# Perturbative quantum dynamics: variants of the Dirac method



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# Perturbative quantum dynamics: variants of the Dirac method

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**Abstract.** A detailed comparative study of the structure and workability of various rearranged versions of the Dirac method of variation of constants for perturbative treatment of quantum dynamics is presented. The variants include a modified strategy proposed recently and also a new rearrangement of this form; both of these contain $\lambda$ dependent phase factors associated with the amplitudes which are determined order-by-order by following a Brillouin-Wigner type perturbation procedure, $\lambda$ being the perturbation parameter. The following classes of perturbation problems are considered: $V$, $(V\exp(\mathrm{i}\omega t)+V^{+}\exp(-\mathrm{i}\omega t))$, $f(t)V$ and $f(t)(V\exp(\mathrm{i}\omega t)+V^{+}\exp(-\mathrm{i}\omega t))$, where $f(t)$ defines some suitable adiabatic 'switching' function. Special attention is paid to (i) the avoidance of divergent parts in the amplitude-correction terms from the schemes, (ii) applicability to cases involving a degenerate initial state and a 'resonant' harmonic perturbation, (iii) use of both exponential and non-exponential forms for $f(t)$ and (iv) possible sources of convergence difficulties in such variants. The merits and demerits of the schemes concerned for the different problems under investigation are also listed, for convenience, in a tabular form.

## 1. Introduction

A perturbative approach to quantum dynamics appears frequently in solving several kinds of problems of physical and chemical interest (see, e.g., the works of Dalgarno (1966) and Langhoff *et al* (1972), and references therein, for detailed expositions). The Dirac method (DM), commonly known as the method of variation of constants (Dirac 1926, 1927), is by far the most popular among the various perturbative developments in vogue, including the method of multiple time scales (Brooks and Scarfone 1969, 1982), the Magnus method (Pechukas and Light 1966), etc (see also Case 1966, Langhoff *et al* 1972), thus enjoying widespread applications since the inception of quantum mechanics. However, it is also true that this method, if applied *straightforwardly*, exhibits some undesirable features; these have been discussed, for example, by Heinrichs (1968), Todorov (1981), Dong (1983), Bhattacharyya (1984), etc.

In the course of a recent analysis (Bhattacharyya 1984) with a view to modifying the DM, it has been found that actually the choice of the wavefunction $\psi_s(\lambda, t)$ in the form

$$\psi_s(\lambda, t)=\sum_m a_m(\lambda, t)\phi_m \exp(-\mathrm{i}\omega_m t), \tag{1.1}$$

to be employed in the Schrödinger equation (SE)

$$H(\lambda, t)\psi_s(\lambda, t)=\mathrm{i}\hbar\, \partial\psi_s(\lambda, t)/\partial t \tag{1.2}$$

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where

$$H(\lambda, t) = H_0 + \lambda V(t), \qquad H_0\phi_m = \hbar\omega_m\phi_m, \tag{1.3}$$

is responsible for the major difficulties which crop up when we use the perturbation expansion

$$a_m(\lambda, t) = a_m^{(0)} + \lambda a_m^{(1)}(t) + \lambda^2 a_m^{(2)}(t) + \ldots \tag{1.4}$$

to obtain the coefficients $\{a_m(\lambda, t)\}$ to some desired orders; as usual, the initial conditions (IC) are defined as

$$a_s^{(0)} = 1, \qquad a_p^{(0)}(p \neq s) = 0, \qquad a_m^{(n)}(t_0) = 0 \qquad (m = s, p, \ldots; n = 1, 2, \ldots) \tag{1.5}$$

to imply that the system, at $t = t_0$, starts evolving from a definite normalised stationary state $\phi_s$. Naturally, then, it is expected that a suitable rearrangement of the form (1.1) for $\psi_s(\lambda, t)$ can generate a *proper* perturbative development. In fact, such an idea motivated studies of Chung (1967), Heinrichs (1968) and Epstein (1969) with the rearranged form given by

$$\psi_s(\lambda, t) = a_s(\lambda, t)\exp(-\mathrm{i}\omega_s t)\chi_s(\lambda, t), \qquad \langle\phi_s|\chi_s(\lambda, t)\rangle = 1, \tag{1.6}$$

which is related to (1.1) in the sense that

$$\chi_s(\lambda, t) = \phi_s + \sum_{m \neq s} A_m(\lambda, t)\phi_m \exp(\mathrm{i}\omega_{sm}t), \qquad A_m(\lambda, t) = a_m(\lambda, t)/a_s(\lambda, t),$$

$$\omega_{sm} = \omega_s - \omega_m. \tag{1.7}$$

Here, the coefficients $\{A_m(\lambda, t)\}$ are expanded as

$$A_m(\lambda, t) = A_m^{(0)} + A_m^{(1)}(t) + \lambda^2 A_m^{(2)}(t) + \ldots \tag{1.8}$$

and the IC (1.5) become

$$A_p^{(0)} = 0 = A_p^{(n)}(t_0) \qquad p \neq s;\ n = 1, 2, \ldots. \tag{1.9}$$

As a result, one finds that $a_s(\lambda, t)$ in (1.6) consists of a nonlinear phase term multiplied by a factor which takes care of normalisation of $\psi_s(\lambda, t)$. An analysis and some applications of this *rearranged* DM (RDM) have been presented by Langhoff *et al* (1972); they also considered a *second* rearranged version where only an overall phase factor is explicitly taken out of $\psi_s(\lambda, t)$. However, we shall see that such RDM have some serious limitations. A different kind of rearrangement (Bhattacharyya 1984) which corresponds really to employing *undetermined phases* within the DM (to be termed henceforth the UPDM) proceeds, instead of (1.1), with the choice

$$\psi_s(\lambda, t) = \sum_m b_m(\lambda, t)\phi_m \exp(-\mathrm{i}\alpha_m t). \tag{1.10}$$

A perturbative development then follows by writing

$$b_m(\lambda, t) = b_m^{(0)} + \lambda b_m^{(1)}(t) + \lambda^2 b_m^{(2)}(t) + \ldots \tag{1.11}$$

and

$$\alpha_m = \omega_m + \lambda\alpha_m^{(1)} + \lambda^2\alpha_m^{(2)} + \ldots; \tag{1.12}$$

here the IC are similar to (1.5): $b_s^{(0)} = 1$, $b_p^{(0)}(p \neq s) = 0$, $b_m^{(n)}(t_0) = 0$ ($m = s, p, \ldots; n = 1, 2, \ldots$). The undetermined $\{\alpha_m^{(n)}\}$ are evaluated by requiring the absence of any divergent term in $\{b_m^{(n)}(t)\}$ at each order of perturbation. This UPDM can treat successfully a number of problems; but it fails, for example, to deal with the case of an adiabatically switched-on harmonic perturbation. Hence, it appears logical and interesting to study the form

$$\psi_s(\lambda, t) = b_s(\lambda, t) \exp(-\mathrm{i}\alpha_s t)\left(\phi_s + \sum_{m \neq s} B_m(\lambda, t)\phi_m \exp(\mathrm{i}\alpha_{sm} t)\right)$$

$$= b_s(\lambda, t) \exp(-\mathrm{i}\alpha_s t)\bar{\chi}_s(\lambda, t), \tag{1.13}$$

with $\alpha_{sm} = \alpha_s - \alpha_m$, $B_m(\lambda, t) = b_m(\lambda, t)/b_s(\lambda, t)$, which bears the same relation to (1.10) as (1.6) does to (1.1). Once again, here, we accordingly use the expansion

$$B_m(\lambda, t) = B_m^{(0)} + \lambda B_m^{(1)}(t) + \lambda^2 B_m^{(2)}(t) + \ldots \tag{1.14}$$

and the IC

$$B_p^{(0)} = 0 = B_p^{(n)}(t_0); \qquad p \neq s;\ n = 1, 2, \ldots. \tag{1.15}$$

We shall call it the *rearranged* UPDM (RUPDM).

The aim of the present work is to investigate the workability of the various variants of the DM stated above; specifically, we shall study in detail the performances of the RDM and the RUPDM. As regards the perturbation problems, we shall consider the more important static and harmonic cases (switched on instantaneously and adiabatically), given by

$$V(t) = V, \tag{1.16}$$

$$V(t) = V\,\mathrm{e}^{\mathrm{i}\omega t} + V^{+}\,\mathrm{e}^{-\mathrm{i}\omega t}, \tag{1.17}$$

$$V(t) = f(t)V \tag{1.18}$$

and

$$V(t) = f(t)(V\,\mathrm{e}^{\mathrm{i}\omega t} + V^{+}\,\mathrm{e}^{-\mathrm{i}\omega t}). \tag{1.19}$$

Here $f(t)$ is an appropriate 'switching' function required to develop the perturbations (from $t = t_0$, $f(t_0) = 0$) over an infinite time interval to the 'full' values, and hence satisfies

$$\mathrm{d}f(t)/\mathrm{d}t \to 0. \tag{1.20}$$

Indeed, of these, perturbations like (1.18) and (1.19) which are developed *adiabatically* have special appeal. Thus, whereas (1.18) is intended to investigate the existence of a quantum adiabatic theorem (Messiah 1961, Todorov 1981) and hence to establish a correspondence between time-independent and time-dependent perturbation theories, the 'steady-state' response of a system to harmonic perturbations is studied through (1.19) for various properties of interest (Dalgarno 1966, Epstein 1969, Young *et al* 1969, Langhoff *et al* 1972). It may be mentioned here that a variety of switching functions can be employed in this context (see below). So, we feel obliged to study them separately in order to examine if there is any inconvenient form or whether all of them furnish equivalent results (see, e.g., Todorov (1981) for a discussion). The interest behind studying the form (1.16) lies, among others, in analysing the long-time behaviour of coherent states (Krivoshlykov *et al* 1982, Brickmann 1983), etc; study of the periodic perturbation (1.17) has also drawn considerable attention in various contexts (Hogg and Huberman 1982, 1983, Yajima 1984). From our scrutiny, it turns out that in fact all the procedures mentioned above have some kind of limitations regarding either the applicability to some particular perturbation $V(t)$ or the ability to tackle some specific form of $f(t)$. So, some remarks on this point are made and a more general scheme is sought.

The paper is organised as follows. Section 2 presents the structure and applications of the RDM. Section 3 deals with the strategy and workability of the RUPDM. Section 4 discusses some more important aspects of all the rearrangements with a view to framing a very general and convenient perturbation scheme. Section 5, finally, summarises the conclusions of the present analysis.

## 2. Rearrangements of the Dirac method

It may be easily seen (see, e.g., Bhattacharyya 1984) that if (1.1) is used in (1.2), with (1.4) and (1.5) to obtain $\{a_m(\lambda, t)\}$, terms appear in $\{a_m^{(n)}(t)\}$ having $t^p$ dependence ($p \geqslant 1$) for either of the perturbations (1.16) and (1.17); here one chooses $t_0 = 0$ and finally finds the long-time behaviour becomes difficult to interpret. For adiabatic perturbations also, the trouble of divergence appears if $f(t)$ is chosen in the form of $\exp(\eta t)$ and finally the limit $\eta \to 0_+$ is taken (Bhattacharyya 1984); another serious difficulty in this context is concerned with the use of non-exponential $f(t)$ leading to the emergence of non-adiabatic terms (Todorov 1981). Hence, we wish to examine here the usefulness of the RDM in detail.

