here since it most likely will cover the majority of practical applications. We also specialize to three cases where analytic solutions can be obtained, namely the case where there is no bridge, the case where the energy band of the bridge is narrow and the case where we have a wide energy band for the bridge.

A. No bridge

If there is no bridge present, the only interaction between the donor and the acceptor is the direct one represented by the matrix element v^{AD} and we have a standard well-understood problem. We include it here only for comparison with the other two cases. Equations (2) can be written in the form of a matrix differential equation

$$i\dot{\mathbf{c}}=\mathbf{M}\mathbf{c}, \tag{16}$$

where $\mathbf{c}$ is a column vector and $\mathbf{M}$ is a real symmetric matrix defined by

$$\mathbf{c}=\begin{bmatrix} c_{\mathrm{D}} \\ c_{\mathrm{A}} \end{bmatrix}, \quad \mathbf{M}=\begin{bmatrix} E_{\mathrm{D}} & v^{\mathrm{AD}} \\ v^{\mathrm{AD}} & E_{\mathrm{A}} \end{bmatrix}. \tag{17}$$

The initial condition is $\mathbf{c}=\mathbf{c}_0=\left[\begin{smallmatrix}1\\0\end{smallmatrix}\right]$ at time $t=0$ and the solution can be written in the form

$$\mathbf{c}(t)=\sum_k \left(\frac{\mathbf{m}_k^T\mathbf{c}_0}{\mathbf{m}_k^T\mathbf{m}_k}\right)\mathbf{m}_k \exp(-i\lambda_k t), \tag{18}$$

where $\mathbf{m}_k$ is an eigenvector of $\mathbf{M}$ associated with eigenvalue λ_k.

From Eq. (18) we can obtain the probabilities defined in Eq. (7) so that $P_{\mathrm{B}}=0$, $P_{\mathrm{D}}=1-P_{\mathrm{A}}$, and

$$P_{\mathrm{A}}(t)=\frac{(v^{\mathrm{AD}})^2}{\Omega^2}\sin^2\,\Omega t,$$

$$\Omega=\tfrac{1}{2}\sqrt{(E_{\mathrm{A}}-E_{\mathrm{D}})^2+4(v^{\mathrm{AD}})^2}. \tag{19}$$

Thus the behavior is oscillatory and, for v^{AD} small compared with $(E_{\mathrm{A}}-E_{\mathrm{D}})$, $P_{\mathrm{A}}(t)$ is negligible. However, in the resonant case when $E_{\mathrm{A}}=E_{\mathrm{D}}$, we have

$$P_{\mathrm{A}}(t)=\sin^2\,\Omega t \quad \text{and} \quad P_{\mathrm{D}}(t)=\cos^2\,\Omega t, \tag{20}$$

so that there is regular transfer backwards and forwards between donor and acceptor.

B. A narrow bridge band

If the states comprising the bridge form a narrow band, we can apply the narrow-band approximation and use a single energy E_{B}, say, for each state, i.e., we take $E_j=E_{\mathrm{B}}$ for each j. Then, provided the bridge contains at least two states, the set of N equations represented by Eq. (2b) can be replaced by just two:

$$i\dot{c}_{\mathrm{BD}}=E_{\mathrm{B}}c_{\mathrm{BD}}+c_{\mathrm{D}} \tag{21a}$$

and

$$i\dot{c}_{\mathrm{BA}}=E_{\mathrm{B}}c_{\mathrm{BA}}+c_{\mathrm{A}}, \tag{21b}$$

since

$$c_j=v_j^{\mathrm{D}}c_{\mathrm{BD}}+v_j^{\mathrm{A}}c_{\mathrm{BA}}. \tag{21c}$$

Using Eq. (21c), Eqs. (2a) and (2c) can be rewritten in terms of c_{BD} and c_{BA}. If there is no direct interaction between the donor and the acceptor so that $v^{\mathrm{AD}}=0$, the equations have the same form as Eq. (16) with

$$\mathbf{c}=\begin{bmatrix} c_{\mathrm{D}} \\ c_{\mathrm{BD}} \\ c_{\mathrm{BA}} \\ c_{\mathrm{A}} \end{bmatrix}, \quad \mathbf{c}_0=\begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix},$$

$$\mathbf{M}=\begin{bmatrix} E_{\mathrm{D}} & v_{\mathrm{BD}} & v_{\mathrm{BDA}} & 0 \\ 1 & E_{\mathrm{B}} & 0 & 0 \\ 0 & 0 & E_{\mathrm{B}} & 1 \\ 0 & v_{\mathrm{BDA}} & v_{\mathrm{BA}} & E_{\mathrm{A}} \end{bmatrix}, \tag{22}$$

where the parameters v_{BD}, v_{BA}, and v_{BDA} are those defined in Eq. (12).

