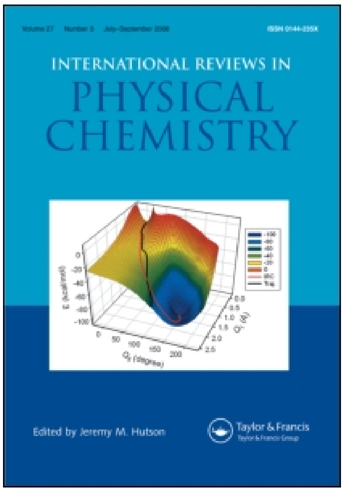

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Gert. D. Billing[a]
[a] Department of Chemistry, H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark

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Classical path method in inelastic and reactive scattering

by GERT D. BILLING

Department of Chemistry, H. C. Ørsted Institute,
University of Copenhagen, 2100 Copenhagen, Denmark

The semiclassical (classical path) method has over the years probably been the most commonly used approximate method for describing many molecular dynamical processes in inelastic, non-adiabatic and recently also in reactive scattering. Here an overview of the development of the theory is given. Its connection to various other approximate dynamic theories such as the eikonal, time-dependent self-consistent field, Gaussian wave packet and the Feynmann path theory is discussed. Various numerical and technical schemes for solving the mixed quantum–classical equations through algebraic, state and grid expansion methods are also given.

1. Introduction

The semiclassical or the classical path (CP) method, which it is sometimes called, is as old as quantum mechanics itself. In this method, classical and quantum mechanics are mixed in such a manner that the solution of a given collision problem is facilitated compared with the exact quantum solution. Early applications (Bohr 1948) of this approach in electron capture theory treat the internuclear motion classically and the electronic motion quantally. This separation was natural because of the small mass of the electron compared with that of the nuclei. Later the approach has been used to treat molecular energy transfer problems. Here the relative translational motion was approximated by a classical trajectory and the time-dependent Schrödinger equation (TDSE) solved for the internal states. Often a simple straight-line trajectory was taken or at least a trajectory which was not coupled to the internal motion was assumed. Later came attempts to couple the trajectory to specific quantum transitions, that is to invoke quantum-mechanical boundary conditions. Also methods where not only the relative motion but also part of the internal motion were treated classically have been suggested. For problems concerning non-adiabatic electronic transitions it was also an obvious choice to quantize the electronic degrees of freedom while treating the remaining within a trajectory approach (for a recent review see Sidis 1990). However, only recently has there been attempts to extend the ideas to reactive scattering and to combined reactive–non-adiabatic problems. We shall in the present paper give a description of how far the CP method has been pushed today. The paper is organized as follows: § 2 considers the CP method within the first-order perturbation treatment of the inelastic transitions. Comparison with quantum expressions suggests the introduction of a mean velocity approach. The same is true for the multichannel ‘derivation’ of the coupled CP equations given in § 3; § 4 introduces a classical treatment of some of the internal degrees of freedom and an algebraic approach to energy transfer problems in the polyatomic molecules; in § 4 the CP theory is derived from first principles by invoking a self-consistent field (SCF) approximation and a variational determination of the initial momentum. Also the Feynman path (FP) formulation can be used to define self-consistent paths. This is discussed in § 6; § 7 shows how the CP method can be introduced in reactive scattering by using hyperspherical coordinates, that is coordinates which treat the various rearrangement channels evenhandedly. Also non-adiabatic transitions give rise to problems, which calls for specific methodology. Some of these are discussed in § 8. The introduction of grid methodology has been the latest development of the method. Grid methods are convenient to use for dissociative and tunnelling degrees of freedom. Unfortunately the method is restricted to only a few dimensions but combined with a classical treatment of some degrees of freedom the methodology has many potentially interesting applications. The last section is devoted to a summary and discussion of future lines of development.

2. First-order theories

First-order theories for inelastic transitions were popular in the 1950s and 1960s, and simple scaling relations for the scaling of rates with the vibrational and rotational quantum numbers are based upon these expressions. In the CP evaluation of the first-order transition probabilities, one assumes a simple path. Consider for example the collision of two diatomic molecules and not too small impact parameters. Here a path of the type

$$R^2 = b^2 + (vt)^2 \tag{1}$$

has been assumed (figure 1). R is the centre-of-mass distance, b the impact parameter and v the velocity of the relative motion. At large impact parameters the inelastic transitions will mainly be governed by the long-range multipole interaction. Here one obtains the following first-order expression for the transition probabilities as (Rabitz and Gordon 1970, Nyeland and Billing 1976)

$$\begin{aligned} P_{\alpha,\alpha'} = {} & \frac{4}{\hbar^2 v^2}(2j'_1+1)(2j'_2+1) \\ & \times \sum_{l_1 l_2 l} \frac{(2l)!}{(2l_1+1)!(2l_2+1)!} b^{-2l} \begin{bmatrix} j_1 & l_1 & j'_1 \\ 0 & 0 & 0 \end{bmatrix}^2 \begin{bmatrix} j_2 & l_2 & j'_2 \\ 0 & 0 & 0 \end{bmatrix}^2 \\ & \times |\langle n_1 | Ql_1 | n'_1 \rangle|^2 |\langle n_2 | Q_{l2} | n'_2 \rangle|^2 \sum_{q=-l}^{l} \frac{x^{2l} K^2_{|q|}(x)}{(l-|q|)!(l+|q|)!}, \end{aligned} \tag{2}$$

where Q_{l_i} is a multipole moment ($l_i = 1$ for a dipole, 2 for a quadrupole, etc.), $l = l_1 + l_2$, K_n is a Bessel function and $x = b\omega/v$. The energy mismatch for the transition is given as

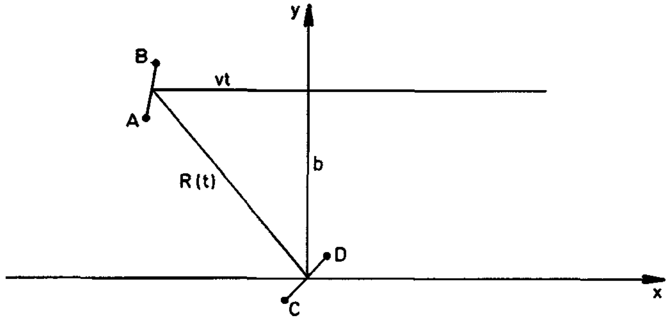

Figure 1. A simple straight-line trajectory is often assumed in the CP method.

$\hbar\omega = |E_{\alpha'} - E_{\alpha}|$, where α is a collective quantum number $\alpha = (n_1 j_1 n_2 j_2)$. The above expression is valid for impact parameters larger than a critical value b_0 which depends upon the transition under consideration and the coupling strength (for example Billing 1987a). At smaller values of b (the close-coupling region) one can for example introduce statistical assumptions or eventually use state expansion methods (see below). The advantage of using this simple theory at large impact parameters is that the contribution to the cross-section from long-range forces can quickly be estimated. Thus we have

$$2\pi \int_{b_0}^{\infty} \mathrm{d}b\, b b^{-2l} x^{2l} K_{|q|}^{2}(x) \approx \frac{\pi^2 v^2}{\omega^2} \exp\left(-\frac{2b_0\omega}{v}\right). \tag{3}$$

At small impact parameters the first-order treatment of rotational transitions rapidly breaks down and hence first-order theories have mainly been used to estimate vibrational or non-adiabatic electronic transitions, where the larger energy mismatch will lead to smaller transition probabilities and hence it is expected that a first-order approach is applicable.

The first-order theory for vibrational excitation processes was based on a collinear collision assumption and a simple trajectory for the relative motion

$$\exp[-\alpha R(t)] = \mathrm{sech}^2(\tfrac{1}{2}\alpha v t), \tag{4}$$

that is an exponential interaction potential ($C \exp(-\alpha r_{\mathrm{AB}})$) with a steepness parameter α was assumed, that is

$$V(R, r) = C \exp[-\alpha(R - \lambda r)], \tag{5}$$

where C is a constant, r the vibrational coordinate and $\lambda = m_{\mathrm{C}}/(m_{\mathrm{B}} + m_{\mathrm{C}})$ for a collinear A + BC collision. The transition probability obtained with this simple (for example Rapp and Kassal 1969) theory is

$$P_{nm} = \frac{U_{mn}^2}{\hbar^4} \frac{(E_m - E_n)^2 4\pi^2 \mu^2}{\alpha^4} \sinh^{-2}\left(\frac{\pi(E_m - E_n)}{v_n a \hbar}\right), \tag{6}$$

where m and n are final and initial vibrational states respectively, E_m is a vibrational energy, μ is the reduced mass, U_{mn} is a transition matrix element $U_{mn} = \langle \phi_m | \exp(\alpha\lambda r) | \phi_n \rangle$, ϕ_n is a vibrational wavefunction and v_n is the initial velocity of the relative motion:

$$\tfrac{1}{2}\mu v_n^2 = E - E_n. \tag{7}$$

It is interesting to compare the first-order CP expression for the transition probability with the corresponding quantum-mechanical expression (Jackson and Mott 1932, Schwartz *et al.* 1952)

$$P_{nm} = \frac{16\pi^2 \mu^2 (E_m - E_n)^2 U_{mn}^2}{\hbar^4 \alpha^4} \frac{\sinh(2\pi k_n/\alpha) \sinh(2\pi k_m/\alpha)}{[\cosh(2\pi k_n/\alpha) - \cosh(2\pi k_m/\alpha)]^2}. \tag{8}$$

Under the assumption that $2\pi k_n/\alpha > 2\pi k_m/\alpha \gg 1$ the last factor can be simplified to

$$\exp\left(-\frac{2\pi(E_m - E_n)}{\alpha\hbar 0{\cdot}5(v_n + v_m)}\right). \tag{9}$$

Under the same conditions the last factor in the CP expression (6) becomes

$$4 \exp\left(-\frac{2\pi(E_m - E_n)}{a\hbar v_n}\right), \tag{10}$$

that is we obtain identical expressions if the initial velocity v_n is substituted by the arithmetic mean value 0·5 (v_n+v_m) for the transition in question. If this velocity is introduced in equation (4) we have the so-called *symmetrized trajectory*, that is each quantum transition $n \rightarrow m$ has its own 'classical trajectory'.