### *2.1. Theory*

Let us note that, if (1.6) is put in (1.2), we obtain

$$\mathrm{i}\hbar a_s \partial\chi_s/\partial t = \{[H(\lambda, t) - \hbar\omega_s]a_s - \mathrm{i}\hbar\partial a_s/\partial t\}\chi_s \tag{2.1}$$

and dividing (2.1) by $a_s$ throughout, we then find

$$\mathrm{i}\hbar\partial\chi_s/\partial t = [H(\lambda, t) - \hbar\omega_s - \mathrm{i}\hbar\partial \ln a_s/\partial t]\chi_s, \tag{2.2}$$

where, for convenience, the $\lambda$ and $t$ dependences of $\chi_s$ and $a_s$ are suppressed. The $\phi_s$ projection part of this equation gives

$$\mathrm{i}\hbar\partial \ln a_s/\partial t = \lambda\langle\phi_s|V(t)|\chi_s\rangle = \lambda\Delta E_s(\lambda, t) \qquad \text{(say)}. \tag{2.3}$$

We now integrate (2.3), noting from (1.5) that $a_s(t_0) = 1$, and write $\Delta E_s(\lambda, t) = \mathrm{Re}\,\Delta E_s(\lambda, t) + \mathrm{i}\,\mathrm{Im}\,\Delta E_s(\lambda, t)$ to arrive at the following expression for $a_s$:

$$a_s(\lambda, t) = \exp\left(-\frac{\mathrm{i}\lambda}{\hbar}\int_{t_0}^{t} \mathrm{Re}\,\Delta E_s(\lambda, t')\,\mathrm{d}t'\right)\exp\left(\frac{\lambda}{\hbar}\int_{t_0}^{t} \mathrm{Im}\,\Delta E_s(\lambda, t')\,\mathrm{d}t'\right). \tag{2.4}$$

We may remark that the first part of (2.4) does not have any observable consequence for ultimately only expectation values with respect to $\psi_s(\lambda, t)$ concern us. To gain the significance of the last part of (2.4), we multiply (2.2) by $\chi_s^*$, integrate over coordinates and subtract from the resulting equation its complex conjugate form. This gives

$$\partial \ln\langle\chi_s|\chi_s\rangle/\partial t = (-2\lambda/\hbar)\,\mathrm{Im}\,\Delta E_s(\lambda, t). \tag{2.5}$$

A second integration of (2.5), now over the time, shows

$$\exp\left(\frac{\lambda}{\hbar}\int_{t_0}^{t} \mathrm{Im}\,\Delta E_s(\lambda, t')\,\mathrm{d}t'\right) = \langle\chi_s|\chi_s\rangle^{-1/2}, \tag{2.6}$$

implying that this part of $a_s$ preserves norm of $\psi_s(\lambda, t)$. The determining equation for $\chi_s$ (which, in turn, means evaluation of $\{A_p(\lambda, t)\}$ in (1.7)) is given by (2.2) and (2.3).

The $\phi_k$ projection part of (2.2), with (2.3), leads to the actual working form:

$$\mathrm{i}\hbar\partial A_k/\partial t = \lambda V^t_{ks}\exp(\mathrm{i}\omega_{ks}t) - \lambda A_k V^t_{ss} + \lambda \sum_{m\neq s} A_m V^t_{km}\exp(\mathrm{i}\omega_{km}t)$$
$$- \lambda A_k \sum_{m\neq s} A_m V^t_{sm}\exp(\mathrm{i}\omega_{sm}t), \tag{2.7}$$

where $V^t_{ij} = \langle\phi_i|V(t)|\phi_j\rangle$ and $A_m \equiv A_m(\lambda, t)$. The perturbative procedure then follows by employing (1.8) in (2.7), with subsequent use of the IC (1.9) to solve the differential equations for $A^{(n)}_k(t)$ $(n = 1, 2, \ldots)$. Notably, from (1.6) and (2.4), one finds that $\psi_s(\lambda, t)$ takes the form

$$\psi_s(\lambda, t) = \exp\left[-\mathrm{i}\left(\omega_s t + \lambda\int_{t_0}^{t}\mathrm{Re}\,\Delta E_s(\lambda, t')\,\mathrm{d}t'/\hbar\right)\right]$$
$$\times\exp\left(\lambda\int_{t_0}^{t}\mathrm{Im}\,\Delta E_s(\lambda, t')\,\mathrm{d}t'/\hbar\right)\chi_s, \tag{2.8}$$

which can equivalently be written as

$$\psi_s(\lambda, t) = \exp\left[-\mathrm{i}\left(\omega_s t + \lambda\int_{t_0}^{t}\mathrm{Re}\,\Delta E_s(\lambda, t')\,\mathrm{d}t'/\hbar\right)\right]\chi_s\langle\chi_s|\chi_s\rangle^{-1/2} \tag{2.9}$$

making use of (2.6); $\Delta E_s(\lambda, t)$ is defined by (2.3).

The implication of (2.9) naturally motivates investigation of the usefulness of another kind of RDM proposed by Langhoff *et al* (1972) where the choice

$$\psi_s(\lambda, t) = \exp\left[-\mathrm{i}\left(\omega_s t + \lambda\int_{t_0}^{t}\Delta\varepsilon_s(\lambda, t')\,\mathrm{d}t'/\hbar\right)\right]\theta_s(\lambda, t), \qquad \|\theta_s(\lambda, t)\| = 1, \tag{2.10}$$

is made, with real $\Delta\varepsilon_s(\lambda, t)$ to ensure extraction of *only* an overall phase factor from $\psi_s(\lambda, t)$. Employing (2.10) in (1.2), we obtain

$$\mathrm{i}\hbar\partial\theta_s/\partial t = [H(\lambda, t) - \hbar\omega_s - \lambda\Delta\varepsilon_s(\lambda, t)]\theta_s, \tag{2.11}$$

where $\theta_s \equiv \theta_s(\lambda, t)$. The $\phi_s$ projection part of this equation gives

$$\Delta\varepsilon_s(\lambda, t) = (\langle\phi_s|V(t)|\theta_s\rangle - \mathrm{i}\hbar\langle\phi_s|\partial\theta_s/\partial t\rangle/\lambda)\langle\phi_s|\theta_s\rangle^{-1} \tag{2.12}$$

Since $\theta_s$ should obviously have the form

$$\theta_s(\lambda, t) = c_s\phi_s + \sum_{m\neq s} c_m\phi_m\exp(\mathrm{i}\omega_{sm}t), \tag{2.13}$$

we put (2.12) and (2.13) in (2.11) to find from the $\phi_k$ projection part the following

$$\mathrm{i}\hbar\partial c_k/\partial t = \lambda c_s V^t_{ks}\exp(\mathrm{i}\omega_{ks}t) + \lambda\sum_{m\neq s} c_m V^t_{km}\exp(\mathrm{i}\omega_{km}t)$$
$$- \lambda c_k\left[V^t_{ss} + \sum_{m\neq s} c_m V^t_{sm}\exp(\mathrm{i}\omega_{sm}t)\left(c_s - \frac{\mathrm{i}\hbar}{\lambda}\frac{\partial\ln c_s}{\partial t}\right)^{-1}\right] \tag{2.14}$$

as the working equation, where $c_p \equiv c_p(\lambda, t)$; $p = m, s, \ldots$. But here we find a difficulty; although (2.14) contains $c_s$, there is no determining equation for it. So, to proceed, we *have to* divide (2.14) throughout by $c_s$ which gives

$$i\hbar\partial C_k/\partial t = \lambda V'_{ks}\exp(i\omega_{ks}t) + \lambda \sum_{m\neq s} C_m V'_{km}\exp(i\omega_{km}t) - \lambda C_k V'_{ss}$$
$$-\lambda C_k \sum_{m\neq s} C_m V'_{sm}\exp(i\omega_{sm}t) \qquad C_k = c_k/c_s,\ k\neq s, \tag{2.15}$$

and $C_k \equiv C_k(\lambda, t)$. Clearly, (2.15) is of the same form as (2.7). Hence, in practice, this second RDM affords *no new route*; one has to follow the first procedure to get $\{C_k\}$ and then rearrange the results accordingly; $|c_s|$ is to be evaluated, understandably, from the normalisation condition. Also, the rearrangement just stated has been found to be somewhat inconvenient (Langhoff *et al* 1972).

### *2.2. Applications*

Guided by the above analysis, we shall now consider the workability of the RDM mentioned *first*. The reason is, if there appears any difficulty with the first form, it will continue to remain in the second form also; moreover, this latter procedure is not as compact as the former one (see, e.g., Langhoff *et al* 1972). So, we proceed with (2.7), making use of (1.8) and (1.9), to obtain the relevant quantities.

*2.2.1.* We first consider the perturbations (1.16) and (1.17). With the choice $t_0 = 0$, we obtain the following results for $V(t) = V$:

$$A_k^{(1)}(t) = -\frac{V_{ks}}{\hbar\omega_{ks}}[\exp(i\omega_{ks}t) - 1], \tag{2.16}$$

$$A_k^{(2)}(t) = \left(\sum_{m\neq s}\frac{V_{km}V_{ms}}{\hbar\omega_{ms}} - \frac{V_{ks}V_{ss}}{\hbar\omega_{ks}}\right)\frac{\exp(i\omega_{ks}t) - 1}{\hbar\omega_{ks}}$$
$$-\sum_{m\neq k,s}\frac{V_{km}V_{ms}}{\hbar^2\omega_{km}\omega_{ms}}[\exp(i\omega_{km}t) - 1] + \frac{V_{ks}(V_{kk} - V_{ss})}{i\hbar^2\omega_{ks}}t \tag{2.17}$$

etc. Clearly, the presence of secular terms (e.g., the last term of (2.17)) from $A_k^{(2)}(t)$ onwards indicates that this rearrangement is *not* useful. Such a conclusion is actually not quite unexpected if we remember that, in this case, perturbative solution free from secular terms is obtained through the use of the UPDM (Bhattacharyya 1984) where $\alpha_m \neq \omega_m$ ($m = s, p, \ldots$) and that this flexibility is absent in the RDM. For the oscillatory perturbation (1.17), it is evident that a similar conclusion will follow. Another objection against the applicability of this procedure to the cases (1.16) and (1.17) is that the assumption required to obtain (2.2) from (2.1),

$$a_s(\lambda, t) \neq 0 \tag{2.18}$$

for *any* $t$ at some fixed value of $\lambda$, is difficult to justify; in other words, it is not at all apparent why $\|\chi_s\|$ should always be finite. This may actually lead to some trouble of convergence. We shall discuss more about this point later.