Before turning to the special case of the initially empty bridge band, we indicate, briefly, how the more general treatment would proceed. In order to obtain $\mathbf{c}$ we need to solve the characteristic equation for $\mathbf{M}$. It turns out that $\mathbf{M}$ has real eigenvalues $\{\lambda_k\}$ and its eigenvectors $\mathbf{m}_k$ form a complete set. Hence, $\mathbf{c}$ can be expressed as a linear combination of the eigenvectors. To determine the time-dependent coefficients in this expansion, we make use of the result that, since the eigenvalues are real, related to the set $\{\mathbf{m}_k\}$ is the biorthogonal set $\{\mathbf{b}_k\}$ of eigenvectors of $\mathbf{M}^T$, the transpose of $\mathbf{M}$. We can then obtain the solution of Eq. (21) in the analogous form to Eq. (18) so that

$$\mathbf{c}(t)=\sum_k \left(\frac{\mathbf{b}_k^T\mathbf{c}_0}{\mathbf{b}_k^T\mathbf{m}_k}\right)\mathbf{m}_k \exp(-i\lambda_k t), \tag{23}$$

and from $\mathbf{c}(t)$ the various probabilities can be found.

As can be seen from Eq. (22), the parameter v_{BDA} occurs in the only nonzero matrix elements of the matrix $\mathbf{M}$ which connect the first two elements of $\mathbf{c}$ to the last two. Thus, it is the only term that can cause c_{A} to change from its initial value of zero, and therefore, is the determining factor for charge transfer to the acceptor. Unfortunately, as we saw in Sec. III, for an initially empty band, the situation we deal with in this paper, $v_{\mathrm{BDA}}=0$ so that it follows that there can be no charge transfer. Of course, this holds only within the narrow-band approximation. Going beyond that approximation, c_{A} might indeed be nonzero but we would expect it to be at most quite small. This implies that a bridge whose effective band was narrow and initially empty would not be a good candidate for facilitating donor–acceptor charge transfer.

We can consider this in more detail by noting that when $v_{\mathrm{BDA}}=0$ the matrix $\mathbf{M}$ can be partitioned into two nonzero 2×2 matrices. Consequently, the original matrix differential equation factors into two separate equations. One involves c_{BA} and c_{A} only and, since initially they are zero and there are no terms which can alter that, they remain zero, showing again that there is no charge transfer to the acceptor. The second equation has the same general form as Eqs. (16) and (17), for the no-bridge case, but with c_{A} replaced by c_{BD}, E_{A} by E_{B} and v^{AD} by v_{BD}. Since the form of solution is the same as in Eqs. (19) and (20), we shall obtain oscillatory behavior with charge transfering backwards and forwards between the donor and the bridge states.

Although this is essentially a reduction to a two-state problem, it is not the conventional two state (DA) reduction since here the states are the donor and a ''virtual state'' formed from the combination of the bridge states. Thus the present results are completely different to those of the conventional model. Perhaps this is not surprising in the case of near resonance $E_D \approx E_B \approx E_A$ where the conventional method might be expected to fail. However, Eq. (22) and the following conclusions apply even when the bridge energies are well separated from the donor and acceptor energies (given that the band is narrow), so that there is the interesting question of the region of validity of the different models and how one merges into the other. We intend to investigate this in some detail in a future publication when we consider, also, the behavior of the narrow band approximation in those circumstances where $v_{BDA} \neq 0$.

C. A wide bridge band

Integrating Eq. (2b) and applying the initial condition $c_j = 0$ leads to

$$c_j(t) = -i \int_0^t (v_j^D c_D + v_j^A c_A) \exp\, iE_j(u-t)\, du. \tag{24}$$

Substituting into Eq. (2a) and rearranging gives

$$i\dot{c}_D = E_D c_D + v^{AD} c_A - i \sum |v_j^D|^2 I_j(c_D) - i \sum v_j^D v_j^A I_j(c_A), \tag{25}$$

and

$$i\dot{c}_A = E_A c_A + v^{AD} c_D - i \sum |v_j^A|^2 I_j(c_A) - i \sum v_j^D v_j^A I_j(c_D), \tag{26}$$

where

$$I_j(c) = \int_0^t c \, \exp\, iE_j(u-t)\, du. \tag{27}$$

With a wide dense band we can use the interaction densities discussed in Sec. III to replace the summations by integration over E and this leads to double integrals of the general form

$$J = \int_0^t c(u) \int_{E_L}^{E_U} \rho(E) \exp\, iE(u-t)\, dE\, du = \int_{-t}^0 c(t+x) \int_{E_L}^{E_U} \rho(E) \exp\, iEx\, dE\, dx. \tag{28}$$