Although various corrections (e.g. anharmonic or 'diagonal distortion' corrections) to the above expressions were known and discussed in the mid-1960s the paper of Secrest and Johnson (1966) where the above collision problem was solved exactly essentially showed that first-order theories were unreliable. An area where first-order expressions for the transition probability has had some success is within non-adiabatic electronic transitions where the transitions often are sufficiently localized to make a local linear trajectory approach sufficiently accurate. The most celebrated result is the Landau–Zener expression for the non-adiabatic transition:

$$P_{12}=\exp\left(-\frac{2\pi V_{12}(R_c)^2}{\hbar v|F_1-F_2|}\right), \tag{11}$$

where v is the velocity with which the crossing point (R_c) is passed and V_{12} is the adiabatic splitting at R_c. The above expression can be obtained using a CP model, quantum (Child 1974) or a wave-packet approach (Henriksen 1992) with a simple linear approximation of the diabatic potential energy curves:

$$V_{ii}=-F_i(R-R_c). \tag{12}$$

First-order theories can be used to give a qualitative impression of the magnitude of the transition probabilities and their dependence of physical parameters as mass, slope of the potential, energy gap, etc., for single quantum transitions. For multiple quantum transitions and high-accuracy work, one has to use methods which involve more numerical work, methods which include higher-order terms and interference effects between the various channels. Such methods are the so-called state expansion methods, where the wavefunction is expanded in a suitable basis set.

3. The eikonal method

We have seen that agreement between the CP and the quantum first-order probabilities can be obtained if the condition $k_m/\alpha \gg 1$ is fulfilled. In this limit we also have $\frac{1}{2}(k_n+k_m)\approx k_m$, that is the CP expression is obtained as the high-energy limit of the quantum-mechanical result. The argument is, however, based upon first-order perturbation theory, which may not be valid in the high-energy limit. Therefore attempts were made to derive the *coupled* CP equations from the corresponding quantum-mechanical equations. This is possible by invoking the eikonal approximation.

The eikonal method owes its name to short-wavelength treatments in optics and the approximation involved can be illustrated by considering the time-independent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dR^2}+V(R)-E\right)\Psi(R)=0, \tag{13}$$

Introducing $\Psi(R)=A(R)\exp(iS(R)/\hbar)$ we obtain

$$A''-A(S')^2+[k^2-U(R)]A=0, \tag{14}$$

$$2A'S'+AS''=0, \tag{15}$$

where the prime and the double prime denote first and second derivative respectively. The fundamental eikonal approximation $A''=0$ can be introduced if

$$\frac{A''}{A} \ll k^2, \tag{16}$$

where $k^2 = 2mE/\hbar^2$. With this approximation we obtain

$$(S')^2 = k^2 - U(R), \tag{17}$$

where $U(R) = 2mV(R)/\hbar^2$. Considering now the multidimensional situation we have the following Schrödinger equation:

$$\left(-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m}\nabla_r^2 + V(\mathbf{r},\mathbf{R}) - E\right)\Psi(\mathbf{r},\mathbf{R}) = 0, \tag{18}$$

Introducing now cylindrical coordinates (figure 2) we obtain

$$\nabla_R^2 = \frac{\partial^2}{\partial\rho^2} + \frac{\partial^2}{\partial Z^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2}. \tag{19}$$

For an A + BC system the total wavefunction is expanded in vibrational–rotational states $(\phi_{vj} Y_{jm})$ of the diatom as

$$\Psi = \sum_{vjmM} \phi_{vj}(r) Y_{jm}(\hat{r}) \Phi_\alpha(\rho, Z) \exp(\mathrm{i}M\phi), \tag{20}$$

where $\alpha = vjmM$ is a collective quantum number and r is the BC bond distance. From the Schrödinger equation we then obtain

$$-\frac{\hbar^2}{2\mu}\left(\nabla^2\Phi_\alpha + \frac{1}{\rho}\frac{\partial\Phi_\alpha}{\partial\rho} - \frac{M_\alpha^2}{\rho^2}\Phi_\alpha\right)\exp(\mathrm{i}M_\alpha\phi) + (E_{vj} - E)\Phi_\alpha \exp(\mathrm{i}M_\alpha\phi)$$

$$= -\sum_{\alpha'} \langle \phi_{vj} Y_{jm} | V_{\mathrm{int}} | \phi_{v'j'} Y_{j'm'} \rangle \Phi_{\alpha'} \exp(\mathrm{i}M_{\alpha'}\phi), \tag{21}$$

where $\nabla^2 = \partial^2/\partial\rho^2 + \partial^2/\partial Z^2$ and $V = v(r) + V_{\mathrm{int}}$. We now introduce

$$\Phi_\alpha = A_\alpha \exp\left(\frac{\mathrm{i}}{\hbar}S_\alpha\right) \tag{22}$$

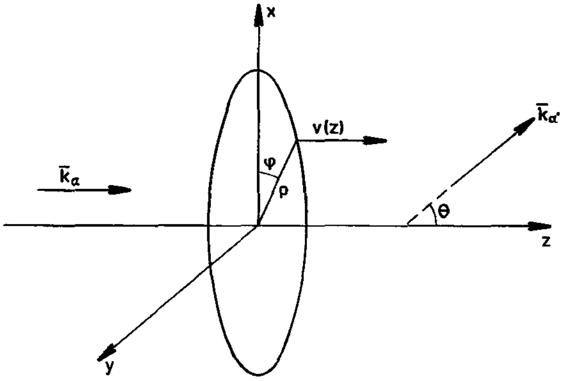

Figure 2. Introduction of cylindrical coordinates for derivation of the eikonal equations.

use the eikonal approximation $\nabla^2 A_\alpha = 0$ and that

$$\frac{1}{2\mu}(\nabla S_\alpha^2 - i\hbar\nabla^2 S_\alpha) = \frac{1}{2\mu}P_\alpha^2(\rho, Z)$$

$$= E - E_{vj} - \langle\alpha|V_{\rm int}|\alpha\rangle, \tag{23}$$

where the angular brackets indicate integration over r, $\hat{r}$ space and where $|\alpha\rangle = \phi_{vj}Y_{jm}$. This finally leads to the following set of coupled equations:

$$\frac{i\hbar}{\mu}\nabla A_\alpha \cdot \nabla S_\alpha + \frac{\hbar^2}{2\mu\rho}\left(\frac{\partial A_\alpha}{\partial\rho} + \frac{i}{\hbar}A_\alpha\frac{\partial S_\alpha}{\partial\rho}\right) - \frac{\hbar^2 M_\alpha^2}{2\mu\rho^2}A_\alpha$$

$$= \sum_{\alpha'\neq\alpha}\langle\alpha|V_{\rm int}|\alpha'\rangle\exp\left(\frac{i}{\hbar}(S_{\alpha'} - S_\alpha)\right)A_{\alpha'}\exp(i\Delta M\,\phi). \tag{24}$$

In order to obtain the T-matrix elements we use the fact that (for example Levine 1969)

$$T_{\alpha',\alpha} = \langle\phi_{v'j'}Y_{j'm'}\exp(-i\mathbf{k}_{\alpha'}\cdot\mathbf{R})|V_{\rm int}|\Psi\rangle, \tag{25}$$

where the angle bracket now denote integration over $\mathbf{R}$, $\mathbf{r}$ space. Introducing the above equations we finally obtain

$$T_{\alpha',\alpha} = (-i)^{M_\alpha}\int_0^\infty d\rho\,\rho J_{M_\alpha}(k_{\alpha'}\rho\sin\theta)[I_1(\rho,\theta) + I_2(\rho,\theta)], \tag{26}$$

where θ is the scattering angle and

$$I_1(\rho,\theta) = \int_0^\infty dZ\exp\left(\frac{iS_\alpha}{\hbar} - ik_{\alpha'}\cos\theta\,Z\right)\frac{i\hbar}{\mu}\nabla A_\alpha\cdot\nabla S_\alpha, \tag{27}$$

$$I_2(\rho,\theta) = \int_0^\infty dZ\exp\left(\frac{iS_\alpha}{\hbar} - ik_{\alpha'}\cos\theta\,Z\right)\left[\left(\langle\alpha|V_{\rm int}|\alpha\rangle - \frac{\hbar^2 M_\alpha^2}{2\mu\rho^2} + \frac{i\hbar}{2\mu\rho}\frac{\partial S_\alpha}{\partial\rho}\right)A_\alpha + \frac{\hbar^2}{2\mu\rho}\frac{\partial A_\alpha}{\partial\rho}\right], \tag{28}$$

where we have used that $\mathbf{k}_{\alpha'} = (k_{\alpha'}\sin\theta, 0, k_{\alpha'}\cos\theta)$, $\mathbf{R} = (\rho\cos\phi, \rho\sin\phi, Z)$ and

$$J_n(z) = \frac{i^{-n}}{\pi}\int_0^\pi d\phi\exp(iz\cos\phi)\cos(n\phi). \tag{29}$$

Thus the ϕ dependence has been integrated out, but the θ dependence is retained. The scattering amplitude is then obtained as

$$f_{\alpha',\alpha}(\theta) = -\frac{\mu}{2\pi\hbar^2}T_{\alpha',\alpha} \tag{30}$$

and the S-matrix elements (Levine 1969) as

$$S_{\alpha',\alpha} = \delta_{\alpha,\alpha} + 2\pi i T_{\alpha',\alpha}. \tag{31}$$