*2.2.2.* For the perturbation (1.18), we now consider the usually prescribed (Epstein 1969, Todorov 1981) form for $f(t)$ which is given by

$$\begin{aligned} f(t) &= e^{\eta t}, \qquad t_0 = -\infty < t \leqslant 0,\ \eta > 0, \\ f(t) &= 1, \qquad t \geqslant 0 \end{aligned} \tag{2.19}$$

and, at the end, the limit $\eta \to 0_+$ is put. With such a function, we find in the adiabatic limit ($\eta \to 0_+$)

$$\lim_{\eta\to 0_+} A_k^{(1)}(t) = -\frac{V_{ks}}{\hbar\omega_{ks}}\exp(\mathrm{i}\omega_{ks}t), \tag{2.20}$$

$$\lim_{\eta\to 0_+} A_k^{(2)}(t) = \left(\sum_{m\neq s}\frac{V_{km}V_{ms}}{\hbar^2\omega_{ms}\omega_{ks}} - \frac{V_{ks}V_{ss}}{\hbar^2\omega_{ks}^2}\right)\exp(\mathrm{i}\omega_{ks}t) + \frac{V_{ks}}{\hbar^2\omega_{ks}^2}(V_{ss}-V_{kk}), \tag{2.21}$$

etc. Hence, $\chi_s(\lambda, t)$ in (1.7) takes the form

$$\lim_{\eta\to 0_+}\chi_s(\lambda,t) = \phi_s + \lambda\sum_{m\neq s}\frac{V_{ms}}{\hbar\omega_{sm}}\phi_m + \lambda^2\sum_{m\neq s}\left(\sum_{n\neq s}\frac{V_{mn}V_{ns}}{\hbar^2\omega_{ms}\omega_{ns}} - \frac{V_{ms}V_{ss}}{\hbar^2\omega_{ms}^2}\right)\phi_m$$
$$+\lambda^2\sum_{m\neq s}\frac{V_{ms}}{\hbar^2\omega_{ms}^2}(V_{ss}-V_{mm})\phi_m\exp(\mathrm{i}\omega_{sm}t) + \mathrm{O}(\lambda^3). \tag{2.22}$$

Let us recall at this point the implication of quantum adiabaticity. What we expect for the perturbation (1.18) is that expectation values like $\langle\psi_s(\lambda,t)|W|\psi_s(\lambda,t)\rangle$, $\|\psi_s(\lambda,t)\|=1$, after the required infinite time interval, should agree with $\langle\bar{\psi}_s|W|\bar{\psi}_s\rangle$, $\|\bar{\psi}_s\|=1$, where $W$ stands for any Hermitian operator corresponding to some observable and $\bar{\psi}_s \equiv \bar{\psi}_s(\lambda)$ satisfies

$$(H_0+\lambda V)\bar{\psi}_s(\lambda) = E_s\bar{\psi}_s(\lambda), \tag{2.23}$$

with the subscript referring to the initial state $\phi_s$ from which the system has been allowed to evolve. In our present context, therefore, we are to show

$$\lim_{\eta\to 0_+}\chi_s(\lambda,t) = \bar{\bar{\psi}}_s(\lambda), \tag{2.24}$$

and then

$$\lim_{\eta\to 0_+}\exp\left(\lambda\int_{t_0}^{t}\mathrm{Im}\langle\phi_s|V(t')|\chi_s(\lambda,t')\rangle\,\mathrm{d}t'/\hbar\right) = \langle\bar{\bar{\psi}}_s|\bar{\bar{\psi}}_s\rangle^{-1/2} \tag{2.25}$$

where $\bar{\bar{\psi}}_s(\lambda)\equiv\bar{\bar{\psi}}_s$ also obeys (2.23), satisfying the 'intermediate' normalisation condition ($\langle\phi_s|\bar{\bar{\psi}}_s\rangle = 1$) like $\chi_s(\lambda, t)$. But, comparing (2.22) with the Rayleigh–Schrödinger (RS) perturbative result for $\bar{\bar{\psi}}_s$ to second order, it is easily seen that (2.24) fails to hold. In fact, this failure is due to the second term (time independent) at the right-hand side of (2.21) and precisely such a type of term has been called 'non-adiabatic' by Todorov (1981). More important, however, is to notice that the normalisation requirement, (2.25), *also* ceases to be obeyed. We find

$$\mathrm{Im}\langle\phi_s|V(t')|\chi_s(\lambda,t')\rangle$$
$$=\lambda\sum_{m\neq s}V_{ms}V_{sm}\left[\left(\frac{1}{\hbar\omega_{ms}} - \frac{\omega_{ms}}{\hbar(\omega_{ms}^2+\eta^2)}\right)f(t')\sin\omega_{sm}t'\right.$$
$$\left. - \frac{\eta}{\hbar(\omega_{ms}^2+\eta^2)}f(t')\cos\omega_{sm}t'\right] + \mathrm{O}(\lambda^2) \tag{2.26}$$

which, after integration in accordance with (2.19), shows that its first-order contribution vanishes in the limit $\eta\to 0_+$. Hence, the left-hand side of (2.25) gives no $\lambda^2$ term; whereas, at the right-hand part of (2.25), a term of $\mathrm{O}(\lambda^2)$ definitely exists (note that, to first order, $\lim_{\eta\to 0_+}\chi_s(\lambda,t) = \bar{\bar{\psi}}_s$). This second observation, we think, is rather surprising in view of the way we arrived at (2.6). Perhaps, the reason behind such a contradiction lies in using the form (2.19) for $f(t)$. In our opinion, (2.19) is somewhat inappropriate in defining adiabaticity because, as long as $\eta \neq 0$, the time $t=0$ has a meaning, but this 'zero' of time loses significance when the adiabatic limit $\eta \to 0_+$ is put. In other words, here the notion of adiabaticity is incompatible with the specification of some $t=0$. So, in what follows, we shall not consider this particular switching function. Instead, as we remarked elsewhere (Bhattacharyya 1984), the form

$$f(t)=e^{\eta t}, \qquad t_0=-\infty<t, \qquad \eta \to 0_+ \tag{2.27}$$

will be used, and we shall actually demonstrate its adequacy.

*2.2.3.* We now consider the function

$$f(t)=t/T, \qquad t_0=0<t, \tag{2.28}$$

once again for the case (1.18), where finally the limits $T\to\infty$, $t/T\to 1$ are to be taken. This type ($t^n/T^n$, $n\geq 1$) of switching functions is known to lead to non-adiabatic terms in the DM (Todorov 1981). The present formulation (RDM) also, in fact, cannot avoid the appearance of such terms. For example, we obtain here the following results:

$$\lim_{\substack{T\to\infty \\ t/T\to 1}} A_k^{(1)}(t) = -\frac{V_{ks}}{\hbar\omega_{ks}}\exp(\mathrm{i}\omega_{ks}t), \tag{2.29}$$

$$\lim_{\substack{T\to\infty \\ t/T\to 1}} A_k^{(2)}(t) = \left(\sum_{m\neq s}\frac{V_{km}V_{ms}}{\omega_{ms}}-\frac{V_{ks}V_{ss}}{\omega_{ks}}\right)\frac{\exp(\mathrm{i}\omega_{ks}t)}{\hbar^2\omega_{ks}}+\frac{V_{ks}}{2\hbar^2\omega_{ks}^2}(V_{kk}-V_{ss}), \tag{2.30}$$

etc. Evidently, just like the previous case, we have a non-adiabatic term in $A_k^{(2)}(t)$ (the last term at the right-hand side of (2.30)) in the adiabatic limit. On the other hand, from the expression

$$A_k^{(1)}(t) = -\frac{V_{ks}}{\hbar T\omega_{ks}}\left(t\exp(\mathrm{i}\omega_{ks}t)-\frac{\exp(\mathrm{i}\omega_{ks}t)-1}{\mathrm{i}\omega_{ks}}\right), \tag{2.31}$$

we find that

$$\mathrm{Im}\langle\phi_s|V(t')|\chi_s(\lambda,t')\rangle = -\lambda\sum_{m\neq s}\frac{V_{ms}V_{sm}}{\hbar T^2\omega_{ms}^2}t'(1-\cos\omega_{sm}t')+\mathrm{O}(\lambda^2) \tag{2.32}$$

and this result, on integration, gives us the left-hand side of (2.25)

$$\exp\left(-\lambda^2\sum_{m\neq s}\frac{V_{ms}V_{sm}}{2\hbar^2\omega_{ms}^2}+\mathrm{O}(\lambda^3)\right). \tag{2.33}$$

The agreement between (2.33) and the right-hand side of (2.25) to $\mathrm{O}(\lambda^2)$ is now apparent from (2.29). Thus, we may conclude that this second case is not as severe as the first one. Indeed, we shall see that the difficulty with the non-adiabatic terms for the $f(t)$ defined by (2.28) *can* be bypassed in the RUPDM.

*2.2.4.* With the results of the above scrutiny in mind, let us now proceed with the form (2.27) for $f(t)$. In this case, we find for the perturbation (1.18), unlike (2.22), the following form for $\chi_s(\lambda, t)$ in the adiabatic limit:

$$\lim_{\eta\to 0_+} \chi_s(\lambda, t) = \phi_s + \lambda \sum_{m\neq s} \frac{V_{ms}}{\hbar\omega_{sm}} \phi_m + \lambda^2 \sum_{m\neq s} \left( \sum_{n\neq s} \frac{V_{mn}V_{ns}}{\hbar^2\omega_{ms}\omega_{ns}} - \frac{V_{ms}V_{ss}}{\hbar^2\omega_{ms}^2} \right)\phi_m$$
$$+ \lambda^3 \sum_{m\neq s} \left( \frac{V_{ms}}{\hbar^2\omega_{ms}^2} \sum_{n\neq s} \frac{V_{sn}V_{ns}}{\hbar\omega_{ns}} - \frac{V_{ms}V_{ss}^2}{\hbar^3\omega_{ms}^3} + \frac{V_{ss}}{\hbar^2\omega_{ms}^2} \sum_{n\neq s} \frac{V_{mn}V_{ns}}{\hbar\omega_{ns}} \right.$$
$$\left. + \frac{V_{ss}}{\hbar\omega_{ms}} \sum_{n\neq s} \frac{V_{mn}V_{ns}}{\hbar^2\omega_{ns}^2} - \sum_{n,p\neq s} \frac{V_{mn}V_{np}V_{ps}}{\hbar^3\omega_{ms}\omega_{ns}\omega_{ps}} \right)\phi_m + \mathrm{O}(\lambda^4). \tag{2.34}$$