To make further progress, we use the Fourier series expansion of $\rho(E)$ and this gives rise to the following integrals:

$$\int_{-2\beta}^{2\beta} \cos\left(\frac{\pi n E}{2\beta}\right) e^{iEx}\, dE = 2\beta[\mathrm{sinc}(2\beta x + n\pi) + \mathrm{sinc}(2\beta x - n\pi)] \tag{29}$$

and

$$\int_{-2\beta}^{2\beta} \sin\left(\frac{\pi n E}{2\beta}\right) e^{iEx}\, dE = -2i\beta[\mathrm{sinc}(2\beta x + n\pi) - \mathrm{sinc}(2\beta x - n\pi)], \tag{30}$$

where $\mathrm{sinc}(x) = \sin(x)/x$. Thus, Eq. (29) can be written

$$J = \frac{1}{2\beta} \int_{-t}^0 c(t+x) \left\{ \frac{1}{2} A_0 4\beta\, \mathrm{sinc}(2\beta x) + \sum_{n=1}^{\infty} [(A_n - iB_n) 2\beta\, \mathrm{sinc}(2\beta x + n\pi) + (A_n + iB_n) 2\beta\, \mathrm{sinc}(2\beta x - n\pi)] \right\} dx. \tag{31}$$

In order to handle Eq. (31), we now use the fundamental feature of the wide-band approximation by taking the limit as β becomes large. From generalized function theory, it follows that, in the limit, sinc can be replaced by a delta function, viz.

$$2\beta\, \mathrm{sinc}(2\beta x - z) \approx \pi \delta(x - z/2\beta) \tag{32}$$

for $z = \pm n\pi$. The range of integration is negative so that only zero or negative values of z contribute to the integral. Since zero is one of the limits of the integral, the corresponding result for $z = 0$ is different and we have

$$2\beta\, \mathrm{sinc}(2\beta x) \approx \frac{\pi}{2}\, \delta(x). \tag{33}$$

Thus, Eq. (31) becomes

$$J = \sum_n a_n c(t - k_n), \tag{34}$$

where

$$k_n = \frac{n\pi}{2\beta}, \quad a_0 = \frac{\pi}{4\beta} A_0, \quad a_n = \frac{\pi}{2\beta} (A_n - iB_n). \tag{35}$$

We will be predominantly concerned with two special cases: (i) where a_0 is the dominant coefficient in Eq. (35); (ii) where a_n is the dominant coefficient for some nonzero n. The former corresponds to the conventional wide-band approximation used in solid-state physics and is the most appropriate approximation for $\rho_D(E)$ and $\rho_A(E)$ since these are usually fairly uniform interaction densities. Let us denote the dominant constants for these two densities by μ_D and μ_A; a full analysis of this case is given in Ref. 18. In contrast, for an initially empty band Eq. (14) should still hold in the limit of the continuous approximation, so that $a_0 = 0$ for $\rho_{AD}(E)$. However, in many cases $\rho_{AD}(E)$ will be accurately approximated by just one term in Eq. (15) corresponding to a dominant frequency of oscillation. (This can be established in any example by a preliminary Fourier analysis of the coefficients $v_j^D v_j^A$.) Writing μ for the dominant a_n and k for the corresponding frequency k_n, the differential equations for c_D and c_A in this situation are

$$\dot{c}_{\mathrm{D}}(t)=-(\mu_{\mathrm{D}}+iE_{\mathrm{D}})c_{\mathrm{D}}(t)-\mu c_{\mathrm{A}}(t-k), \tag{36}$$

$$\dot{c}_{\mathrm{A}}(t)=-(\mu_{\mathrm{A}}+iE_{\mathrm{A}})c_{\mathrm{A}}(t)-\mu c_{\mathrm{D}}(t-k), \tag{37}$$