The above equations can be simplified by neglecting the ρ dependence of A_α and S_α, that is they depend only parametrically upon the initial ρ value (Flannery 1969, Byron 1971, Micha 1983). Thus the coupled equations (24) simplify to

$$i\hbar\frac{dA_\alpha}{dZ}v_\alpha(Z) = \sum_{\alpha'\neq\alpha}\langle\alpha|V_{\rm int}|\alpha'> A_{\alpha'}(Z)\exp\left(\frac{i}{\hbar}(S_{\alpha'} - S_\alpha)\right). \tag{32}$$

This set of equations can be rewritten in terms of a time-dependent theory by introducing a trajectory, such that

$$\frac{dA_\alpha}{dt}=\frac{dA_\alpha}{dZ}\frac{dZ}{dt} \tag{33}$$

and

$$\begin{aligned} S_{\alpha'}-S_\alpha &= \int dZ\,(P_{\alpha'}-P_\alpha) \\ &= \frac{1}{2\mu}\int dt\,(P_{\alpha'}^2-P_\alpha^2) \\ &= \int dt\,(E_\alpha+V_{\alpha,\alpha}-E_{\alpha'}-V_{\alpha',\alpha'}), \end{aligned} \tag{34}$$

where we in the last equation have introduced

$$\frac{dZ}{dt}=\frac{1}{2\mu}(P_\alpha+P_{\alpha'}), \tag{35}$$

but in order to convert equation (32) to the usual CP equation we have to introduce $dZ/dt=v_\alpha$ and hence this 'derivation' of the time-dependent CP equations from the time-independent equations can only be valid if $v_\alpha \approx v_{\alpha'}$, that is in the high-energy limit. This conclusion is then the same as that obtained when deriving the CP equations from the time-independent Schrödinger equation (for example Delos *et al.* 1972, Delos and Thorson 1972 and Wartell and Cross 1971). This has also led to the statement that the CP equations are valid only in high-energy limit where this requirement is met. However, it is possible as we shall see below, by introducing a variational approach, to extend the region of validity considerably.

4. State expansion methods

As mentioned above the paper by Secrest and Johnson (1966) essentially showed that first-order approximations to the transition probability for vibrational excitation of diatomic molecules were of limited value, except that they of course provide some qualitative insight in the processes. However, for instance scaling of the probabilities with vibrational quantum number, the importance of the multiquantum and transitions in excited molecules could not be predicted. Here we need to expand the wavefunction for the system in many target states and to solve a set of coupled equations within either the exact quantum or the semiclassical framework. Thus treating the relative motion classically the wavefunction for the quantum, that is internal degrees of freedom are expanded in a complete set of states, defined as eigenfunctions to part of the Hamiltonian, that is

$$\psi(R.r,t)=\sum_n \alpha_n(t)\phi_n(r). \tag{36}$$

In order to couple the classical motion $R(t)$ to the quantum system it was suggested (Rapp and Kassal 1969) that the Ehrenfest averaged potential should be introduced, that is the classical equations of motion should be solved with the potential

$$V_{\text{eff}}(R,t)=\langle\psi|V(R,r,t)|\psi\rangle, \tag{37}$$

where the angular brackets indicate integration over the quantum coordinate r. However, the results obtained using this approach were not satisfactory (for example Billing (1973)) but, if the above-mentioned symmetrization of the initial velocity was also introduced, the results were improved drastically (Billing 1975a). Although this approach (the symmetrized Ehrenfest approach) was later tested on a number of systems for inelastic vibrational as well as rotational and rotational–vibrational transitions it was based upon an *ad-hoc* prescription until it was shown that it can be derived from first principles (see § 5).

In the CP method, one solves a set of coupled first-order differential equations in the expansion coefficients compared with a set of second-order differential equations in the exact quantum-mechanical approach. Although the first-order differential equations are solved without any numerical problems the method is limited to about 1–2000 states at present. For three-dimensional treatment of collision problems and especially for molecule–molecule scattering problems the number of energetically accessible target states soon runs into the thousands or millions. Hence it is important to introduce some techniques which can also handle this situation. Within the CP framework, two suggestions have been made in order to facilitate the situation, namely.

(*a*) that the rotational motion and eventually some of the vibrational motions of the molecule(s) should also be treated classically and
(*b*) that an operator approach should be introduced for the vibrational degrees of freedom.

4.1. *Classical treatment of rotation*

If the rotational motion is included by classical dynamics, the quantum problem reduces to that of collinear collisions and hence both atom–diatom and diatom–diatom collision problems are easily handled (Billing 1984a, b). Thus for an A + BC problem the Hamiltonian is divided in the following way:

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + v(r) + \frac{j(t)^2}{2m}\left(\frac{1}{r^2} - \frac{l}{r_e^2}\right), \tag{38}$$

$$H_1 = \frac{j(t)^2}{2mr_e^2} + \frac{1}{2\mu}\left(P_R^2 + \frac{l^2}{R^2}\right) + V_{\text{eff}}(R,\gamma), \tag{39}$$

$$H_2 = V(R,r,\gamma) - V_{\text{eff}}(R,\gamma), \tag{40}$$

where m is the reduced mass, $v(r)$ the intramolecular potential, r the bond distance, r_e the equilibrium bond distance and $j(t)$ the rotational angular momentum of the BC molecule. The reduced mass of the relative motion is μ, the centre-of-mass distance is R and the angle between r and R is γ. As before, the effective potential, which couples the quantum and classical degrees of freedom, is obtained by averaging over the quantum coordinate r, that is

$$V_{\text{eff}} = \langle\psi|V(R,r,\gamma)|\psi\rangle. \tag{41}$$

The wavefunction ψ can be explained in eigenfunctions to $\hat{H}_0$ or eventually on a grid (see below). The eigenstates depend upon time through $j(t)$, giving rise to rotational–vibrational coupling. If the wavefunction is expanded in eigenstates, we have to solve a set of equations for these expansion coefficients (transition amplitudes) and the classical equations of motion for the rotational and translational motion simultaneously (for further details see Billing 1984a, b). From the amplitudes we obtain partial cross-sections as

$$\sigma_{n_ij_i\to n_fj_f}(E,J)=\frac{\pi}{k^2_{n_ij_i}}\frac{1}{2j_i+1}\sum_{l_i=|J-j_i|}^{J+j_i}P_{\alpha\beta}(U,J), \tag{42}$$

where J is the total angular momentum, and n_i and j_i are initial vibrational quantum number and rotational classical action. The wavenumber is obtained from

$$k^2_{n_ij_i}=\frac{2\mu(E-E_{n_i}-E_{j_i})}{\hbar^2}. \tag{43}$$

The probability $P_{\alpha\beta}$ is obtained as

$$P_{\alpha\beta}=\frac{1}{\mathrm{N}}\sum_i{}'|a^{(i)}_{n_f}|^2, \tag{44}$$

where N is the number of trajectories, $a^{(i)}_{n\mathrm{f}}$ is the amplitude for a transition from quantum state n_i to quantum state n_f, under the ith trajectory and $\alpha=(n_\mathrm{i}, j_\mathrm{i}, l_\mathrm{i})$. For the rotational motion, 'box' quantization is introduced, that is the sum is restricted to trajectories with $j(t\to\infty)$ in the interval $[j_\mathrm{f}-\delta; j_\mathrm{j}+\delta]$, where $\delta=1$ for homonuclear and $\frac{1}{2}$ for heteronuclear molecules. The scattering angle is obtained from the classical trajectories, that is

$$\cos\theta=\frac{\mathbf{P}_R\cdot\mathbf{P}'_R}{P_RP'_R}, \tag{45}$$

where $\mathbf{P}_R$ and $\mathbf{P}'_R$ are the initial and final momentum vectors respectively. Thus we can obtain an expression for the differential cross-section as

$$\sin\theta\frac{\mathrm{d}\sigma_{n_ij_i\to n_fj_f}}{\mathrm{d}\Omega}=\sum_J{}'(2J+1)\sigma_{n_ij_i\to n_fj_f}, \tag{46}$$

where the prime indicates that only trajectories with scattering angle in the interval $[\theta-\frac{1}{2}\Delta\theta;\ \theta+\frac{1}{2}\Delta\theta]$ are used. The energy U in the above equation is defined as the 'classical' energy, that is the sum of translational and rotational energy in this case. The 'symmetrization' or detailed balance correction is then made in a manner similar to that introduced in the collinear collision case. This symmetrization corresponds to defining the total energy E in terms of the classical energy U by the following equation (Billing 1984a):

$$E=E_{n_i}+U+\tfrac{1}{2}(E_{n_f}-E_{n_i})+\frac{(E_{n_f}-E_{n_i})^2}{16U}. \tag{47}$$

We notice that the smallest allowed value of the 'classical' energy is min $U=\frac{1}{4}(E_{n_f}-E_{n_i})$ for which $E=E_{n_f}$. The above expression (46) for the differential cross-section is given as the classical 'elastic' potential scattering differential cross-section multiplied by a quantum probability for a given final state. At small scattering angles this expression is expected to fail (McCann and Flannery 1973). Here the multichannel eikonal treatment, which, as we have seen is very much related to the CP method, can provide a better description of the differential cross-section.