This is our desired result. We may well note that (2.34) can also be written as

$$\lim_{\eta\to 0_+} \chi_s(\lambda, t) = \phi_s + \lambda\phi_s^{(1)} + \lambda^2\phi_s^{(2)} + \lambda^3\phi_s^{(3)} + \mathrm{O}(\lambda^4)$$
$$= \bar{\bar{\psi}}_s + \mathrm{O}(\lambda^4) \tag{2.35}$$

where $\phi_s^{(i)}$ denotes the $i$th-order RS perturbation correction term (to $\phi_s$) for $\bar{\bar{\psi}}_s$ that obeys (2.23), with $\langle\phi_s|\bar{\bar{\psi}}_s\rangle = 1$. Thus, we see that (2.24) is verified to third order, and we expect that this equality will hold to all orders. It now remains only to check whether (2.25) is also obeyed. To proceed, we consider for simplicity that $V_{ij} = V_{ji}$ and find

$$\lim_{\eta\to 0_+} \langle\chi_s(\lambda, t)|\chi_s(\lambda, t)\rangle = \langle\bar{\bar{\psi}}_s|\bar{\bar{\psi}}_s\rangle = 1 + \lambda^2 \sum_{m\neq s} \frac{V_{ms}^2}{\hbar^2\omega_{ms}^2}$$
$$+ 2\lambda^3 \left( \sum_{m\neq s} \frac{V_{ms}^2 V_{ss}}{\hbar^3\omega_{ms}^3} - \sum_{m,n\neq s} \frac{V_{ms}V_{mn}V_{ns}}{\hbar^3\omega_{ms}^2\omega_{ns}} \right) + \mathrm{O}(\lambda^4); \tag{2.36}$$

whereas the $\mathrm{Im}\,\Delta E_s(\lambda, t)$ part becomes

$$\mathrm{Im}\langle\phi_s|V(t)|\chi_s(\lambda, t)\rangle = -\lambda \sum_{m\neq s} \frac{V_{ms}^2}{\hbar(\eta^2+\omega_{ms}^2)} \eta\, \mathrm{e}^{2\eta t} - \lambda^2 \sum_{m\neq s} \frac{V_{ms}\eta\, \mathrm{e}^{3\eta t}}{\hbar^2(4\eta^2+\omega_{ms}^2)}$$
$$\times \left( 3\omega_{ms} \frac{V_{ms}V_{ss}}{\eta^2+\omega_{ms}^2} - \sum_{n\neq s} (2\omega_{ns}+\omega_{ms}) \frac{V_{mn}V_{ns}}{\eta^2+\omega_{ns}^2} \right) + \mathrm{O}(\lambda^3) \tag{2.37}$$

which, on integration, gives the left-hand side of (2.25) under the adiabatic limit as

$$\exp\left[ -\frac{\lambda^2}{2\hbar^2} \sum_{m\neq s} \frac{V_{ms}^2}{\omega_{ms}^2} - \frac{\lambda^3}{\hbar^3} \sum_{m\neq s} \frac{V_{ms}}{\omega_{ms}^2} \left( \frac{V_{ms}V_{ss}}{\omega_{ms}} - \sum_{n\neq s} \frac{V_{mn}V_{ns}}{\omega_{ns}} \right) + \mathrm{O}(\lambda^4) \right]. \tag{2.38}$$

From (2.36) and (2.38), it is clear that (2.25) is satisfied up to the third order, and again we expect that this agreement will continue to hold to any order. So, we are now in a position to conclude that (2.27) *is* the proper adiabatic switching function, at least in so far as the success of the RDM is concerned. For the sake of completeness, however, it may be of some interest to evaluate the phase part of $\psi_s(\lambda, t)$, the exponential factor at the right-hand side of (2.9). Calculation shows that $\mathrm{Re}\,\Delta E_s(\lambda, t)$ is of the form

$$\mathrm{Re}\,\Delta E_s(\lambda, t) = V_{ss}\, \mathrm{e}^{\eta t} - \lambda \sum_{m\neq s} \frac{V_{ms}^2\omega_{ms}}{\hbar(\eta^2+\omega_{ms}^2)} \mathrm{e}^{2\eta t} + \lambda^2 \sum_{m\neq s} \frac{V_{ms}\, \mathrm{e}^{3\eta t}}{\hbar^2(4\eta^2+\omega_{ms}^2)}$$
$$\times \left( \frac{V_{ms}V_{ss}}{\eta^2+\omega_{ms}^2}(2\eta^2-\omega_{ms}^2) - \sum_{n\neq s} \frac{V_{mn}V_{ns}}{\eta^2+\omega_{ns}^2}(2\eta^2-\omega_{ms}\omega_{ns}) \right) + \mathrm{O}(\lambda^3). \tag{2.39}$$

Integrating (2.39) and taking subsequently the limit $\eta\to 0_+$, we find that the overall phase factor becomes

$$\exp[-i(\omega_s+\lambda\omega_s^{(1)}+\lambda^2\omega_s^{(2)}+\lambda^3\omega_s^{(3)}+O(\lambda^4))t]$$
$$\times\lim_{\eta\to 0_+}\exp\left[-i\left(\frac{\lambda}{\eta}\omega_s^{(1)}+\frac{\lambda^2}{2\eta}\omega_s^{(2)}+\frac{\lambda^3}{3\eta}\omega_s^{(3)}+O(\lambda^4)\right)\right] \tag{2.40}$$

where $\hbar\omega_s^{(i)}$ stands for the $i$th-order Rayleigh-Schrödinger (RS) perturbation correction term for $E_s$ in (2.23), i.e.,

$$E_s\equiv E_s(\lambda)=\hbar\omega_s+\lambda\hbar\omega_s^{(1)}+\lambda^2\hbar\omega_s^{(2)}+\dots; \tag{2.41}$$

understandably, the second exponential part in (2.40) accounts for the divergent phase.

*2.2.5.* Having established the suitability of (2.27) as the adiabatic switching function in the present context, we now consider the perturbation (1.19) and use (2.27). The coefficients in this case become

$$A_k^{(1)}(t)=\frac{1}{i\hbar}\left(\frac{V_{ks}\exp\{[i(\omega_{ks}+\omega)+\eta]t\}}{i(\omega_{ks}+\omega)+\eta}+\frac{V_{sk}^*\exp\{[i(\omega_{ks}-\omega)+\eta]t\}}{i(\omega_{ks}-\omega)+\eta}\right), \tag{2.42}$$

$$A_k^{(2)}(t)=\left(\frac{V_{ss}V_{ks}}{i(\omega_{ks}+\omega)+\eta}-\sum_{m\neq s}\frac{V_{km}V_{ms}}{i(\omega_{ms}+\omega)+\eta}\right)\frac{\exp\{[i(\omega_{ks}+2\omega)+2\eta]t\}}{\hbar^2[i(\omega_{ks}+2\omega)+2\eta]}$$
$$+\left(\frac{V_{ss}V_{sk}^*}{i(\omega_{ks}-\omega)+\eta}+\frac{V_{ss}^*V_{ks}}{i(\omega_{ks}+\omega)+\eta}-\sum_{m\neq s}\frac{V_{km}V_{sm}^*}{i(\omega_{ms}-\omega)+\eta}\right.$$
$$\left.-\sum_{m\neq s}\frac{V_{mk}^*V_{ms}}{i(\omega_{ms}+\omega)+\eta}\right)\frac{e^{(i\omega_{ks}+2\eta)t}}{\hbar^2(i\omega_{ks}+2\eta)}$$
$$+\left(\frac{V_{ss}^*V_{sk}^*}{i(\omega_{ks}-\omega)+\eta}-\sum_{m\neq s}\frac{V_{mk}^*V_{sm}^*}{i(\omega_{ms}-\omega)+\eta}\right)\frac{\exp\{[i(\omega_{ks}-2\omega)+2\eta]t\}}{\hbar^2[i(\omega_{ks}-2\omega)+2\eta]}, \tag{2.43}$$

etc. So, in the adiabatic limit, $\chi_s(\lambda, t)$ takes the form

$$\lim_{\eta\to 0_+}\chi_s(\lambda,t)=\phi_s-\frac{\lambda}{\hbar}\sum_{m\neq s}\left(\frac{V_{ms}}{\omega_{ms}+\omega}e^{i\omega t}+\frac{V_{sm}^*}{\omega_{ms}-\omega}e^{-i\omega t}\right)\phi_m$$
$$+\frac{\lambda^2}{\hbar^2}\sum_{m\neq s}\left[\left(\sum_{n\neq s}\frac{V_{mn}V_{ns}}{\omega_{ns}+\omega}-\frac{V_{ss}V_{ms}}{\omega_{ms}+\omega}\right)\frac{e^{2i\omega t}}{\omega_{ms}+2\omega}\right.$$
$$+\left(\sum_{n\neq s}\frac{V_{mn}V_{sn}^*}{\omega_{ns}-\omega}-\frac{V_{ss}V_{sm}^*}{\omega_{ms}-\omega}+\sum_{n\neq s}\frac{V_{nm}^*V_{ns}}{\omega_{ns}+\omega}-\frac{V_{ss}^*V_{ms}}{\omega_{ms}+\omega}\right)\frac{1}{\omega_{ms}}$$
$$\left.+\left(\sum_{n\neq s}\frac{V_{nm}^*V_{sn}^*}{\omega_{ns}-\omega}-\frac{V_{ss}^*V_{sm}^*}{\omega_{ms}-\omega}\right)\frac{e^{-2i\omega t}}{\omega_{ms}-2\omega}\right]\phi_m+O(\lambda^3). \tag{2.44}$$

Notably, putting $\omega=0$, with $V^\dagger=V$, we get back the results for the static case $2f(t)V$. Of importance is to see now the form of $a_s(\lambda, t)$ given by (2.4). Again, for simplicity, we choose $V^\dagger=V$ and $V_{ij}=V_{ji}$, and then find

$$\lim_{\eta\to 0_+}\exp\left(-\frac{i\lambda}{\hbar}\int_{-\infty}^{t}\mathrm{Re}\,\Delta E_s(\lambda,t')\,dt'\right)$$
$$=\lim_{\eta\to 0_+}\exp\left\{\left(-\frac{i\lambda}{\hbar}\right)\left[2V_{ss}\frac{\sin\omega t}{\omega}-\lambda\sum_{m\neq s}\frac{V_{ms}^2\omega_{ms}}{\hbar(\omega_{ms}^2-\omega^2)}\right.\right.$$

$$\times\left(\frac{\sin 2\omega t}{\omega}+\frac{1}{\eta}+2t\right)+O(\lambda^2)\Bigg]\Bigg\} \tag{2.45}$$

corresponding to the first exponential part of (2.4), and

$$\lim_{\eta\to 0_+} \exp\left(\frac{\lambda}{\hbar}\int_{-\infty}^{t} \operatorname{Im} \Delta E_s(\lambda, t')\,\mathrm{d}t'\right)$$
$$=\exp\left[-\lambda^2 \sum_{m\neq s} \frac{V_{ms}^2}{\hbar^2}\left(\frac{1}{2(\omega_{ms}+\omega)^2}+\frac{1}{2(\omega_{ms}-\omega)^2}+\frac{\cos 2\omega t}{\omega_{ms}^2-\omega^2}\right)+O(\lambda^3)\right] \tag{2.46}$$

which agrees with the right-hand side of (2.6) to $O(\lambda^2)$, we have checked. Also, secular terms do not appear to invalidate this procedure. However, it is not quite clear whether the condition (2.18) is satisfied throughout in this case.

### *2.3. Summary*

We summarise our findings of this section as follows.

(i) The second kind of RDM does not have any practical advantage; so, we shall henceforth consider the first kind only.

(ii) The RDM does not successfully work for the perturbations (1.16) and (1.17) because of the appearance of secular terms.

(iii) The form (2.19) for $f(t)$ does not appear to be appropriate; we shall not use it afterwards.

(iv) The procedure concerned fails to efficiently handle the form (2.28) for $f(t)$ in the course of dealing with (1.18); a similar conclusion hence follows for the case (1.19).

(v) For the perturbation (1.18), with $f(t)$ given by (2.27), results show that the RDM is not useful if $\phi_s$ is degenerate (i.e., when some $\omega_{sr}=0$).

(vi) From the results for the perturbation (1.19) with the switching function (2.27), we find that this scheme again ceases to work either when there is an initial degeneracy (see, e.g., the $O(\lambda^2)$ term in (2.44)) or when a resonant oscillatory field ($n\omega = \pm\omega_{rs}$; $n = 1, 2, \ldots$) acts.