where $c_{\mathrm{D}}(0)=1$ and $c_{\mathrm{A}}(0)=0$. We are considering the case where the electron is excited instantaneously at $t=0$ and Eqs. (36) and (37) are to be solved for $t>0$. However, because of the delay terms, in order to solve the equations we must impose the conditions $c_{\mathrm{D}}(t)=c_{\mathrm{A}}(t)=0$ for $t<0$. While superficially these equations resemble those found in the conventional two-state (DA) problem, in reality they are very different because of the time delay $c_{\mathrm{A}}(t-k)$ in Eq. (36) and $c_{\mathrm{D}}(t-k)$ in Eq. (37). As will be seen, with $k\neq 0$ there is no simple oscillatory transfer of charge between the donor and the acceptor, but a much more complex behavior arises including an initial exponential decay in $c_{\mathrm{D}}(t)$. Also Eqs. (36) and (37) do not conserve charge since, for $t>0$, $|c_{\mathrm{D}}(t)|^2+|c_{\mathrm{A}}(t)|^2$ need not equal 1, and frequently does not. It does not mean that the charge has been lost from the system, but only that it has transferred to the bridge. Thus, it is important to recognize that we are not assuming that all of the $c_j(t)$ for the bridge states are zero; rather that within the wide-band approximation, Eqs. (36) and (37) do not themselves completely describe the system, but they must be supplemented by Eq. (24).

Similar considerations apply to the energy of the system. At $t=0$, energy is fed into the system in order to place the electron into the donor level but after that, for $t>0$, energy is conserved and the dynamics will be reversible back to $t=0$. From these equations we have

$$c_{\mathrm{D}}(t)=e^{-(\mu_{\mathrm{D}}+iE_{\mathrm{D}})t}\left[1-\int_0^t \mu e^{(\mu_{\mathrm{D}}+iE_{\mathrm{D}})x}c_{\mathrm{A}}(x-k)dx\right], \tag{38}$$

$$c_{\mathrm{A}}(t)=-e^{-(\mu_{\mathrm{A}}+iE_{\mathrm{A}})t}\int_0^t \mu e^{(\mu_{\mathrm{A}}+iE_{\mathrm{A}})x}c_{\mathrm{D}}(x-k)dx. \tag{39}$$

From Eq. (39) we may deduce that $c_{\mathrm{A}}(t)$ remains at its initial value of 0 until $t=k$. Furthermore, in $0\leqslant t\leqslant 2k$ we have

$$c_{\mathrm{D}}(t)=e^{-(\mu_{\mathrm{D}}+iE_{\mathrm{D}})t}. \tag{40}$$

Since $\mu_{\mathrm{D}}<0$, $c_{\mathrm{D}}(t)$ decreases initially, the rate depending on the ratio of the strength of the interaction to the bandwidth; at $t=2k$ there is a new contribution from the second term in Eq. (38).

It is likely that in practical applications the behavior of the system at times near $t=0$ will be most significant and, provided k is not too small, this implies that we can concentrate on the interval between $t=0$ and $t=2k$. We now have enough information to describe qualitatively the pattern of electron transfer in this time interval. For the first half of the interval, the interaction between bridge and acceptor is, in effect, ''turned off'' so that only the bridge and donor play any part. During this time, the electron density on the donor is decreasing at a rate governed by μ_{D} [Eq. (46)] and, as a consequence, the lost electron density will be transferred to the bridge at the same rate. Up to the time $t=k$, the electron density on the acceptor is zero but, at $t=k$, the bridge–acceptor interaction ''kicks in'' and charge can transfer to the acceptor from the bridge. The rate at which and the extent to which this occurs is governed by Eq. (39) and it is clear, as would be expected, that the key parameter is μ, although μ_{A} is also important since that tends to encourage the return of charge back to the bridge. In the interval $[0,2k]$, charge is continually lost from the donor at a uniform rate but at $t=2k$, the second term in Eq. (38) has an effect and it is possible for some charge to be transferred back to the donor from then on.

A more quantitative account can be given by using Laplace transforms to obtain explicit solutions. The simplest solution arises for the most important case namely that of resonance ($E_{\mathrm{D}}=E_{\mathrm{A}}=0$) when the Laplace transforms of Eqs. (36) and (37) are

$$s\overline{c_{\mathrm{D}}}-1=-\mu_{\mathrm{D}}\overline{c_{\mathrm{D}}}-\mu e^{-sk}\overline{c_{\mathrm{A}}}, \tag{41}$$

$$s\overline{c_{\mathrm{A}}}=-\mu_{\mathrm{A}}\overline{c_{\mathrm{A}}}-\mu e^{-sk}\overline{c_{\mathrm{D}}}. \tag{42}$$