The basis functions in which the total wavefunction are expanded will often depend parametrically on the classical variables, that is the basis functions are obtained as

$$\hat{H}_0(\hat{p}, q; P, Q)\phi_n(q; P, Q) = E_n(P, Q)\phi_n(q; P, Q), \tag{48}$$

where P, Q denote classical and $\hat{p}, q$ quantum variables. The coupled equations for the expansion amplitudes in

$$\psi = \sum_n \phi_n(q; P, Q) a_n(t) \exp\left(-\frac{\mathrm{i}}{\hbar} \int E_n(P, Q)\,\mathrm{d}t \right) \tag{49}$$

are then

$$\mathrm{i}\hbar \dot{a}_n = \sum_n a_n(t)(\langle \phi_m | H_1 | \phi_n \rangle - \mathrm{i}\hbar \langle \phi_m | \dot{\phi}_n \rangle) \exp[\mathrm{i}(\theta_m - \theta_n)], \tag{50}$$

where we have used that

$$H = H_1(q; P, Q) + \hat{H}_0, \tag{51}$$

$$\theta_n(t) = \frac{1}{\hbar} \int_{t_0}^{t} E_n(P(t'), Q(t'))\,\mathrm{d}t'. \tag{52}$$

The time dependence of the basis functions should also be included when deriving the equations of motion from the Ehrenfest averaged potential:

$$H_{\mathrm{eff}} = \langle \psi | H | \psi \rangle, \tag{53}$$

yielding the equations of motion

$$\dot{P} = -\left\langle \psi \left| \frac{\partial H}{\partial R} \right| \psi \right\rangle + \left\langle \psi H \left| \frac{\partial \psi}{\partial R} \right. \right\rangle + \left\langle \frac{\partial \psi}{\partial R} \right| H \psi \right\rangle, \tag{54}$$

$$\dot{R} = \left\langle \psi \left| \frac{\partial H}{\partial P} \right| \psi \right\rangle - \left\langle \psi H \left| \frac{\partial \psi}{\partial P} \right. \right\rangle - \left\langle \frac{\partial \psi}{\partial P} \right| H \psi \right\rangle. \tag{55}$$

A large reduction in the basis set size is also obtained by treating the rotational projection states classically but quantizing the rotational angular momentum (for example Billing 1986, 1987a).

4.2. *The operator approach*

We have seen that the eikonal and the CP approach leads to a set of coupled equations

$$\mathrm{i}\hbar \frac{\mathrm{d}A_\alpha}{\mathrm{d}t} = \sum_{\alpha' \neq \alpha} \langle \alpha | V_{\mathrm{int}} | \alpha' \rangle A_\alpha(t) \exp\left(\frac{\mathrm{i}}{\hbar} (W_{\alpha\alpha} - W_{\alpha'\alpha'}) \right), \tag{56}$$

where $W_{nn} = \int \mathrm{d}t\,(E_n + V_{nn})$ and $A_\alpha = \delta_{I\alpha}$. The index n only runs over quantum states of that part of the problem which is treated quantally. Equations (56) can be expressed in a matrix form as

$$\mathrm{i}\hbar \frac{\mathrm{d}\mathbf{U}(t, t_0)}{\mathrm{d}t} = \mathbf{V}\mathbf{U}(t, t_0). \tag{57}$$

The solution can formally be written as

$$\mathbf{U}(t, t_0) = \exp[\mathbf{A}(t, t_0)], \tag{58}$$

where $\mathbf{A} = \Sigma_i \mathbf{A}_i$ and

$$\mathbf{A}_1 = -\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} \mathrm{d}t'\,\mathbf{V}, \tag{59}$$

$$\mathbf{A}_2 = \frac{1}{2\hbar^2}\int_{t_0}^{t} \mathrm{d}t' \int_{t_0}^{t'} \mathrm{d}t''\,\mathbf{V}(t'), \mathbf{V}(t'')], \text{etc.} \tag{60}$$

For closed Lie algebraic groups of operators $\{H_j\}$ (Miller 1968) we can introduce the operator representation of the evolution operator as

$$U(t, t_0) = \prod_i \exp\,[\alpha_j(t, t_0)H_j], \tag{61}$$

where the functions α_j are obtained by solving a time-dependent matrix equation of the order $M \times M$, where M is the number of operators. Thus, for systems where the Hamiltonian is of the type

$$H = \sum_k \hbar\omega_k(a_k a_k^+ + \tfrac{1}{2}) + \sum_k (f_k^+ a_k^+ + f_k^- a_k) + \sum_{k<k'} (F_{kk'}^+ a_{k'}^+ a_k + F_{kk'}^- a_k^+ a_{k'}), \tag{62}$$

where a_k^+ and a_k are the creation and annihilation operators for mode k, and $f_k^{\pm}$ and $F_{kk'}^{\pm}$ are the linear and quadratic forces respectively, it is possible to use this 'operator' approach to solve the TDSE algebraically (Pechukas and Light 1966, Billing 1980). This has been the basis for a semiclassical treatment of energy transfer in polyatomic molecules (Billing 1984a), molecule surface scattering (Billing 1982) and the reaction path approach to chemical reactions (Billing 1984c). The operator solution, that is the solution within the harmonic approximation, can serve either as an approximate but often realistical model for a large system or as a zeroth-order approximation on which the 'true' anharmonic can be expanded. Higher-order terms are then included by the perturbation technique. This approach is however, only applicable for not too highly excited polyatomic molecules. Since the harmonic basis in principle forms a complete set, a simple overlap model in which the harmonic basis is projected onto the anharmonic asymptotically could be suggested. This method has recently been used successfully for energy transfer in the CF_4 molecule (Billing 1990).

Some times the interaction can be approximated by a 'nearest-neighbour' coupling model, that is

$$\mathrm{i}\hbar\dot{A}_{In} = V_1 \exp(\pm\mathrm{i}\omega t)\,\delta_{n',n\mp 1} A_{In'}. \tag{63}$$

Here the coupling matrix can be diagonalized by an analytical transformation yielding (for example Billing 1975b)

$$A_{n\to n'} = J_{n-n'}\left(\int_{-\infty}^{\infty} \mathrm{d}t\, V_1(t)\cos\omega t\right), \tag{64}$$

where J_n is a Bessel function.

The CP method given so far has been based upon a symmetrized or detailed balance corrected Ehrenfest approach and we have seen that this to some extent is justified by the first-order expressions and/or the 'eikonal' derivation. The method combines the use of an average potential of the type (41) with an energy mapping (47), where U means the total classical energy. In the next section we wish to put the energy mapping, which so far has been an *ad hoc* correction to the CP theory, on a more firm theoretical ground.

5. Connection to the time-dependent self-consistent field method

It has recently been demonstrated (Muckerman *et al.* in press, Billing 1993a) that one can arrive at a CP theory by introducing a single-configuration SCF approach, that is by assuming a separability between coordinates r and R and introduce a trial function of the type

$$\Psi(r,R,t)=\psi(r,t)\Phi(R,t), \tag{65}$$

where r denote the vibrational coordinate of a diatomic molecule and R the translational coordinate for the relative motion. Introducing a Gaussian-type wave-packet (GWP) for the latter motion, that is

$$\Phi(R,t)=\exp\left(\frac{i}{\hbar}\{\gamma(t)+P(t)[R-R(t)]+A(t)[R-R(t)]^2\}\right) \tag{66}$$

and inserting this the trial function in the TDSE

$$i\hbar\frac{\partial\Psi}{\partial t}=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+v(r)-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2}+H_1(r,R)\right)\Psi(r,R,t), \tag{67}$$

where m is the reduced mass of the diatomic molecule and μ the reduced mass for the motion of the atom A relative to the diatomic molecule BC. By equating terms of power $\Phi(R,t)[R-R(t)]^n(n=0,1,2)$, one obtains the following set of equations:

$$\dot{R}(t)=\frac{P(t)}{\mu}, \tag{68}$$

$$-\dot{P}(t)=\langle\psi|\frac{\partial H_1(r,R)}{\partial R}\bigg|_{R=R(t)}|\psi\rangle, \tag{69}$$

$$-\dot{A}(t)=\frac{2A(t)^2}{\mu}+\tfrac{1}{2}\langle\psi|\frac{\partial^2 H_1(r,R)}{\partial R^2}\bigg|_{R=R(t)}|\psi\rangle \tag{70}$$

$$\dot{\gamma}(t)=\frac{P(t)^2}{\mu}+\frac{i\hbar A(t)}{\mu}, \tag{71}$$

where the angular brackets indicate integration over the coordinate r. Furthermore the following equation for $\psi(r,t)$ was obtained:

$$i\hbar\frac{\partial\psi}{\partial t}=F(t)\psi+[H_0+H_1(r,R(t))]\psi(r,t), \tag{72}$$

where $F(t)$ is a phase factor given by

$$F(t)=\dot{\gamma}-P(t)\dot{R}(t)+\frac{P(t)^2}{2\mu}-\frac{i\hbar A(t)}{\mu} \tag{73}$$

and

$$H_0=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+v(r). \tag{74}$$

Using equations (68) and (71) we see that $F(t)=0$. Equation (72) can be solved by expanding in eigenstates to H_0 or by grid methods (see below). Expanding in eigenstates to H_0 we obtain

$$i\hbar\dot{a}_n=E_n a_n(t)+\sum_m\langle\phi_n|H_1(r,R(t))|\phi_m\rangle a_m(t), \tag{75}$$

where $a_m(t\rightarrow -\infty)=\delta_{mI}$ and I denotes the initial internal state. Thus we see that the CP equations arises (from first principles) if a single-configuration SCF trial function is introduced and if the GWP description of the relative motion holds. However, it is important to realize that the GWP represents not only a spread in coordinate but also a spread in momentum space that is one is running all energies with one wavepacket. In order to extract information on the probability for a quantum transition $I\rightarrow F$ at a given energy we should project the initial and final total wavefunction $\Psi(r,R,t)$ $(t\rightarrow \pm\infty)$ on an incoming wave $\psi_I(r)\exp(-ik_IR)$ and outgoing wave $\psi_F(r)\exp(+ik_FR)$ respectively. The transition probability is then obtained as a ratio of the outgoing and incoming fluxes, that is as

$$P_{I\rightarrow F}=F_{\rm kin}\left(\left|\int \mathrm{d}R\exp(-ik_FR)\,\Phi(R,t)\right|^2\Big/\left|\int dR\exp(ik_IR)\,\Phi(R,-t)\right|^2\right)|a_F(t)|^2 \quad (76)$$

where $t\rightarrow\infty$, k_I is the wavenumber given by

$$\frac{\hbar^2k_I^2}{2\mu}=E-E_I \quad (77)$$

and $F_{\rm kin}$ a kinematic factor which quantum-mechanically would be $F_{\rm kin}=k_F/k_I$ but semiclassically (Muckerman *et al.*) is $F_{\rm kin}=P(-t)^2/P_IP_F$, where $P_I=\hbar k_I$. The above projection is that normally used in wave-packet calculations (for example Jolicard and Billing 1991) but, if a GWP is assumed to hold at all times (and not only initially), then the integral can be evaluated analytically to give