## 3. Rearrangement of the Dirac method with undetermined phase

We have mentioned in § 1 that the UPDM (Bhattacharyya 1984) works in a number of cases. But, whereas for perturbations like (1.16) and (1.17) the method applies directly, one has to proceed through some *indirect* route to treat the adiabatic case (1.18), and moreover the method apparently shows difficulty in handling a problem like (1.19). So, here we wish to study the RUPDM for which $\psi_s(\lambda, t)$ is given by (1.13); the procedure will turn out to be of value, as we shall see just now, in dealing with some important problems which the RDM fails to tackle.

### *3.1. Theory*

To proceed, let us first have a glance at the basic structure of the RUPDM. Following the earlier development ((2.1)–(2.9)), we put (1.13) in (1.2) and divide the result throughout by $b_s(\lambda, t)$ to obtain

$$\mathrm{i}\hbar\partial\bar{\chi}_s/\partial t = [H(\lambda, t) - \hbar\alpha_s - \mathrm{i}\hbar\partial \ln b_s/\partial t]\bar{\chi}_s, \tag{3.1}$$

where again $\bar{\chi}_s \equiv \bar{\chi}_s(\lambda, t)$, $b_s \equiv b_s(\lambda, t)$. Clearly, implicit here is the assumption that

$$b_s(\lambda, t) \neq 0. \tag{3.2}$$

The $\phi_s$ projection part of (3.1) leads to

$$b_s(\lambda, t) = \exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} F_s(\lambda, t')\,\mathrm{d}t'\right) \tag{3.3}$$

after integration, which can be rewritten as

$$b_s = \exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} \mathrm{Re}\, F_s(\lambda, t')\,\mathrm{d}t'\right)\exp\left(\int_{t_0}^{t} \mathrm{Im}\, F_s(\lambda, t')\,\mathrm{d}t'/\hbar\right), \tag{3.4}$$

where

$$F_s(\lambda, t) = \langle\phi_s|H(\lambda, t)|\bar{\chi}_s\rangle - \hbar\alpha_s. \tag{3.5}$$

From (3.1) and (3.3), it is easy to see that

$$\exp\left(\int_{t_0}^{t} \mathrm{Im}\, F_s(\lambda, t')\,\mathrm{d}t'/\hbar\right) = \langle\bar{\chi}_s|\bar{\chi}_s\rangle^{-1/2} \tag{3.6}$$

like the previous result (2.6); we also note that (3.1) takes the form

$$\mathrm{i}\hbar\partial\bar{\chi}_s/\partial t = [H(\lambda, t) - \langle\phi_s|H(\lambda, t)|\bar{\chi}_s\rangle]\bar{\chi}_s \tag{3.7}$$

and the $\phi_k$ projection part of this equation gives

$$\mathrm{i}\hbar\partial B_k/\partial t = B_k(\hbar\omega_{ks} - \hbar\alpha_{ks}) + \lambda V_{ks}^t \exp(\mathrm{i}\alpha_{ks}t) - \lambda B_k V_{ss}^t + \lambda \sum_{m\neq s} B_m V_{km}^t \exp(\mathrm{i}\alpha_{km}t) - \lambda B_k \sum_{m\neq s} B_m V_{sm}^t \exp(\mathrm{i}\alpha_{sm}t) \tag{3.8}$$

with $B_k \equiv B_k(\lambda, t) = b_k(\lambda, t)/b_s(\lambda, t)$, which is actually the working equation. For a perturbative procedure to develop, we only need additionally (1.12), (1.14) and (1.15); then, the resulting set of perturbation equations are solved order-by-order.

### 3.2. Applications

It is clear from (3.8) that the RUPDM reduces to the RDM for the choice $\alpha_p = \omega_p$. But, we shall here use (1.12) and, for convenience, deliberately suppress the $\lambda$ dependence of $\alpha_{mn}$ in $\exp(\mathrm{i}\alpha_{mn}t)$ (Bhattacharyya 1984) to evaluate the undetermined $\{\alpha_{ms}^{(n)}\}$. Thus, our scheme resembles the stationary Brillouin–Wigner (BW) perturbation theory (see, e.g., Bhattacharyya 1982) in some sense. The strategy will be more transparent as we treat below specific problems.

*3.2.1.* We first consider the perturbation (1.18), with (2.28), to immediately see the usefulness of the RUPDM. From the first-order equation

$$\mathrm{i}\hbar\partial B_k^{(1)}(t)/\partial t = V_{ks}^t \exp(\mathrm{i}\alpha_{ks}t) \tag{3.9}$$

we find that

$$B_k^{(1)}(t) = -\frac{V_{ks}}{\hbar\alpha_{ks}T}\left(t\exp(\mathrm{i}\alpha_{ks}t) - \mathrm{i}\,\frac{\exp(\mathrm{i}\alpha_{ks}t) - 1}{\alpha_{ks}}\right) \tag{3.10}$$

which shows, in the adiabatic limit we have

$$\lim_{\substack{T\to\infty \\ t/T\to 1}} B_k^{(1)}(t) = -\frac{V_{ks}}{\hbar\alpha_{ks}}\exp(\mathrm{i}\alpha_{ks}t). \tag{3.11}$$

The second-order equation

$$\mathrm{i}\hbar\partial B_k^{(2)}(t)/\partial t = -B_k^{(1)}(t)\hbar\alpha_{ks}^{(1)} - B_k^{(1)}(t)V'_{ss} + \sum_{m\neq s} B_m^{(1)}(t)V'_{km}\exp(\mathrm{i}\alpha_{km}t) \tag{3.12}$$

then gives

$$\begin{aligned} B_k^{(2)}(t) = &-\frac{\hbar\alpha_{ks}^{(1)}V_{ks}}{\hbar^2\alpha_{ks}^2 T}\left(2\mathrm{i}\frac{\exp(\mathrm{i}\alpha_{ks}t)-1}{\alpha_{ks}} + t\exp(\mathrm{i}\alpha_{ks}t)\right) + \frac{V_{ss}V_{ks}}{\hbar^2\alpha_{ks}^2T^2}\left(3\frac{\exp(\mathrm{i}\alpha_{ks}t)-1}{\alpha_{ks}^2}\right. \\ &\left. -3\mathrm{i}t\frac{\exp(\mathrm{i}\alpha_{ks}t)}{\alpha_{ks}} - t^2\exp(\mathrm{i}\alpha_{ks}t)\right) - \sum_{m\neq s}\frac{V_{km}V_{ms}}{\hbar^2\alpha_{ks}\alpha_{ms}T^2}\left[\left(\frac{2}{\alpha_{ks}}+\frac{1}{\alpha_{ms}}\right)\right. \\ &\left.\times\left(\frac{\exp(\mathrm{i}\alpha_{ks}t)-1}{\alpha_{ks}} - \mathrm{i}t\exp(\mathrm{i}\alpha_{ks}t)\right) - t^2\exp(\mathrm{i}\alpha_{ks}t)\right] \\ &+\sum_{m\neq k,s}\frac{V_{km}V_{ms}}{\hbar^2\alpha_{ms}^2\alpha_{km}T^2}\left(\frac{\exp(\mathrm{i}\alpha_{km}t)-1}{\alpha_{km}} - \mathrm{i}t\exp(\mathrm{i}\alpha_{km}t)\right) \\ &+\frac{V_{ks}t}{\hbar^2\alpha_{ks}^2T}\left(\frac{V_{kk}-V_{ss}}{2T}t - \hbar\alpha_{ks}^{(1)}\right). \end{aligned} \tag{3.13}$$

The undetermined $\alpha_{ks}^{(1)}$ is now evaluated from (3.13) by requiring that $B_k^{(2)}(t)$ would *not* contain any constant term in the adiabatic limit. Indeed, this will be our general strategy for the evaluation of any $\alpha_{ks}^{(n)}$. Following such a prescription, we find

$$\hbar\alpha_{ks}^{(1)} = \tfrac{1}{2}(V_{kk} - V_{ss}), \tag{3.14}$$

and hence,

$$\lim_{\substack{T\to\infty \\ t/T\to 1}} B_k^{(2)}(t) = \frac{1}{\hbar^2\alpha_{ks}}\left(\sum_{m\neq s}\frac{V_{km}V_{ms}}{\alpha_{ms}} - V_{ks}\frac{V_{kk}+V_{ss}}{2\alpha_{ks}}\right)\exp(\mathrm{i}\alpha_{ks}t). \tag{3.15}$$

Similarly, from the third-order equation, we obtain

$$\hbar\alpha_{ks}^{(2)} = \frac{1}{3\hbar}\left(\sum_{m\neq s}\frac{V_{ms}V_{sm}}{\alpha_{ms}} + \frac{V_{ks}V_{sk}}{\alpha_{ks}}\right) \tag{3.16}$$

and

$$\begin{aligned} \lim_{\substack{T\to\infty \\ t/T\to 1}} B_k^{(3)}(t) = &\left(-\frac{\hbar\alpha_{ks}^{(2)}V_{ks}}{\hbar^2\alpha_{ks}^2} + \frac{V_{ks}}{4\hbar^3\alpha_{ks}^3}(V_{kk}^2 - V_{ss}^2) - \frac{\hbar\alpha_{ks}^{(1)}}{\hbar^3\alpha_{ks}^2}\sum_{m\neq s}\frac{V_{km}V_{ms}}{\alpha_{ms}}\right. \\ &+\sum_{n\neq k,s}\frac{V_{kn}V_{ns}\hbar\alpha_{ns}^{(1)}}{\hbar^3\alpha_{ns}^2\alpha_{ks}} + \frac{V_{ss}}{\hbar\alpha_{ks}}\sum_{n\neq k,s}\frac{V_{kn}V_{ns}}{\hbar^2\alpha_{ns}^2} \\ &\left.-\sum_{\substack{m\neq s\\ n\neq k,s}}\frac{V_{kn}V_{nm}V_{ms}}{\hbar^3\alpha_{ks}\alpha_{ms}\alpha_{ns}} + \frac{V_{ks}}{\hbar^2\alpha_{ks}^2}\sum_{m\neq s}\frac{V_{ms}V_{sm}}{\hbar\alpha_{ms}}\right)\exp(\mathrm{i}\alpha_{ks}t). \end{aligned} \tag{3.17}$$

Thus, we do not have here any non-adiabatic term, unlike the RDM. It may also be checked by using (1.13), (3.11), (3.15) and (3.17) that

$$\lim_{\substack{T\to\infty \\ t/T\to 1}} \bar{\chi}_s(\lambda, t) = \bar{\bar{\psi}}_s + O(\lambda^4); \tag{3.18}$$

we just require (1.12), (3.14) and (3.16) to properly expand the denominators in order to achieve this end. Hopefully, (3.18) will be satisfied to all orders. To check whether (3.6) is satisfied, we evaluate $\langle\bar{\chi}_s|\bar{\chi}_s\rangle$ in the adiabatic limit and find, considering $V_{ij} = V_{ji}$, that

$$\lim_{\substack{T\to\infty \\ t/T\to 1}} \langle\bar{\chi}_s|\bar{\chi}_s\rangle = 1 + \lambda^2 \sum_{m\neq s} \frac{V_{ms}^2}{\hbar^2\alpha_{ms}^2} + \lambda^3 \times \sum_{m\neq s} \left( V_{ms}^2 \frac{V_{mm}+V_{ss}}{\hbar^3\alpha_{ms}^3} - 2\frac{V_{ms}}{\hbar^2\alpha_{ms}^2} \sum_{n\neq s} \frac{V_{mn}V_{ns}}{\hbar\alpha_{ns}} \right) + O(\lambda^4). \tag{3.19}$$