Solving these equations we obtain

$$\overline{c}_{\mathrm{D}}=\frac{s+\mu_{\mathrm{A}}}{\Delta},\quad \overline{c_{\mathrm{A}}}=\frac{-\mu e^{-sk}}{\Delta}, \tag{43}$$

where

$$\Delta=(s+\mu_{\mathrm{D}})(s+\mu_{\mathrm{A}})-\mu^2e^{-2ks}. \tag{44}$$

Inverting the Laplace transforms leads to the explicit expressions

$$c_{\mathrm{D}}=e^{-\mu_{\mathrm{D}}t}+\sum_{m=1}^{\infty} f_m(t-2mk)u(t-2mk), \tag{45}$$

$$c_{\mathrm{A}}=\sum_{m=1}^{\infty} g_m[t-(2m-1)k]u[t-(2m-1)k], \tag{46}$$

where $u(t)$ is the Heaviside function and the functions f_m and g_m are defined recursively. Thus, for any given finite interval $0\leqslant t\leqslant T$ analytic formula may be obtained. For example, if we consider $T=3k$, then we only require explicit expressions for $f_1(t)$ and $g_1(t)$. For $\mu_{\mathrm{D}}\neq\mu_{\mathrm{A}}$ these are given by

$$f_1(t)=\frac{\mu^2}{(\mu_{\mathrm{D}}-\mu_{\mathrm{A}})^2}[(e^{-\mu_{\mathrm{A}}t}-e^{-\mu_{\mathrm{D}}t}) -(\mu_{\mathrm{D}}-\mu_{\mathrm{A}})te^{-\mu_{\mathrm{D}}t}], \tag{47}$$

$$g_1(t)=\frac{\mu}{\mu_{\mathrm{D}}-\mu_{\mathrm{A}}}(e^{-\mu_{\mathrm{D}}t}-e^{-\mu_{\mathrm{A}}t}). \tag{48}$$

From these equations we see that the charge density $|c_{\mathrm{A}}|^2$ on the acceptor is indeed zero until $t=k$; after that it equals $|g_1(t-k)|^2$ until $t=3k$. Thus, it will increase from its zero value at $t=k$, continuing to increase either until $t=3k$ or until it reaches a maximum at the turning point of $g_1(t-k)$,

TABLE I. Comparison of the narrow-band approximation for $N=10$ with the numerical results for $\beta=0.1$ and $\beta=0.0001$.

	$\beta=0.0001$		$\beta=0.1$		
t	P_D	P_A	P_D	P_A	$\cos^2\frac{\sqrt{3}}{2}t$
0.1	0.9851	0	0.9851	0	0.9851
0.2	0.9412	0	0.9412	0	0.9412
0.5	0.6696	0	0.6697	0	0.6696
1	0.1150	0	0.1154	0.0001	0.1150
1.5	0.0693	0	0.0681	0.0035	0.0693
2	0.5928	0	0.5849	0.0106	0.5928
5	0.9748	0	0.9136	0.0642	0.9748
6	0.2345	0	0.2191	0.0115	0.2345

TABLE II. Comparison of nonresonant behavior for varying interaction strengths with $\beta=0.001$ and $N=2$.

	$V_N^D=V_1^D=1$		$V_N^D=V_1^D=0.1$	
t	P_D	P_A	P_D	P_A
0.1	0.9851	0	0.9999	0
0.2	0.9414	0	0.9994	0
0.5	0.6766	0	0.9963	0
1	0.1945	0	0.9863	0
1.5	0.2816	0	0.9724	0
2	0.8060	0	0.9584	0
5	0.9094	0	0.9836	0
6	0.1488	0	0.9998	0
10	0.6758	0	0.9535	0

provided that turning point occurs before $t=3k$. In the latter case, charge will begin to flow back from the acceptor to the bridge. The behavior of the donor charge density is exactly as discussed earlier up to the time $t=2k$. After that, when $f_1(t-2k)$ has to be included, it will depend on the relative magnitudes of the various parameters.

For completeness, we give the results for the special case where the donor–bridge interaction and the acceptor–bridge are the same so that $\mu_{\mathrm{D}}=\mu_{\mathrm{A}}$. They are

$$f_1(t)=\tfrac{1}{2}\mu^2t^2e^{-\mu_{\mathrm{D}}t},\quad g_1(t)=-\mu te^{-\mu_{\mathrm{D}}t}. \tag{49}$$

A similar analysis can be carried out in the nonresonant situation and for the more general case when all the terms in Eq. (15) are included. However, the expressions become increasingly complex so that they are useful only for an interval $0\leqslant t\leqslant T$ and when there are only a few dominant coefficients a_n in Eq. (15) with $k<T$.