$$P_{I\rightarrow F}=\left(\frac{g(t)}{g(-t)}\right)^{1/2}\exp\{-g(t)[P(t)-p_F]^2+g(-t)[P(-t)+p_I]^2\}\,F_{\rm kin}|a_F(t)|^2 \quad (78)$$

where

$$g(t)=\frac{\mathrm{Im}\,[A(t)]}{2\hbar|A(t)|^2}. \quad (79)$$

If the TDSE had been solved exactly instead of approximately by assuming a single SCF configuration and assuming a GWP at all times, then the above transition probability would be independent of the initial centre of the GWP $P(-t)=P_0$ and of the initial width $A(-t)$ (Jolicard and Billing 1991). However, owing to the approximations introduced in the solution method we cannot expect this to be the case for equation (78). Thus the transition probability will depend on these parameters but Muckerman *et al.* (in press) and Billing (1993a) have demonstrated that we can define optimum or best momentum P_0^* (figure 3) such that the probability is independent of the width parameter α_0, that is the best momentum is defined variationally by

$$\left.\frac{\partial P_{I\rightarrow F}}{\partial\alpha_0}\right|_{P(-t)=P_0^*}=0, \quad (80)$$

where α_0 is most conveniently (from a numerical point of view) taken as the width at the turning point $(P(t=0)=0)$, that is such that $\mathrm{Im}\,[A(t=0)]=\alpha_0$ and $\mathrm{Re}\,[A(t=0)]=0$ (Billing 1993a). It has turned out that the P_0^* defined variationally is at low energies very close to the arithmetic mean value, that is close to

$$P_{\rm av}=\tfrac{1}{2}(P_I+P_F). \quad (81)$$

Thus this derivation (from first principles) gives not only the CP equations but also a natural definition of the initial momentum to be used, a momentum which we see is

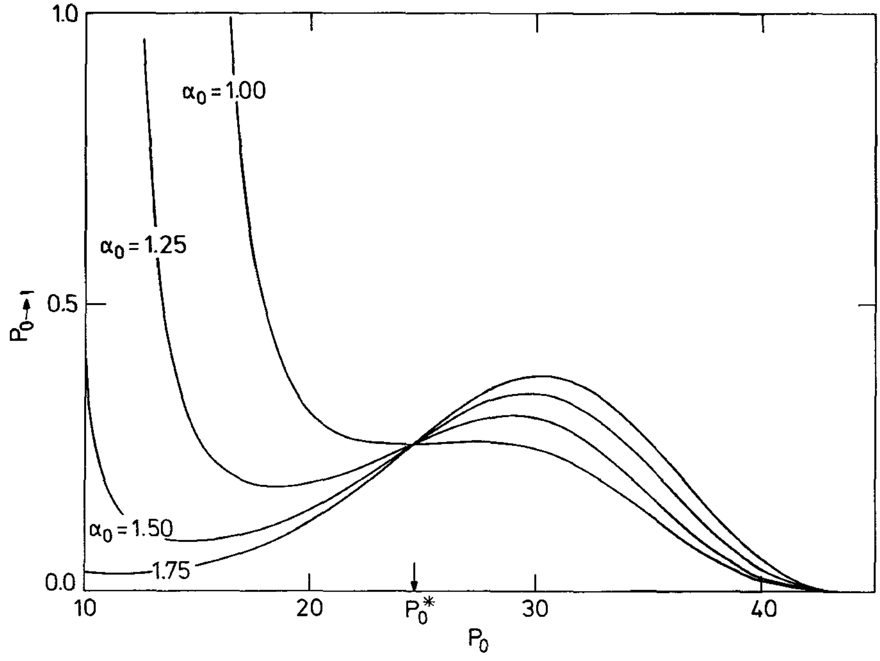

Figure 3. Variational determination of P_0, the initial momentum in the CP theory (from Muckerman *et al.* (in press). The transition probability P_{01} is independent of α_0(width of the wave packet for $P_0=P_0^*$.

otherwise not defined in the CP theory. Furthermore correction terms involving the width of the wave bracket arise. However, what is more important is that it gives an indication when the CP theory will break down, that is when the single-configuration approximation no longer holds. This is the case at higher energies when the two coordinates R and r are strongly mixed and hence the separability approximation invoked by the product-type wavefunction (65) is no longer valid. In order to improve the SCF approach, one can either introduce more configurations, that is use the multiconfiguration method or try to optimize or improve the single-configuration method. The latter can be done either by using a variational procedure to determine free parameters or by looking for coordinates where the separability is larger or a combination of the two methods. We have seen that the derivation of the CP equations given here does not invoke or assume a classical picture. Rather the quantum-mechanical equations of motion do give equations which are classical like and we have seen that the equations are best in the low-energy range, where the separability assumption is expected to hold and where the search from the best momentum converges fast. The CP equations are, however, as we have seen also valid in the other energy limit, that of high energies, where the transition probability becomes independent of the exact nature of the trajectory, that is when $E-E_I\approx E-E_F$. In the intermediate-energy range it is necessary to improve the method by looking for self-consistent trajectories, that is trajectories which are tied to a specific quantum transition. The variational CP method given in the present section is only one way of looking for self-consistent trajectories. Another approach which can be used is based upon a derivation given by Pechukas (1969) using the FP integral representation of quantum mechanics.

6. Connection to the Feynman path method

In the previous section we showed that the CP theory arises when the SCF trial wavefunction is mapped onto quantum-mechanical boundary conditions, that is no assumptions about a classical path was assumed. However, in the FP formulation of quantum mechanics (Feynman and Hibbs 1965) the classical limit arises naturally from the stationary phase of the path integral. What Pechukas (1969) suggested was then to treat part of the system (r) in an ordinary quantum-mechanical fashion while treating the R system within a path integral approach. By looking for the stationary phase, subject to the boundary conditions that the r system should start in a given quantum state I and end in F, an effective path was obtained, that is the stationary phase defines the 'classical' trajectory subject to quantum boundary conditions set by the transition that one considers. This specific trajectory is one which should be used as the 'classical path' when calculating the probability for a given transition. The self-consistent trajectories obtained in this manner lose the energy corresponding to the transition under consideration that is

$$-\Delta E_{\mathrm{kin}}=\lim_{t\to\infty}\left(\frac{1}{2\mu}[P(-t)^2-P(t)^2]\right)=E_F-E_I. \tag{82}$$

Thus the classical part of the system will by the quantum boundary conditions see a system going from the initial state I to F with unit probability. However, when this trajectory is used in the CP equations for the quantum amplitudes (75), we do of course not obtain unit probability for the transition.

The stationary phase defines a trajectory $R(t)$ which is obtained by using the effective potential

$$V_{\mathrm{eff}}=\mathrm{Re}\left(\frac{\langle\psi_F(t_1,t)|H_1(r,R)|\psi_I(t,t_0)\rangle}{\langle\psi_F(t_1,t)|\psi_I(t,t_0)\rangle}\right), \tag{83}$$

where Re denotes the real value, the brackets $\langle\ \rangle$ denote an integration over r, $\psi_I(t,t_0)$ is a wavefunction evolving from the state I forward in time from t_0 to t and $\psi_F(t_1,t)$ is a wavefunction evolving backwards in time from t_1 to t starting in state F. In a state expansion approach these wavefunctions are obtained by solving a set of equations (75) using $R(t)$ obtained from the Hamiltonian equations of motion:

$$\dot{R}(t)=\frac{P(t)}{\mu}, \tag{84}$$

$$\dot{P}(t)=-\frac{\partial V_{\mathrm{eff}}}{\partial R}. \tag{85}$$

Since the effective potential is 'non-local', this can only be done iteratively and problems with convergence of the solution have occurred (Penner and Wallace 1973, 1975, Jolicard 1984). It was later shown (Billing 1987b) that these self-consistent trajectories might be complex, that more than one solution often existed and that phase interference between the trajectories should then be taken into account.

By considering the simple problem of a linearly forced oscillator, Billing (1987b) was able to suggest an alternative formulation of an effective potential which would lead to self-consistent trajectories, namely

$$V_{\mathrm{eff}}=V_0(R)+\eta\langle\psi_I(t,t_0)|V_1(r,R)|\psi_I(t,t_0)\rangle, \tag{86}$$

where we have assumed that the interaction potential can be divided as follows:

$$H_1(r,R) = V_0(R) + V_1(r,R), \tag{87}$$

but V_0 could eventually be absent. The parameter η is defined by

$$\eta = \frac{E_F - E_I}{\Delta E_{\mathrm{cl}}}, \tag{88}$$

where

$$\Delta E_{\mathrm{cl}} = -\int_{t_0}^{t_1} \mathrm{d}t \frac{\partial}{\partial t} \langle \psi_I(t,t_0) | V_1(r,R) | \psi_I(t,t_0) \rangle. \tag{89}$$

We note that $\eta = 1$ gives the usual CP equations with the Ehrenfest averaged potential and that the energy lost by the classical degree of freedom is given as

$$\frac{1}{2\mu}[P(t_0)^2 - P(t_1)^2] = \eta \int_{t_0}^{t_1} \frac{\partial}{\partial t} \langle \psi_I(t,t_0) | V_1(r,R) | \psi_I(t,t_0) \rangle = E_F - E_I, \tag{90}$$

that is just as in the FP formulation of Pechukas. The above effective potential is, however, considerably simpler to use and also easier to generalize to more complicated systems. We note that the equations of motion still have to be solved iteratively since the denominator of η depends upon the whole trajectory from t_0 to t_1. However, it is easy to make the iterative scheme converge using a Newton–Raphson search for the value of η for which self-consistency is obtained. Another important point is that the potential defined by equation (86) is actually the same as obtained in the previous section using the SCF method, but it contains the factor η, that is it involves a scaled Ehrenfest potential. Thus we see that yet another improvement in the single-configuration SCF approach involves the use of a variationally determined 'SCF potential'. The advantages of the single-configuration approach over the multi-configuration method is that it provides the quantum basis for a mixed quantum–classical description and that the classical limit is easily obtained, but cases are known for which the simple single-configuration method fails and a multiconfiguration method should be introduced (for example Makri and Miller 1987a, b, and Kotler *et al.* 1988, 1991).