On the other hand, calculation shows

$$\lim_{\substack{T\to\infty \\ t/T\to 1}} \int_0^t \operatorname{Im} F_s(\lambda, t')\,dt' = -\frac{\lambda^2}{2} \sum_{m\neq s} \frac{V_{ms}^2}{\hbar\alpha_{ms}^2} + \lambda^3 \sum_{m\neq s} \frac{V_{ms}}{\hbar^2\alpha_{ms}^2} \times\left( \sum_{n\neq s} \frac{V_{mn}V_{ns}}{\alpha_{ns}} - V_{ms}\frac{V_{mm}+V_{ss}}{2\alpha_{ms}} \right) + O(\lambda^3), \tag{3.20}$$

and it is clear from (3.19) and (3.20) that (3.6) is satisfied to $O(\lambda^3)$; once again, we hope that this will hold to all orders. Finally, the overall phase term, as (1.13) and (3.4) reveal,

$$\exp(-i\alpha_s t)\exp\left(-i\int_0^t \operatorname{Re} F_s(\lambda, t')\,dt'/\hbar\right) \tag{3.21}$$

becomes

$$\exp\left[-\frac{i}{\hbar}\left(\hbar\omega_s + \frac{\lambda}{2}V_{ss} - \frac{\lambda^2}{3}\sum_{m\neq s}\frac{V_{ms}^2}{\hbar\alpha_{ms}} + O(\lambda^4)\right)t\right] \tag{3.22}$$

under the specified limiting situation. Let us note here that actually the phase (3.22) is infinite because adiabaticity ($T\to\infty$, $t/T\to 1$) requires $t\to\infty$. Thus, although we have found a somewhat different expression for the phase factor following the UPDM in this particular case (Bhattacharyya 1984), it does not really matter; one may view this difference as being equivalent to the fact that $\exp(i\times\text{constant})\psi_s(\lambda, t)$ is also a solution of (1.2) if $\psi_s(\lambda, t)$ is one.

*3.2.2.* We now reconsider the case (1.18), but with $f(t)$ given by (2.27), in order to arrive at a form which works even if the initial state is degenerate. It is evident that here the RUPDM does not *apparently* lead to any improvement if we follow the previous strategy to evaluate $\{\alpha_{ms}^{(n)}\}$, because in this case the RDM works successfully. So, we shall have to adopt a somewhat *different* scheme to exploit the *flexibility* of the RUPDM. Thus, our endeavour will be to choose the $\{\alpha_{ms}^{(n)}\}$ in such a way that the final results resemble a BW type of development in the static limit. To achieve this end, we first note that the first-order equation gives

$$B_k^{(1)}(t) = \frac{V_{ks}}{i\hbar}\frac{\exp[(i\alpha_{ks}+\eta)t]}{i\alpha_{ks}+\eta}. \tag{3.23}$$

From (3.23) and the second-order perturbation equation, we then find

$$B_k^{(2)}(t) = \frac{\hbar\alpha_{ks}^{(1)} V_{ks}}{\hbar^2(i\alpha_{ks}+\eta)^2}\exp[(i\alpha_{ks}+\eta)t] + \frac{V_{ks}V_{ss}}{\hbar^2(i\alpha_{ks}+\eta)(i\alpha_{ks}+2\eta)}\exp[(i\alpha_{ks}+2\eta)t]$$

$$-\sum_{m\neq s}\frac{V_{km}V_{ms}}{\hbar^2(i\alpha_{ms}+\eta)(i\alpha_{ks}+2\eta)}\exp[(i\alpha_{ks}+2\eta)t]. \tag{3.24}$$

Since we wish to have the coefficients such that

$$\lim_{\eta\to 0_+}\bar{\chi}_s(\lambda, t) = \bar{\bar{\psi}}_s(\lambda) = \phi_s + \lambda\psi_s^{(1)} + \lambda^2\psi_s^{(2)} + \dots \tag{3.25}$$

is obeyed order-by-order, where $\psi_s^{(i)}$ stands for the $i$th-order BW perturbative result, we shall examine the structure of $\lim_{\eta\to 0_+} B_k^{(n)}(t)$ at each step. From (3.24) we see that

$$\lim_{\eta\to 0_+} B_k^{(2)}(t) = \sum_{m\neq s}\frac{V_{km}V_{ms}}{\hbar^2\alpha_{ms}\alpha_{ks}}\exp(i\alpha_{ks}t) \tag{3.26}$$

*only* if we choose

$$\hbar\alpha_{ks}^{(1)} = -V_{ss}. \tag{3.27}$$

Similarly, from the third-order equation, we obtain $B_k^{(3)}(t)$ and note that the requirement

$$\lim_{\eta\to 0_+} B_k^{(3)}(t) = -\sum_{m,n\neq s}\frac{V_{km}V_{mn}V_{ns}}{\hbar^3\alpha_{ks}\alpha_{ms}\alpha_{ns}}\exp(i\alpha_{ks}t) \tag{3.28}$$

is satisfied only when the choice

$$\hbar\alpha_{ks}^{(2)} = \sum_{m\neq s}\frac{V_{ms}V_{sm}}{\hbar\alpha_{ms}} \tag{3.29}$$

is made. Thus we have

$$\lim_{\eta\to 0_+}\bar{\chi}_s(\lambda, t) = \phi_s + \lambda\sum_{m\neq s}(B_m^{(1)}(t) + \lambda B_m^{(2)}(t) + \dots)\phi_m\exp(i\alpha_{sm}t)$$

$$= \phi_s - \lambda\sum_{m\neq s}\frac{V_{ms}}{\hbar\alpha_{ms}}\phi_m + \lambda^2\sum_{m,n\neq s}\frac{V_{mn}V_{ns}}{\hbar^2\alpha_{ms}\alpha_{ns}}\phi_m$$

$$-\lambda^3\sum_{m,n,p\neq s}\frac{V_{mn}V_{np}V_{ps}}{\hbar^3\alpha_{ms}\alpha_{ns}\alpha_{ps}}\phi_m + \dots, \tag{3.30}$$

and from (3.27) and (3.29) we can write

$$\begin{aligned}\hbar\alpha_k &= \hbar\alpha_k^{(0)} = \hbar\omega_k,\\ \hbar\alpha_s &= \hbar\omega_s + \lambda V_{ss} - \lambda^2\sum_{m\neq s}\frac{V_{ms}V_{sm}}{\hbar\alpha_{ms}} + \dots\end{aligned} \tag{3.31}$$

which reveal that indeed a BW type of scheme has emerged; hence (3.25) is obeyed, at least to third order which we have checked. The normalisation requirement (3.6) has also been checked to $O(\lambda^3)$ and found satisfied. In fact, we obtained for the left-hand side of (3.6) the expression

$$\exp\left(-\frac{\lambda^2}{2}\sum_{m\neq s}\frac{V_{ms}^2}{\hbar^2\alpha_{ms}^2} + \lambda^3\sum_{m,n\neq s}\frac{V_{ms}V_{mn}V_{ns}}{\hbar^3\alpha_{ms}^2\alpha_{ns}} + O(\lambda^4)\right) \tag{3.32}$$

in the adiabatic limit, assuming, of course, that $V_{ij} = V_{ji}$, for simplicity; it agrees with the right-hand side of (3.6) as may be seen from (3.30).

It is worth noting in this context that the above strategy for the evaluation of $\{\alpha_{ms}^{(n)}\}$ which corresponds, in effect, to having a BW form for the un-normalised wavefunction $\bar{\chi}_s(\lambda, t)$, as (3.25) shows, is by no means *unique.* In fact, this non-uniqueness associated with non-zero choices for $\{\alpha_{ms}^{(n)}\}$, $n \geq 1$, just reflects various possible ways, with different partitionings of the final Hamiltonian $H = H_0 + \lambda V$, of arriving at the state $\bar{\bar{\psi}}_s = \lim_{\eta \to 0_+} \bar{\chi}_s(\lambda, t)$ by resumming its perturbation series. For example, a still more resummed version than the one given by (3.30) and (3.31) is possible if we choose

$$\hbar\alpha_{ks}^{(1)} = V_{kk} - V_{ss}, \tag{3.33}$$

instead of (3.27), to obtain from (3.24)

$$\lim_{\eta \to 0_+} B_k^{(2)}(t) = \sum_{m \neq k,s} \frac{V_{km} V_{ms}}{\hbar^2 \alpha_{ks} \alpha_{ms}} \exp(\mathrm{i}\alpha_{ks} t). \tag{3.34}$$

Solving the third-order equation, we then calculate $B_k^{(3)}(t)$ and choose

$$\hbar\alpha_{ks}^{(2)} = \sum_{m \neq s} \frac{V_{sm} V_{ms}}{\hbar\alpha_{ms}} - \sum_{m \neq k,s} \frac{V_{km} V_{mk}}{\hbar\alpha_{ms}} \tag{3.35}$$

to find

$$\lim_{\eta \to 0_+} B_k^{(3)}(t) = -\sum_{\substack{m \neq k,s \\ n \neq k,m,s}} \frac{V_{km} V_{mn} V_{ns}}{\hbar^3 \alpha_{ks} \alpha_{ms} \alpha_{ns}} \exp(\mathrm{i}\alpha_{ks} t). \tag{3.36}$$

Thus, here we have

$$\lim_{\eta \to 0_+} \bar{\chi}_s(\lambda, t) = \phi_s - \lambda \sum_{m \neq s} \frac{V_{ms}}{\hbar\alpha_{ms}} \phi_m + \lambda^2 \sum_{\substack{m \neq s \\ n \neq m,s}} \frac{V_{mn} V_{ns}}{\hbar^2 \alpha_{ms} \alpha_{ns}} \phi_m$$

$$- \lambda^3 \sum_{\substack{m \neq s \\ n \neq m,s \\ p \neq m,n,s}} \frac{V_{mn} V_{np} V_{ps}}{\hbar^3 \alpha_{ms} \alpha_{ns} \alpha_{ps}} \phi_m + \mathrm{O}(\lambda^4), \tag{3.37}$$

where

$$\hbar\alpha_{ks} = \hbar\omega_{ks} + \lambda(V_{kk} - V_{ss}) + \lambda^2 \left( \sum_{m \neq s} \frac{V_{sm} V_{ms}}{\hbar\alpha_{ms}} - \sum_{m \neq k,s} \frac{V_{km} V_{mk}}{\hbar\alpha_{ms}} \right) + \mathrm{O}(\lambda^3). \tag{3.38}$$

It is easy to see by employing (3.38) in (3.37) that the latter equation can also be written in the form

$$\lim_{\eta \to 0_+} \bar{\chi}_s(\lambda, t) = \phi_s + \lambda\psi_s^{(1)} + \lambda^2 \psi_s^{(2)} + \lambda^3 \psi_s^{(3)} + \mathrm{O}(\lambda^4), \tag{3.39}$$

as required. We have also checked the validity of (3.6) to $\mathrm{O}(\lambda^3)$. Once again, this resummed version also applies *even if* the initial state is degenerate.