V. NUMERICAL ILLUSTRATIONS USING A TIGHT-BINDING MODEL

To illustrate the theoretical results obtained we introduce a standard Huckel, tight-binding model for the bridge so treating it as a long chain molecule with N atoms. We have in the notation of Sec. III, see especially Eq. (8),

$$(\alpha-E_j)b_{jr}+\beta(b_{jr+1}+b_{jr-1})=0,\quad r=1,\ldots,N. \tag{50}$$

The solution of this eigenvalue problem is

$$E_j=\alpha+2\beta\cos\theta_j,\quad b_{jr}=\sin r\theta_j,\quad \text{where}\quad \theta_j=\frac{j\pi}{N+1}. \tag{51}$$

For this model the bandwidth is 4β and without loss of generality we may choose $\alpha=0$.

If we take the donor and the acceptor at opposite ends of the chain, so that the donor only interacts significantly with atom 1 and the acceptor only interacts significantly with atom N, then the important parameters which determine the interaction strengths are b_{j1} and b_{jN} and they are related so that

$$b_{j1}=\sin\theta_j=(-1)^jb_{jN}, \tag{52}$$

which verifies Eq. (14). The other parameters for this model are E_{D}, E_{A}, V_l^{D} and V_N^{A}, where

$$V_1^{\mathrm{D}}=\langle\psi_{\mathrm{D}}|H|\omega_l\rangle,\quad V_N^{\mathrm{A}}=\langle\psi_{\mathrm{A}}|H|\omega_N\rangle, \tag{53}$$

and we have absorbed the band normalization constant into the definitions of ω_l and ω_N. The direct interaction v^{AD} is taken to be zero throughout these calculations and we are primarily concerned with the wide and narrow bandwidths corresponding to large or small values of β, respectively.

First, we use the numerical model to confirm the validity of the narrowband approximations. To examine this we consider $N=10$ when $\beta=0.1$ and when $\beta=0.0001$. For each of the calculations we take $E_{\mathrm{D}}=E_{\mathrm{A}}=0$, and since we have a completely empty band, then Eq. (14) holds. In Table I, we compare these with the theoretical results obtained from Eq. (23) where we have $v_{\mathrm{BDA}}=0$ and $v_{\mathrm{BD}}=v_{\mathrm{BA}}=3/2$. This leads to

$$P_{\mathrm{D}}=\cos^2\frac{\sqrt{3}}{2}t\quad\text{and}\quad P_{\mathrm{A}}=0. \tag{54}$$

As we can see in Table I, there is perfect agreement for $\beta=0.0001$ but there is also good agreement for the more realistic value $\beta=0.1$. However, for the latter P_{A} becomes more significant as t increases. In Table II, we consider the results of a similar calculation in a situation where $E_{\mathrm{D}}=E_{\mathrm{A}}=1$ so that although the donor and the acceptor are in resonance they are not in resonance with the bridge. We consider two cases where $V_N^{\mathrm{A}}=V_1^{\mathrm{D}}=1$ and $V_N^{\mathrm{A}}=V_1^{\mathrm{D}}=0.1$ and in each case $\beta=0.001$. The numerical results show that in the former case we have oscillatory behavior, whereas for the latter calculation any oscillatory behavior is very small and $P_{\mathrm{D}}\approx1$.

Now we turn to wide band calculations and in Fig. 1 we plot P_{D} and P_{A} for $t\geqslant0$ in the case $\beta=10$, $V_N^{\mathrm{A}}=V_1^{\mathrm{D}}=1$, $E_{\mathrm{D}}=E_{\mathrm{A}}=0$ where the bridge is assumed to have $N=50$ states. This clearly confirms the analysis given for the wide band approximation with $k\approx2.5$. For $0\leqslant t\leqslant5$ the behavior of c_{D} is best described by Eq. (40) but the pattern changes abruptly for $t\approx5$ when in the additional term in Eq. (38) has an effect. In the interval $0\leqslant t\leqslant2.5$ we may take $c_{\mathrm{A}}=0$ but at $t\approx2.5$, in accordance with the predicted behavior from Eq.