When the single-configuration method breaks down, it is then the standard procedure to introduce more configurations. However, a possible different avenue does exist, namely to look for quantum corrections to the SCF scheme. Such quantum corrections are those discussed in this and the previous sections; the first resulted in a

Table 1. Possible mixed quantum–classical methods in the treatment of three-body rearrangement processes using hyperspherical coordinates.

ρ	ϕ	θ	γ	References
Q	Q	Q	Q	Kupperman (1975), Kress *et al.* (1990) Launay and Le Dourneuf (1990), Billing and Markovic (1993)
Q	Q	Q	C	Markovic and Billing (1993)
C	Q	Q	Q	Markovic and Billing (1994)
C	Q	Q	C	Muckerman *et al.* (1988)
C	Q	C	C	Jolicard *et al.* (1994)
C	C	C	C	Johnson (1983), Gross and Billing (1993)

variational determination of the best initial momentum and the second in a scaled Ehrenfest potential. Both methods introduce additional quantum aspects compared with the primitive SCF method. The advantage of this avenue is that the classical limit in terms of trajectories is still contained in the formulation. Yet another way of improving the SCF method is to look for variables where the system is separable (by nature) such that the product-type wavefunction can be assumed to hold. In this respect it is especially important not to introduce the separation between degrees of freedom, which are coupled strongly. Such modes should be treated within the same dynamic description (classically or quantally) before deciding how to partition the degrees of freedom. By changing the coordinates it is sometimes possible to make the system more separable.

7. Reactive scattering

As mentioned, it is sometimes desirable to introduce a special coordinate system before the SCF separation is made. An example of this is reactive scattering, where the various channels are strongly coupled in the transition state region. Hence one should look for variables which treat the reaction channels evenhandedly. Such coordinates are the hyperspherical coordinates (for example Johnson 1980, 1983a, b). A mixed quantum–classical description (table 1) of three-body rearrangement processes has been suggested (Muckerman *et al.* 1988, Markovic and Billing 1992a, b) using a classical mechanical treatment of for example the motion along the hyperradius and of the rotation of the hyperplane in space, that is of the Euler angles α, β and γ. The hyperspherical coordinates ρ, θ and ϕ are defined implicitly through the Jacobi coordinates. Thus the variables ρ, θ, ϕ specify the shape and size of the ABC triangle. Its orientation in space is given by three Euler angles mentioned above. Within these variables, one obtains the following (Johnson 1983a, b) Hamiltonian:

$$\hat{H}=\frac{1}{2\mu}\left(\hat{P}_\rho^2+\frac{4\hat{L}^2(\theta,\phi)}{\rho^2}\right)+\frac{\hat{J}_z(\hat{J}_z-4\cos\theta\,\hat{P}_\phi)}{2\mu\rho^2\sin^2\theta}$$
$$+\frac{\hat{J}^2-\hat{J}_z^2+\sin\theta\,(\hat{J}_+^2+\hat{J}_-^2)}{\mu\rho^2\cos^2\theta}+\Delta V(\rho,\theta)+V(\rho,\theta,\phi), \tag{91}$$

where

$$\hat{L}^2(\theta,\phi)=-\hbar^2\left(\frac{\partial^2}{\partial\theta^2}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right), \tag{92}$$

$$\hat{J}_z=\frac{\hbar\,\partial}{\mathrm{i}\,\partial\gamma}, \tag{93}$$

$$\Delta V(\rho,\theta)=-\frac{\hbar^2}{2\mu\rho^2}\left(\frac{1}{4}+\frac{4}{\sin^2(2\theta)}\right) \tag{94}$$

and $J_\pm$ are the raising and lowering operators working on the rotational wavefunctions $D^J_{MK}(\alpha,\beta,\gamma)$ in which the total wavefunction can be expanded. We note that the Hamiltonian is independent of the two Euler angles α and β. Hence the corresponding momenta are constants of motion J and M, respectively. Thus the complete quantum problem is four dimensional (4D) but by treating for example the motion along the hyperradius classically (by substituting the operator P_ρ by its classical analogue it is possible to reduce the problem to a three-dimensional 3D quantum problem.

Furthermore a classical treatment also of the Euler angles brings the problem down to a two-dimensional (2D) quantum-mechanical problem. Such problems are easily handled by grid methods (see below) and this approach then has the advantage that the problem can be solved for multisurface situations arising when non-adiabatic electronic transitions are of interest. The 2D quantum problem, where θ and ϕ are quantized can be shown asymptotically to correspond to a quantum treatment of the rotational and vibrational motion but a classical treatment of the rotational projection (magnetic) quantum number (Muckerman *et al.* 1988). One drawback of the hyperspherical coordinates is, however, that they are not appropriate asymptotic coordinates, that is one usually has to shift to other (e.g. Jacobi) coordinates when the hyperradius becomes large. How large depends upon the masses of the three particles. If the wavefunction is known in the full 4D space, a projection onto other coordinates is no problem but, if a semiclassical approximation is used, the wavefunction is only represented in part of space, say θ and ϕ. Then it becomes necessary to work with mixed Jacobi–hyperspherical coordinates in order to perform the asymptotic propagation (Muckerman *et al.* 1988, Markovic and Billing 1992a, b). If only the hyperangles θ and ϕ are quantized we obtain a mixed quantum–classical Hamiltonian:

$$H_{\text{mixed}} = \hat{H}_0(\theta,\phi;\rho) + \frac{P_\rho^2}{2\mu} + \hat{H}_1(\theta,\phi,t;J), \tag{95}$$

where

$$\hat{H}_0(\theta,\phi;\rho) = \frac{2}{\mu\rho^2}\hat{L}^2(\theta,\phi) + \Delta V(\rho,\theta) + V(\rho,\theta,\phi) \tag{96}$$

and

$$\hat{H}_1 = \frac{P_\gamma(P_\gamma + 4i\hbar\cos\theta\,\partial/\partial\phi)}{2\mu\rho^2\sin^2\theta} + \frac{J^2 - P_\gamma^2}{\mu\rho^2\cos^2\theta}[1+\sin\theta\cos 2\gamma)]. \tag{97}$$

For $\rho\rightarrow\infty$ the Hamiltonian reduces to

$$\begin{aligned} H_{\text{mixed}}(\rho\rightarrow\infty) = {} & -\frac{2\hbar^2}{\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{1}{x}\frac{\partial}{\partial x} - \frac{1}{4x^2}\right) \\ & -\frac{2\hbar^2}{\mu x^2}\left(\frac{\partial^2}{\partial\eta^2} + \frac{1}{4\sin^2\eta} + \frac{1}{4}\right) + \frac{P_J^2 - P_\gamma^2}{\mu x^2\sin^2\eta}[1+\cos(2\gamma)], \end{aligned} \tag{98}$$

where x is a vibrational coordinate $x = 2r/d_i$, d_i is a constant depending on the arrangement channel (Muckerman *et al.* 1988) and η is the angle between the diatom bond axis and the vector from the atom to the centre of mass of the diatom. The eigenfunction to the above equation is

$$\phi_{vj}(x,\eta;\nu) = \frac{1}{x^{1/2}}(-\sin\eta)^{1/2}g_{vj}(x)P_j^\nu(\cos\eta), \tag{99}$$

where P_j^ν is an associated Legendre polynomial with continuous value of ν, that is

$$\nu = \frac{\cos\gamma}{\hbar}(P_J^2 - P_\gamma^2)^{1/2}. \tag{100}$$

The 'adiabatic' eigenfunctions to $\hat{H}_0$ depend parametrically on the classical coordinate ρ, that is

$$\hat{H}_0(\theta,\phi;\rho)\psi_n(\theta,\phi;\rho) = E_n(\rho)\psi_n(\theta,\phi;\rho), \tag{101}$$

where n denote a vibrational–rotational state (v,j). In the semiclassical approach the total wavefunction is expanded in these eigenfunctions:

$$\Psi(\theta,\phi,t)=\sum_n a_n(t)\psi_n(\theta,\phi;\rho(t)). \tag{102}$$

Inserting in the TDSE we obtain a set of coupled equations in the expansion coefficients, that is

$$\dot{a}_m(t)=-\sum_n a_n(t)\exp\left[\mathrm{i}\,\Delta_{nm}(t)\right]\left(\dot{\rho}\langle\psi_m|\frac{\partial}{\partial\rho}|\psi_n\rangle+\frac{\mathrm{i}}{\hbar}\langle\psi_m|\hat{H}_1|\psi_n\rangle\right), \tag{103}$$

where

$$\Delta_{nm}(t)=\frac{1}{\hbar}\int_{-\infty}^{t}\left[E_m(\rho(t'))-E_n(\rho(t'))\right]\mathrm{d}t'. \tag{104}$$

The various vibrational–rotational states are coupled through $\hat{H}_1$ and the non-adiabatic coupling term $\langle\psi_n|\partial/\partial\rho|\psi_m\rangle$. For P_γ values different from P_J the eigenfunctions to H_0 are not appropriate asymptotic eigenfunctions. Rather one should re-expand the total wavefunction in the eigenstates (99).