*3.2.3.* For the adiabatically developed oscillatory perturbation (1.19), a similar scheme can be followed by choosing the form (2.27) for $f(t)$ to arrive at results which desirably work in situations where application of the RDM leads to troubles. The expressions for the first few orders of $\{B_k^{(n)}(t)\}$ and $\{\alpha_{ks}^{(n)}\}$ are given below without going into the detail:

$$\lim_{\eta \to 0_+} B_k^{(1)}(t) = -\frac{1}{\hbar} \left( \frac{V_{ks}}{\alpha_{ks} + \omega} \exp[\mathrm{i}(\alpha_{ks} + \omega)t] + \frac{V_{sk}^*}{\alpha_{ks} - \omega} \exp[\mathrm{i}(\alpha_{ks} - \omega)t] \right), \tag{3.40}$$

$$\lim_{\eta\to 0_+} B_k^{(2)}(t)=\frac{1}{\hbar^2}\Bigg[\left(\sum_{m\neq s}\frac{V_{km}V_{ms}}{\alpha_{ms}+\omega}-\frac{V_{ss}V_{ks}}{\alpha_{ks}+\omega}\right)\frac{\exp[\mathrm{i}(\alpha_{ks}+2\omega)t]}{\alpha_{ks}+2\omega}$$
$$+\left(\sum_{m\neq s}\frac{V_{km}V^*_{sm}}{\alpha_{ms}-\omega}-\frac{V_{ss}V^*_{sk}}{\alpha_{ks}-\omega}+\sum_{m\neq s}\frac{V^*_{mk}V_{ms}}{\alpha_{ms}+\omega}-\frac{V^*_{ss}V_{ks}}{\alpha_{ks}+\omega}\right)\frac{\exp(\mathrm{i}\alpha_{ks}t)}{\alpha_{ks}}$$
$$+\left(\sum_{m\neq s}\frac{V^*_{mk}V^*_{sm}}{\alpha_{ms}-\omega}-\frac{V^*_{ss}V^*_{sk}}{\alpha_{ks}-\omega}\right)\frac{\exp[\mathrm{i}(\alpha_{ks}-2\omega)t]}{\alpha_{ks}-2\omega}\Bigg], \tag{3.41}$$

etc where

$$\hbar\alpha_{ks}=\hbar\omega_{ks}+\frac{\lambda^2}{\hbar}\left[\sum_{m\neq s}\left(\frac{V_{ms}V^*_{ms}}{\alpha_{ms}+\omega}+\frac{V_{sm}V^*_{sm}}{\alpha_{ms}-\omega}\right)-\frac{V_{ss}V^*_{ss}}{\alpha_{ks}}\right]+\mathrm{O}(\lambda^4). \tag{3.42}$$

We see that (3.40) and (3.41) are structurally similar to (2.42) and (2.43), respectively, in the adiabatic limit, so that the validity of (3.6) to $\mathrm{O}(\lambda^2)$ follows immediately; only, here we have $\{\alpha_{rs}\}$ in the denominators in place of $\{\omega_{rs}\}$ appearing in the RDM. But, in effect, the presence of such $\{\alpha_{rs}\}$, which obey an equation like (3.42), makes this scheme, the RUPDM, fruitful in dealing with situations involving a degeneracy or resonance. It may also be noted that the perturbation equations for this problem are of such a nature that only even order terms in $\lambda$ at the right-hand side of (3.42) will survive. Thus, the structural similarity with the results of the RDM mentioned just above will be lost from $B_k^{(3)}(t)$ onwards.

*3.2.4.* The perturbation (1.16) will now be considered. Applying the RUPDM straightforwardly, we obtain from the first-order equation

$$B_k^{(1)}(t)=-\frac{V_{ks}}{\hbar\alpha_{ks}}[\exp(\mathrm{i}\alpha_{ks}t)-1]. \tag{3.43}$$

From the second-order equation we remove the secular terms by choosing

$$\hbar\alpha_{ks}^{(1)}=V_{kk}-V_{ss} \tag{3.44}$$

and find

$$B_k^{(2)}(t)=\sum_{m\neq k,s}\frac{V_{km}V_{ms}}{\hbar\alpha_{ms}}\left(\frac{\exp(\mathrm{i}\alpha_{ks}t)-1}{\hbar\alpha_{ks}}-\frac{\exp(\mathrm{i}\alpha_{km}t)-1}{\hbar\alpha_{km}}\right). \tag{3.45}$$

Similarly, at the third order, we take

$$\hbar\alpha_{ks}^{(2)}=\sum_{m\neq s}\frac{V_{ms}V_{sm}}{\hbar\alpha_{ms}}-\sum_{m\neq k}\frac{V_{km}V_{mk}}{\hbar\alpha_{mk}} \tag{3.46}$$

to arrive at

$$B_k^{(3)}(t)=\left(-\frac{V_{ks}}{\alpha_{ks}}\alpha_{ks}^{(2)}-\sum_{\substack{m\neq k,s\\ n\neq m,s}}\frac{V_{km}V_{mn}V_{ns}}{\hbar\alpha_{ms}\hbar\alpha_{ns}}+\frac{V_{ks}}{\hbar\alpha_{ks}}\sum_{m\neq s}\frac{V_{ms}V_{sm}}{\hbar\alpha_{ms}}\right)\frac{\exp(\mathrm{i}\alpha_{ks}t)-1}{\hbar\alpha_{ks}}$$
$$+\left[\sum_{\substack{m\neq k,s\\ n\neq m,s}}\frac{V_{km}V_{mn}V_{ns}}{\hbar\alpha_{ns}}\left(\frac{1}{\hbar\alpha_{ms}}-\frac{1}{\hbar\alpha_{mn}}\right)-\frac{V_{ks}}{\hbar\alpha_{ks}}\sum_{m\neq k,s}\frac{V_{ms}V_{sm}}{\hbar\alpha_{ms}}\right]\frac{\exp(\mathrm{i}\alpha_{km}t)-1}{\hbar\alpha_{km}}$$
$$+\sum_{\substack{m\neq k,s\\ n\neq k,m,s}}\frac{V_{km}V_{mn}V_{ns}}{\hbar\alpha_{ns}\hbar\alpha_{mn}}\frac{\exp(\mathrm{i}\alpha_{kn}t)-1}{\hbar\alpha_{kn}}$$
$$+\frac{V_{ks}}{\hbar\alpha_{ks}}\sum_{m\neq s}\frac{V_{ms}V_{sm}}{\hbar\alpha_{ms}}\frac{\exp(\mathrm{i}\alpha_{sm}t)-1}{\hbar\alpha_{sm}}. \tag{3.47}$$

It is easy to check that these results agree with those obtained by employing the UPDM (Bhattacharyya 1984) remembering the relation $B_k(\lambda, t) = b_k(\lambda, t)/b_s(\lambda, t)$. In fact, here the RUPDM allows one *also* to calculate $b_s(\lambda, t)$ perturbatively; it can be performed as follows. We put (1.13) in (1.2) to obtain from the $\phi_s$ projection part of the resulting equation

$$\mathrm{i}\hbar \partial b_s/\partial t = (\langle \phi_s | H(\lambda, t) | \bar{\chi}_s \rangle - \hbar\alpha_s) b_s \tag{3.48}$$

which we rewrite, for the case (1.16), as

$$\begin{aligned} \mathrm{i}\hbar\partial(b_s^{(0)} + \lambda b_s^{(1)}(t) + \lambda^2 b_s^{(2)}(t) + \ldots)/\partial t \\ = \Big(\lambda V_{ss} + \lambda^2 \sum_{m \neq s} (B_m^{(1)}(t) + \lambda B_m^{(2)}(t) + \ldots) V_{sm} \exp(\mathrm{i}\alpha_{sm} t) \\ - \lambda(\hbar\alpha_s^{(1)} + \lambda\hbar\alpha_s^{(2)} + \ldots)\Big)(b_s^{(0)} + \lambda b_s^{(1)}(t) + \lambda^2 b_s^{(2)}(t) + \ldots). \end{aligned} \tag{3.49}$$

As usual, we now solve it order-by-order by choosing $\{\alpha_s^{(n)}\}$ such that no constant terms appear at any order. Thus, we find

$$\hbar\alpha_s^{(1)} = V_{ss} \tag{3.50}$$

and

$$b_s^{(1)}(t) = 0 \tag{3.51}$$

from the first-order equation. At the next order, we obtain

$$\hbar\alpha_s^{(2)} = -\sum_{m \neq s} \frac{V_{ms} V_{sm}}{\hbar\alpha_{ms}} \tag{3.52}$$

and

$$b_s^{(2)}(t) = \sum_{m \neq s} \frac{V_{ms} V_{sm}}{\hbar^2 \alpha_{ms}^2} [\exp(\mathrm{i}\alpha_{sm} t) - 1]. \tag{3.53}$$

The procedure can be continued easily and the results thus obtained agree with those obtained through the UPDM, as expected. Notably, only if we proceed with (3.48) to calculate $b_s(\lambda, t)$ we find the undetermined phases $\{\alpha_s^{(n)}\}$ separately, and hence $\{\alpha_k^{(n)}\}$ also; otherwise, $\{\alpha_{ks}^{(n)}\}$ are obtained, as we have seen. However, it is not *mandatory* to follow this perturbative scheme for $b_s(\lambda, t)$ in the RUPDM; rather, the advantage here is that one need not actually compute it. This is because, the really relevant part of $b_s(\lambda, t)$, as (3.4) and (3.6) show, only accounts for the proper normalisation of $\bar{\chi}_s(\lambda, t)$. Using (3.43) and (3.45), we have also checked the validity of (3.6) to $O(\lambda^3)$ for the case of a real $V$.

Clearly, this procedure can also be successfully applied to deal with the perturbation (1.17); secular terms will not appear and the results which one would obtain are obvious from the work of Bhattacharyya (1984) on UPDM. So, we are not going to explicitly work them out here, within the RUPDM.

### 3.3. Summary

Our observations may now be summarised as follows.

(i) The RDM may be viewed as a special case of the RUPDM; hence, the latter one is more general.

(ii) This procedure works successfully for the perturbation (1.18) with the switching function (2.28). Moreover, results show that no difficulty will arise even if the initial state becomes degenerate. Understandably, then, the RUPDM will also work for the case (1.19) if the form (2.28) is used as $f(t)$.

(iii) From the results for the perturbation (1.18), where $f(t)$ is given by (2.27), we again find no difficulty with degeneracy. It is also evident from our work that here a specific choice for the unknown phases $\{\alpha_{ks}^{(n)}\}$ corresponds actually to working with a particular partitioning of the total Hamiltonian in a time-independent context to obtain that perturbed stationary state which the present scheme gives in the adiabatic limit.

(iv) The perturbation (1.19), with (2.27) as $f(t)$, is also successfully treated by this procedure even when the unperturbed initial state is degenerate or the applied perturbation corresponds to a resonant one.

(v) The RUPDM can also be successfully employed to deal with the case (1.16), and hence the one given by (1.17).