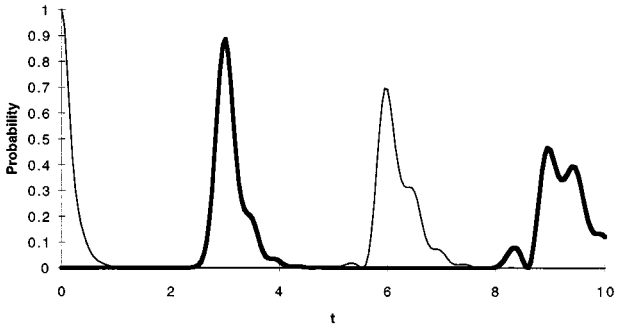

FIG. 1. The probabilities for the donor and the acceptor occupancy when $N=50$, $\beta=10$, and the donor and acceptor are both in resonance with the center of the band.

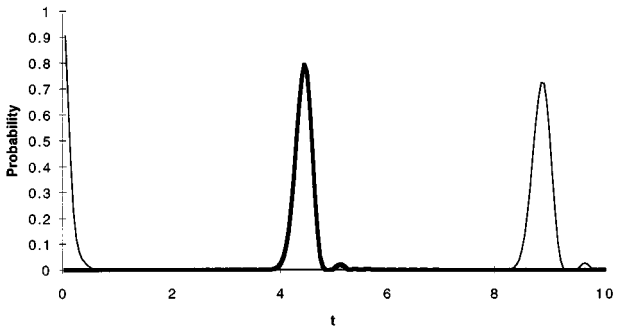

FIG. 3. The probabilities for the donor and acceptor occupancy when $N=80$, $\beta=10$, and the donor and acceptor are both in resonance with the center of the band.

(39), c_A becomes nonzero. A Fourier analysis of $v_j^D v_j^A$ confirms a dominant frequency at $k\approx 2.5$; there are other dominant frequencies for $k>7.5$ but the earlier analysis is sufficient for $0\leqslant t\leqslant 3k$.

In Fig. 2 we plot P_D and P_A for $t\geqslant 0$ where $\beta=10$, $V_N^A=V_1^D=1$, $E_D=0$ and $E_A=10$ so that the acceptor is not in resonance with the centre of the band. The same pattern of results is found but the magnitude of P_A is reduced. The corresponding plots in Fig. 3 are with the same parameter values as for Fig. 1 but with $N=80$ states. The pattern is again apparent with $k\approx 4$ and again a Fourier analysis confirms a dominant peak in this region. For the long chain model the localized states are assumed to be significant on the individual atoms (or molecules) making up the chain, so that by increasing N the chain becomes longer and the donor more geographically separated from the acceptor. Consequently, the time taken for the first significant charge transfer to the acceptor is greater. In the final figure (Fig. 4) the parameters are as for Fig. 1 except $\beta=5$ and again $N=50$. The reduction in the size of β means that the ratio of the interaction strength to the bandwidth has increased so that the initial decay of c_D is more pronounced. Another effect is that the dominant frequency has been doubled to $k\approx 5$ and the same initial behavior is observed. In this figure the calculations are extended to $t=100$.

These calculations illustrate that the numerical techniques used provide accurate and stable results. This is discussed in more detail in the appendix.

VI. CONCLUSION

We have shown that the wide-band and narrow-band approximations lead to analytic approximations, which are in good agreement with the numerical calculations and which provide insight into the effect of the parameters of the model. This has been illustrated for the simplest model where the matrix elements are time independent and where we have one completely empty band. The behavior can be expected to be very different if we have a partially filled band. In future work, we hope to incorporate these generalizations and to consider the effects of an interacting bath, so we would no longer have an isolated system, and also treat the effect of an applied field on the system.

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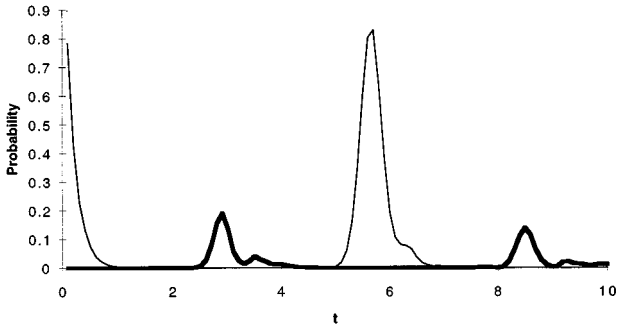

FIG. 2. The probabilities for the donor and acceptor occupancy when $N=50$, $\beta=10$, and only the donor is in resonance with the center of the band.