8. Non-adiabatic transitions

Non-adiabatic transitions involve more than a single electronic state and in this case the classical treatment of the 'slow' nuclear motion and a quantum treatment, of the 'fast' electronic motion becomes a natural and obvious procedure. Thus the quantum–classical approach for these types of problems dates back as mentioned in the introduction to the early days of quantum mechanics. For the electronic degrees of freedom we obtain a TDSE

$$H_{\mathrm{el}}(\mathbf{r},\mathbf{R}(t))\Phi(\mathbf{r},t)=\mathrm{i}\hbar\frac{\partial\Phi(\mathbf{r},t)}{\partial t}. \tag{105}$$

The electronic wavefunction can be expanded for example in an adiabatic basis set as

$$\Phi(\mathbf{r},t)=\sum_n a_n(t)\phi_n(\mathbf{r};\mathbf{R})\exp\left(\frac{1}{\mathrm{i}\hbar}\int E_n(\mathbf{R})\,\mathrm{d}t\right), \tag{106}$$

which yields a set of coupled equations in the expansion coefficients:

$$\mathrm{i}\hbar\dot{a}_n=\sum_m a_m\langle\phi_n|-\mathrm{i}\hbar\frac{\partial}{\partial t}\Big|\phi_m\rangle\exp\left(\frac{1}{\mathrm{i}\hbar}\int\mathrm{d}t\,(E_n-E_m)\right). \tag{107}$$

The non-adiabatic coupling term can be written as

$$\langle\phi_n|-\mathrm{i}\hbar\frac{\partial}{\partial t}|\phi_m\rangle=-\mathrm{i}\hbar\left\langle\phi_n|\frac{\partial\phi_m}{\partial\mathbf{R}}\right\rangle\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t}. \tag{108}$$

So far the only assumption is that some path can be prescribed for the nuclear motion. However, the most important and intriguing point is which path. Tully and Preston (1971) mention in their original paper that they do not know how to solve this problem in general but refer to the self-consistent trajectory method of Pechukas (1969) as a possibility. Instead they suggest obtaining the trajectory from the following simple effective potential.

$$V_{\mathrm{eff}}=\sum_n|a_n|^2E_n(\mathbf{R}), \tag{109}$$

where E_n is an adiabatic energy surface. Initially the above expression is correct. The trajectory starts on one specific surface since $(a_n(t \to \infty) = \delta_{nI})$ but, as the amplitudes on some of the other surfaces grow, the trajectory ought to split in several components, each following a specific adiabatic surface. In general we cannot expect a single average path to be able to account correctly for the quantum electronic coherence connected with these processes.

A method, in which the trajectory splitting is included is the trajectory surface hopping (TSH) method. In the TSH method the system evolves on an adiabatic potential surface and the trajectory is allowed to jump at the avoided crossings with a probability obtained either from a simple Landau–Zener expression (see § 2) or from the squared amplitudes $|a_n(t)|^2$. After a transition, for example from a lower to an upper surface, the new classical momentum on the upper surface is readjusted so as to give energy conservation (Stine and Muckerman 1978, Miller and George 1972). The TSH method is easy to use but it is often based on the validity of the Landau–Zener probability and also that the transitions are sufficiently localized. In the complex-values time method due to Miller and George (1972) actual crossings between the adiabatic surfaces are searched for in complex coordinate space. In the high-energy limit the model is equivalent to the TSH method (Stine and Muckerman 1976). The formal advantage of the complex trajectory method is that it defines a Hamiltonian which brings the trajectory continuously from one surface to the next. However, in practical calculations it has been less useful since it requires knowledge about the potential energy surface in complex space and also a search for all-'important', that is contributing, paths and that interference effects between them are included properly.

The TSH approach has been 'generalized' in a model proposed by Tully (1990). Here the system is allowed to switch from one surface (k) to another (j) at any point along the trajectory according to the criterion

$$\frac{\Delta t b_{jk}}{a_{kk}} > \xi, \tag{110}$$

where ξ is a random number between zero and unity. The time interval which is Δt integrated over, $a_{kk} = |a_k|^2$ and the terms b_{jk} can be obtained from the CP equations (107) using the fact that

$$\dot{a}_{kk} = \sum_{j \neq k} b_{kj}. \tag{111}$$

The model then assumes a sudden switch from one adiabatic surface to another just as the TSH method and the equations of motion during the infinitely narrow transition period are not known and hence not solved. A Hamiltonian which allows a gradual change can be obtained using the FP formulation (Webster *et al.* 1991) in a small time interval Δt, in which the transition is assumed to take place. Therefore, the trajectory may bifurcate in a number of paths and the procedure is only simple to use if interference effects between the various paths satisfying the quantum boundary conditions can be neglected (Billing 1987b).

The FP formulation has also been used successfully to define a mean path by Freed (1975), Laing and Freed (1979) and Herman and Freed (1983). As mentioned previously, the problem with the trajectory obtained from the FP formulation is that the effective potential governing the nuclear motion is non-local, that is the equations of motion have to be solved iteratively. The iterative scheme can in some cases diverge and there may be more than one solution to the equations (Billing 1987b). However, if the FP formulation is considered in the short-time limit, it is possible to introduce suitable approximations for the transition amplitudes, which makes it easier to obtain the path. Consider for example a system with the Lagrangian

$$L=\tfrac{1}{2}m\dot{r}^2+\tfrac{1}{2}\mu\dot{R}^2-v(r)-V(r,R), \tag{112}$$

where we wish to treat the *r* motion exactly and the *R* motion within a FP formulation. Thus we can introduce the reduced propagator (Pechukas 1969) as

$$K_{nm}(R,t;R',t')=\int\delta R(t)\exp\left(\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}L\,\mathrm{d}t''\right)\alpha_{nm}(R(t)), \tag{113}$$

where *L* is the Lagrangian given by

$$L=\frac{1}{2\mu}\dot{R}^2-V_0(R) \tag{114}$$

and α_{nm} is the amplitude for the *n*-to-*m* transition in the *r* system induced by the 'trajectory' $R(t)$. The semiclassical trajectory is then defined in the usual FP sense as the solution to

$$\delta S(R(t))=0, \tag{115}$$

where

$$S=\int_{t'}^{t}\mathrm{d}t''\{L(\dot{R},R,t'')+\hbar\, Im ln(\alpha_{nm})]\}, \tag{116}$$

where the imaginary part is taken so as to obtain a real trajectory. In cases where α_{nm} is known analytically, it is then easy to obtain the effective potential governing the *R* motion. This is the case for solvable models such as the linearly forced harmonic oscillator (Billing 1987b). Also in the short-time limit it is possible to introduce a simple expression for the amplitude α_{nm} using for example the Magnus (1954) expansion where

$$\alpha_{nm}=\langle\phi_n|\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}\hat{H}(t'')\,\mathrm{d}t''\right)|\phi_m\rangle+\text{higher-order terms} \tag{117}$$

and

$$H(t)=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}+v(r)+V_1(r,R(t)). \tag{118}$$

We have assumed that the interaction potential can be split in $V(r,R)=V_0(R)+V_1(r,R)$. In each time interval the matrix

$$\mathbf{A}(t,t')=\int_{t'}^{t}\mathrm{d}t''(\mathbf{L}-\mathbf{V}_0-\mathbf{H}) \tag{119}$$

is diagonalized and the reduced propagator obtained as

$$\mathbf{K}(R,t;R',t')=\int\delta R(t'')\,\mathbf{U}\exp(\mathrm{i}\mathbf{D}(t,t'))\mathbf{U}^+ \tag{120}$$

and

$$\mathbf{U}^+\mathbf{H}\mathbf{U}=\mathbf{D}. \tag{121}$$

Here we have used the notation $\mathbf{V}_0 = V_0\mathbf{I}$, $\mathbf{L} = L(\dot{R}, R, t)\mathbf{I}$ and $\mathbf{H}_{nm} = \langle \phi_n | \hat{H} | \phi_m \rangle$. The path integral is evaluated by stationary phase method, that is

$$K_{nm} = \sum_{p} \int \delta(R(t))\, U_{np} \exp[\mathrm{i}D_{pp}(t, t')]\, U^{*}_{mp} \tag{122}$$

defines p paths by

$$\delta S_{pp}|_{R=R_P} = 0. \tag{123}$$

For the two state cases (relevant for many non-adiabatic problems), one obtains (Laing and Freed 1979, Freed 1975, Herman and Freed 1983) that the trajectories are governed by the following two effective potentials:

$$V_{\pm} = \tfrac{1}{2}(V_{11} + V_{22}) \pm \tfrac{1}{2}\frac{(V_{11} - V_{22}) + 2\alpha V_{12}}{(1+\alpha^2)^{1/2}}, \tag{124}$$

where

$$\alpha = 2\int_{t'}^{t} \mathrm{d}t''\, V_{12}(t'') \Big/ \int_{t'}^{t} \mathrm{d}t''\, (V_{11} - V_{22}), \tag{125}$$

the V_{ii} denote the diabatic potential surface and the V_{12} denote the coupling between them. We notice that α depends upon the trajectory for the entire time interval, that is the equations of motion are solved iteratively, but the iterative scheme for the equations of motion

$$\tfrac{1}{2}\mu \ddot{R} = -\nabla V_{\pm} \tag{126}$$

converges rapidly owing to the small time step taken. The stationary phase defines the trajectory and the path integral is evaluated by a second-order expansion around this trajectory (Feynman and Hibbs 1965). The combined Feynman–Magnus method has features common to the TSH method in that the transition takes place at specific times defined by the Magnus time intervals. The final result should then be independent of the size of these. This will obviously be the case for very small time steps where the Magnus expansion with only a single term included is accurate. In this limit it is possible to invoke the short-time approximation when evaluating the propagator $K(x_2t_2;\, x_1t_1)$. However, for many-dimensional problems it becomes numerically cumbersome to work directly with the propagator. It is advantageous to propagate the wavefunction, that is to introduce the fact that

$$\phi(x_2, t_2) = \int \mathrm{d}x_1\, K(x_2t_2; x_1t_1)\phi(x_1, t_1). \tag{127}$$