## 4. Discussion

It goes without saying that the RDM, the UPDM and the RUPDM are basically various rearrangements of the DM. For a given problem, we consider some particular scheme *convenient* if it is able to just directly avoid the appearance of specific undesirable terms (e.g., terms proportional to $t^n (n \geq 1)$ or $\eta^{-1}$, etc, in the cases considered) from the amplitudes at any order of the perturbation; otherwise, one has to actually take the trouble of ultimately rearranging such unphysical terms to a meaningful form and this task may be quite intricate. We may emphasise, if this *a posteriori* rearrangement is not performed, several problems may appear. For example, application of the DM or the RDM to the problem (1.16) shows oscillatory behaviour of the so-called 'survival probability' at first order and does not respect the spectrum of $H$; but we know that this probability will decay if the spectrum of $H$ is continuous (see, e.g., Bhattacharyya 1983). Moreover, it appears from the $t^n$-proportional amplitude-correction terms that perturbative developments are valid for short times only (see, e.g., Bhattacharyya (1984) and references therein for a discussion) which should not have been the case (Bohm 1951). On the other hand, these difficulties are naturally avoided in the UPDM or in the RUPDM owing to the appearance of eigenenergy differences corresponding to the *perturbed* Hamiltonian in the amplitude-correction terms (so that for the case of a continuum, the inapplicability of such a perturbative approach becomes apparent) and the absence of any secular terms, respectively. Keeping these in mind, we see from the results presented here that only the RUPDM works desirably in all the cases under study.

Removal of the types of undesirable terms mentioned above from the solutions at each order, however, does *not* guarantee the convergence of a procedure. In case of the RUPDM, for example, if the condition (3.2) is not obeyed, difficulty with the convergence of the expansion (1.14) becomes obvious because the series concerned has to then represent functions with infinite values, though it may be true that the correction terms of any order remain finite. But, except for the problem (1.18), it is difficult to justify (3.2). Actually, for the perturbation (1.16), it can be shown that situations may arise to disobey (3.2). To be specific, let us choose a two-level problem as an example and write

$$H\bar{\psi}_1 = \hbar\bar{\omega}_1\bar{\psi}_1, \qquad H\bar{\psi}_2 = \hbar\bar{\omega}_2\bar{\psi}_2, \qquad H \equiv H(\lambda), \qquad \|\bar{\psi}_1\| = 1 = \|\bar{\psi}_2\|, \tag{4.1}$$

$$\phi_s = C_1\bar{\psi}_1 + C_2\bar{\psi}_2, \qquad \|\phi_s\| = 1. \tag{4.2}$$

In this case, calculation shows that

$$\langle \phi_s | \psi_s(\lambda, t)\rangle = 0, \tag{4.3}$$

and hence (3.2) ceases to be obeyed, when

$$|C_1| = |C_2| = 1/\sqrt{2} \qquad t = (2n+1)\pi/(\bar{\omega}_2 - \bar{\omega}_1), \qquad n = \pm 1, \pm 2, \ldots \tag{4.4}$$

For the cases (1.17) and (1.19), however, it is not easy to assert whether (3.2) will always be satisfied. But, it is clear that the RUPDM also is not *quite* free from all the difficulties of a perturbative approach. Needless to mention, the RDM suffers from similar troubles owing to the requirement (2.18).

It seems worthwhile to briefly comment on the performances of the methods under scrutiny before proceeding further. Hence, the main features relevant to our study (see also Bhattacharyya 1984) are given below in a tabular form, for convenience.

| Perturbation | Method | Comments |
|---|---|---|
| (1.16) | DM | inconvenient |
| | RDM | inconvenient |
| | UPDM | convenient, BW type, applicable to degenerate cases, no obvious convergence difficulty |
| | RUPDM | convenient, BW type, applicable to degenerate cases, convergence difficulty in specific situations |
| (1.17) | DM | inconvenient |
| | RDM | inconvenient |
| | UPDM | convenient, BW type, applicable to degenerate and resonant cases, no obvious convergence difficulty |
| | RUPDM | convenient, BW type, applicable to degenerate and resonant cases, convergence difficulty may appear |
| (1.18) with (2.27) | DM | inconvenient |
| | RDM | convenient, RS type, inapplicable to degenerate cases, no obvious convergence difficulty |
| | UPDM | convenient but indirect, BW type, applicable to degenerate cases, no obvious convergence difficulty |
| | RUPDM | convenient, BW type but flexible, applicable to degenerate cases, no obvious convergence difficulty |
| (1.18) with (2.28) | DM | inconvenient |
| | RDM | inconvenient |
| | UPDM | convenient but indirect, BW type, applicable to degenerate cases, no obvious convergence difficulty |
| | RUPDM | convenient, BW type, applicable to degenerate cases, convergence difficulty in specific situations |

| Perturbation | Method | Comments |
|---|---|---|
| (1.19) with (2.27) | DM | inconvenient |
| | RDM | convenient, RS type, inapplicable to degenerate and resonant cases, convergence difficulty may appear |
| | UPDM | inconvenient |
| | RUPDM | convenient, BW type, applicable to degenerate and resonant cases, convergence difficulty may appear |
| (1.19) with (2.28) | DM | inconvenient |
| | RDM | inconvenient |
| | UPDM | inconvenient |
| | RUPDM | convenient, BW type, applicable to degenerate and resonant cases, convergence difficulty may appear |

Understandably, compared to the UPDM, the RUPDM suffers from an additional difficulty with convergence since in this approach we work with $\{B_m(\lambda, t)\}$, and *not* with $\{b_m(\lambda, t)\}$. So, it is natural to investigate whether the UPDM itself can somehow be *modified* to directly bypass the undesirable terms for the adiabatic cases (1.18) and (1.19), because then we can definitely consider the UPDM as a general scheme.

To explore the above possibility, we first proceed with (1.18) and (2.28). The perturbation equations in this case suggest that the desirable result can be obtained if we choose (i) $\alpha_s^{(n)}$ in such a way that no divergent terms in $b_s^{(n)}(t)$ exist in the adiabatic limit and (ii) $\alpha_k^{(n)}(k \neq s)$ such that no constant terms in $b_k^{(n+1)}(t)$ appear, again in the same limit. But, when we consider (1.18) and (2.27), difficulties become apparent. Actually, in this case, two types of disturbing terms, proportional separately to $t^n (n \geqslant 1)$ and $\eta^{-1}$, are present. Of these, only the latter type of terms can be avoided, and to achieve this end we have to render the IC more general. For example, the following choice of the IC

$$b_s(t_0) = e^{iX(\lambda)}, \qquad b_p^{(0)} = 0 = b_p^{(n)}(t_0), \qquad p \neq s, n = 1, 2, \ldots, \tag{4.5}$$

instead of the one given below (1.12), where

$$X(\lambda) = \lambda x_1 + \lambda^2 x_2 + \ldots \tag{4.6}$$

will serve our purpose. The unknown $x_i$ is to be then determined from the equation for $b_s^{(i)}(t)$ such that $b_s^{(i)}(t_0)$ cancels the $\eta^{-1}$-proportional terms present in $b_s^{(i)}(t)$ in the limit $\eta \to 0_+$. However, the $t^n$-proportional terms cannot be bypassed. Hence, an *a posteriori* rearrangement has to be performed. It is more important to note in this context that one can *still* proceed straightforwardly to efficiently handle this problem, but then the form of $\psi_s(\lambda, t)$ has to be chosen properly. Thus, starting from a *very general* choice

$$\psi_s(\lambda, t) = \sum_m b_m(\lambda, t)\phi_m \exp(-i\alpha_m t) \exp(-iZ_m(\lambda, t)), \tag{4.7}$$

where the $Z_m$ part takes care of *nonlinear* time-dependent phase, if any, we have found that if one chooses

$$\alpha_m = \omega_m \tag{4.8}$$

and

$$Z_m(\lambda, t) = Z(\lambda, t) = \lambda z_1 e^{\eta t}/\eta + \lambda^2 z_2 e^{2\eta t}/2\eta + \dots \tag{4.9}$$

in the case concerned, no trouble would arise. Notably, the extra phase in (4.7) can then be rewritten as

$$e^{-iZ(\lambda,t)} = \exp\left(-i \int_{-\infty}^{t} (\lambda z_1 e^{\eta t'} + \lambda^2 z_2 e^{2\eta t'} + \dots)\, dt'\right) \tag{4.10}$$

which implies that it vanishes at $t = t_0 = -\infty$. In the adiabatic limit, however, $Z(\lambda, t)$ contributes to $\psi_s(\lambda, t)$ by providing a $t$-proportional and a divergent ($\sim\eta^{-1}$) part expressed as powers of the exponential given by (4.10). From the equation for $b_s^{(i)}(t)$, $z_i$ can easily be evaluated by requiring the absence of any $t$- *and* $\eta^{-1}$-proportional terms at each order. But, though the form (4.7) is a very general one, and one can legitimately call the corresponding perturbative development as a *generalised* UPDM (GUPDM), the choices (4.8) and (4.9) are understandably quite specific. Thus, if we consider a perturbation like (1.19), with (2.27), we have to search for a proper starting form of $Z_m(\lambda, t)$ afresh. In this sense, the GUPDM is of little practical value; a wise *a priori* guess about the structure of $Z_m(\lambda, t)$ for a given form of the perturbation determined its success.

## 5. Conclusion

The motivation behind our study has been to compare the domains of validity of the various rearranged versions of the method of variation of constants. Among other things, we have thoroughly examined the RDM and demonstrated the superiority of the RUPDM over it. Adiabatic perturbations have been given more importance; specifically, based on the realisation that the results of an adiabatic passage should not depend on the choice of the form for $f(t)$, we have considered the applicability of two different types of switching functions, (2.27) and (2.28). It is evident that any non-exponential form like $t^n/T^n$, $n > 1$ (Todorov 1981), can also be successfully used in cases where (2.28) works. It is also worth noting that the increased flexibility of the UPDM and the RUPDM relative to the DM and the RDM, respectively, can be advantageously exploited by proceeding through a Brillouin–Wigner (BW) type development, and this has become possible owing to the *improper* nature (Sharma 1976) of the BW series.

It turns out from the present analysis that the RUPDM is best suited for dealing with such adiabatically developed perturbations as (1.18) and (1.19). However, if we wish to successfully apply the GUPDM directly in order to avoid convergence difficulty *on all counts*, choice of $Z_m(\lambda, t)$ in (4.7) becomes crucial. This choice is actually determined by the nature of the perturbations concerned. For the cases (1.16) and (1.17), of course, the GUPDM applies in its simplest (UPDM) form (1.10). Thus, the strategy behind the development of a successful time-dependent perturbation scheme appears to be very different from that behind the same of a stationary one. In this latter case, various partitionings of the total Hamiltonian correspond to different ways of resumming of the perturbation series, whereas, in the former one, the rearranged series are found to have correspondences with the choices of the starting form for $\psi_s(\lambda, t)$ to be employed in the SE, and *also* the IC (see, e.g., the discussion around (4.5)). A clear delineation of this important point has already been given in § 3.2.2.

Finally, we must mention that, unless the form of $Z_m(\lambda, t)$ in (4.7) is sufficiently general, such added troubles as non-uniform passage from a diabatic to an adiabatic perturbation, etc (Bhattacharyya 1984) may also appear, and hence one has to be cautious in the course of studying the limiting situations.

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While our work was in progress, we learnt that Professor P A M Dirac had passed away. We humbly dedicate this paper to his revered memory.

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