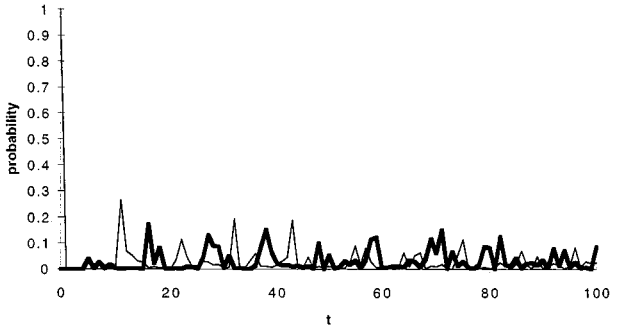

FIG. 4. The probabilities for the donor and acceptor occupancy when $N=50$, $\beta=5$, and both the donor and the acceptor are in resonance with the center of the band.

APPENDIX: AN ANALYSIS OF THE NUMERICAL PROCEDURE

The numerical calculations in this paper have were carried out using a 5th-order Runge–Kutta method for solving Eq. (2) with various values of the step-length h. The results were found to be accurate and stable. The stability of such a procedure for a large number of equations (a maximum of 80 in the results presented here), needs careful analysis and in this Appendix we examine this problem for the particular form of equations given in Eq. (2). The exact solution can be written in the form of Eq. (18) where $\mathbf{M}$ is a real $(N+2)\times(N+2)$ matrix. Denoting the approximate solution obtained by $\mathbf{c}$ we have

$$\hat{\mathbf{c}}(h)=\mathbf{c_0}+\tfrac{1}{6}(\mathbf{k_1}+2\mathbf{k_2}+2\mathbf{k_3}+\mathbf{k_4})=\mathbf{G}\mathbf{c_0}, \tag{A1}$$

where

$$\mathbf{k_1}=-ih\mathbf{M}\mathbf{c_0}, \tag{A2a}$$

$$\mathbf{k_2}=-ih\mathbf{M}(\mathbf{c_0}+\tfrac{1}{2}\mathbf{k_1}), \tag{A2b}$$

$$\mathbf{k_3}=-ih\mathbf{M}(\mathbf{c_0}+\tfrac{1}{2}\mathbf{k_2}), \tag{A2c}$$

and

$$\mathbf{k_4}=-ih\mathbf{M}(\mathbf{c_0}+\mathbf{k_3}). \tag{A2d}$$

Expanding by Taylor's theorem gives

$$\mathbf{c}(h)=\left[\mathbf{G}-i\,\frac{h^5}{120}\,\mathbf{M}^5\,\exp(-i\mathbf{M}t_0)\right]\mathbf{c_0}, \tag{A3}$$

where $0<t_0<h$ so that, since for all t, $\|\mathbf{c}\|=1$,

$$\|\mathbf{c}(h)-\hat{\mathbf{c}}(h)\|<\frac{h^5}{120}\|\mathbf{M}\|^5. \tag{A4}$$

This result is simply the truncation error at each stage and since the method is 5th, order is automatically $O(h^5)$. To examine stability we seek to establish that

$$\|\mathbf{c}(nh)-\hat{\mathbf{c}}(nh)\|<\frac{h^5}{120}\,n\|\mathbf{M}\|^5. \tag{A5}$$

This holds for $n=1$ since this is just the truncation error so that we can proceed by induction. Assuming that Eq. A5 holds we need to establish the equivalent result with $n+1$ replacing n. We have that

$$\begin{aligned}
&\|\mathbf{c}[(n+1)h]-\hat{\mathbf{c}}[(n+1)h]\| \\
&\quad=\|e^{-ih\mathbf{M}}\mathbf{c}(nh)-\mathbf{G}\hat{\mathbf{c}}(nh)\| \\
&\quad\leqslant\|\mathbf{G}\hat{\mathbf{c}}(nh)-e^{-ih\mathbf{M}}\hat{\mathbf{c}}(nh)\|+\|e^{-ih\mathbf{M}}[\mathbf{c}(nh)-\hat{\mathbf{c}}(nh)]\| \\
&\quad\leqslant\frac{h^5}{120}\,\|\mathbf{M}\|^5+\|\mathbf{c}(nh)-\hat{\mathbf{c}}(nh)\| \\
&\quad\leqslant\frac{h^5}{120}\,(n+1)\|\mathbf{M}\|^5.
\end{aligned} \tag{A6}$$

Consequently the result holds for all n and if the time scale T is such that $Nh=T$ we have

$$\|\mathbf{c}(T)-\hat{\mathbf{c}}(T)\|\leqslant\frac{T}{120}\,\|\mathbf{M}\|^5h^4=O(h^4). \tag{A7}$$

Thus, for any time scale T, we may choose N to obtain a solution of accuracy $O(h^4)$ and this verifies the stability of the method applied to the solution of Eq. (2).

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