For $t_2 = t_1 + \Delta t$ we have (Makri and Miller 1987a, b)

$$K(x_2t_2; x_1t_1) = \left(\frac{m}{2\pi \mathrm{i}\hbar\, \Delta t}\right)^{1/2} \exp\left(\frac{\mathrm{i}m\, \Delta x^2}{2\hbar\, \Delta t} - \frac{\mathrm{i}}{\hbar}\frac{\Delta t}{\Delta x}\int_{x_1}^{x_2} \mathrm{d}x\, V(x)\right). \tag{128}$$

We note that the propagator is highly oscillatory in the limit $\Delta t \rightarrow \infty$. The integral (127) can be evaluated if a second-order expansion of the potential around $x = \frac{1}{2}(x_1 + x_2)$ is introduced and if the wavefunction is expressed in a Fourier series, that is

$$\phi(x_1, t_1) = \sum_{k=-N/2}^{N/2} c_k \exp(-\mathrm{i}\theta_k x_1). \tag{129}$$

The result is

$$\phi(x_2, t_1+\Delta t)=\left(\frac{1}{1-\alpha\,\Delta t^2}\right)^{1/2}\exp\left(-\frac{\mathrm{i}}{\hbar}\Delta t\, V(\bar{x})\right)\sum_k d_k \exp(-\mathrm{i}\theta_k x_2), \tag{130}$$

where

$$a=\frac{1}{12m}\frac{\mathrm{d}^2V}{\mathrm{d}x^2}\bigg|_{x=\bar{x}}, \tag{131}$$

$$d_k=c_k\exp\left(-\frac{\mathrm{i}\hbar\,\Delta t}{2m}\theta_k^2\Big/(1-a\,\Delta t^2)\right). \tag{132}$$

We note that the last factor can be evaluated by performing the inverse Fourier transform with the coefficients c_k replaced by d_k and that the poor behaviour with respect to Δt has disappeared. Therefore it is advantageous to work directly with the propagation of the wavefunction itself rather than the propagator. Such propagation schemes will be discussed in the next section.

9. Grid methods

The possibility of introducing a discrete representation of the wavefunction on a grid and thereby being able easily to treat dissociative and reactive coordinates has been important for the further development of the classical path method. Furthermore, since in the grid as in the CP method one considers and solves the TDSE, grid methods makes it easy to introduce additional quantization, that is to quantize degrees of freedom which otherwise would have been treated classically. In this manner, one obtains an approach where classical mechanics is mixed with a quantum (operator or state expansion) technique and a quantum grid expansion (Billing 1991).

Thus classical mechanics should be used for translational and rotational degrees of freedom (of heavy molecules), state (or quantum operator) expansion for electronic and vibrational degrees of freedom and grid methods for reactive or dissociative coordinates.

The grid methods are based upon the evaluation of the kinetic energy terms by a fast Fourier transform (FFT) or a discrete variable representation methodology combined with a method for the time propagation, for example Kossloff, 1988, Feit *et al.* 1982 and Park and Light (1986). In grid methods, one obviously operates with a finite grid and a finite number of grid points. This gives some restrictions as far as the energy resolution and the physical dimensions of the system which can be studied. In order to avoid unphysical reflection near the boundaries, it is necessary to introduce an absorbing optical potential near the edges of the grid. Usually about 30% of the grid is used for the optical potential. Only with a reasonably soft optical potential is it possible to absorb both low- and high-energy components of a scattered wave packet (Neuhauser and Baer 1989).

Thus considering a wavefunction $\phi(x)$ on a grid from 0 to $x_{\max}$ the wavefunction is represented on the grid as

$$\phi_i=\phi(x_i),\ \text{where } x_i=i\,\Delta x+\tfrac{1}{2}\Delta x,\quad i=0,\ldots,N-1 \tag{133}$$

and $\Delta x=x_{\max}/N$. Since the Hamiltonian may contain singular terms at the boundaries the grid points are shifted with $\frac{1}{2}\Delta x$. The Fourier transform is now given as (Press *et al.* 1986)

$$\phi(x_j)=\left(\frac{1}{N}\right)^{1/2}\sum_{k=0}^{N-1} c_k\exp\left(-\frac{\mathrm{i}2\pi kj}{N}\right), \tag{134}$$

where $j=0, 2, \ldots, N-1$. The wavenumbers are given by (Press *et al.* 1986)

$$k_i=\frac{2\pi}{\Delta x}\frac{i}{N}, \quad i\leqslant\tfrac{1}{2}N+1, \tag{135}$$

$$k_i=\frac{2\pi}{\Delta x}\frac{i-N}{N}, \quad i>\tfrac{1}{2}N+1. \tag{136}$$

The derivatives of the wavefunction can easily be obtained by multiplying the fourier component c_k with k_i and making the inverse FFT. Once the effect of the momentum operators has been calculated at each grid point, we can propagate the solution in time by using for example the Lanczos reduction technique (Park and Light 1986). In the grid representation we can write the TDSE as

$$i\hbar\dot{\phi}=\mathbf{H}\phi, \tag{137}$$

where ϕ is a vector of length N containing the wavefunction at the N grid points and $\mathbf{H}$ is an $N\times N$ matrix. We now define a transformation matrix $\mathbf{T}$ which tridiagonalizes $\mathbf{H}$:

$$\mathbf{T}=[\phi_0, \phi_1, , \ldots, \phi_{N-1}]. \tag{138}$$

The vectors ϕ_k where ϕ_0 is the initial wavefunction are found by using the Lanczos recursion scheme:

$$\mathbf{H}\phi_0=\alpha_0\phi_0+\beta_1\phi_1, \tag{139}$$

$$\mathbf{H}\phi_k=\beta_k\phi_{k-1}+\alpha_k\phi_k+\beta_{k+1}\phi_{k+1}, \tag{140}$$

where $k=1, \ldots$. The transformation matrix $\mathbf{T}$ transforms $\mathbf{H}$ to a tridiagonal matrix of dimension $L\times L$, where L is the number of recursions. This matrix is then diagonalized and the wavefunction at time $t+\Delta t$ given as in

$$\phi(t+\Delta t)=\mathbf{TS}\exp\left(-\frac{\mathrm{i}}{\hbar}\mathbf{D}\,\Delta t\right)\mathbf{S}^{+}\mathbf{T}^{+}\phi(t), \tag{141}$$

where $\mathbf{S}$ is the matrix diagonalizing the tridiagonal matrix and $\mathbf{D}$ is the diagonal matrix containing the eigenvalues. The advantage of the FFT method for evaluating the kinetic energy terms is that it scales favourably with the number N of grid points, namely as $N\log N$. However, at present it is not possible to treat more than a few (three to four) degrees of freedom in this manner. This appears also not be be necessary, since the grid methods have to be introduced only for the coordinates in which bond breaking or dissociation occur, that is situations where other methods as state expansion methods need a large number of continuum state in order to obtain convergence. Again the restrictions inherent in any quantum approach for molecular dynamics makes it necessary to invoke some approximations. Here the CP method is an obvious possibility since it introduces an approximate classical description for degrees of freedom which are difficult or even impossible to resolve experimentally. Thus these degrees of freedom should be averaged over by Monte Carlo technique; this is most easily done by running trajectories over the phase space in question. Furthermore the introduction of classical dynamics does in most cases not introduce any dynamic constraints in that part of the system which is described classically. Other methods which are based on a full quantum-mechanical description of the system must in order to obtain the same reduction in the complexity for the solution of the dynamic equations introduce approximations which may act as severe constraints on the dynamics (Billing 1993b, Gianturco *et al.* 1993).

10. Discussion and future development

As mentioned above, the part of the system which is described by classical mechanics is described dynamically 'correct', where by correct we mean without constraints imposed on the Hamiltonian. However, to use classical dynamics is of course an approximate way of describing the system. Hence classically forbidden events are not accounted for properly, if at all. If one now quantizes that part of the system which is not described well by classical mechanics, one should think that an adequate approach is obtained. This philosophy is actually the one on which the CP method is based. However, the two dynamics are of such a different nature that the mere division of the system into two parts treated within different dynamics is itself an *additional* approximation. Thus it is not obvious how the dynamics of the two systems should be coupled together. We have seen that several possibilities exist; each of these define an effective potential which incorporates various aspects of the quantum–classical coupling. If the energy of the classical system is large, then the perturbation from the quantum subsystem on the dynamics may be negligible. Hence the effective potential can be taken as just V_0 (as for example defined in equation 86) and the classical dynamics are independent of the quantum system. In the opposite limit, at low energies, the system may be in the dynamically separable limit where we can introduce a single-configuration wavefunction and hence derive an Ehrenfest effective potential describing the interaction combined with a variational determination of the momentum. In the intermediate-energy range where the classical and quantum systems are coupled strongly together we can use either the FP approach, which has to be solved iteratively, or a quantum-corrected SCF approach (Billing 1993a). However, it is also important to realize that the validity of the CP approach can be extended by treating strongly coupled degrees of freedom within the same dynamic approach. Thus at low energies, rotational and vibrational motion should be quantized and the 'SCF separability' put between the translational and the internal motion. At higher energies the rotational and translational motion will be strongly coupled and hence these two degrees of freedom should be treated classically and the 'SCF separation' made between the vibrational degree of freedom and the other two. Thus it is possible to extend the range of validity of the SCF and the classical path method by this simple recipe. However, in some cases the situation is not so simple. For reactive scattering problems, vibrational degrees of freedom in one channel are translational in another and hence special coordinates which do not discriminate between the various arrangement channels have to be introduced before the separation is made. Even so the problem with the single-trajectory approach, which arises from the GWP SCF scheme, is that the path cannot bifurcate in situations where it should, that is when the quantum probability (the wave packet) in various physical distinct regions become large. This happens in reactive scattering problems and for electronic non-adiabatic transitions. In such cases there does not at present exist a completely satisfactory CP approach. A possibility is to introduce a multiconfiguration GWP SCF approach which would define more than one path. Future research in the development of the CP theory should therefore deal with the above-mentioned situations in an attempt to extend the range of validity of the CP approach, without sacrificing the need for computational simplicity.

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