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SECOND-ORDER EXPRESSION OF BORN PROBABILITIES BY PARTITIONING AND LAPLACE TRANSFORM METHODS

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Abstract

The formalism and first- and second-order approximations for a perturbation-theoretical treatment of the time-dependent solutions of the Schrödinger equation are discussed in the context of possible applications to hydrogen-bonded systems. Equations are proposed that can help to model the essential features of such systems.

The treatment of tunnelling in a double-minimum system, e.g. a hydrogen bridge, interacting with an environment is an important problem [1–3]. The transfer of a proton initially localized in one of the two wells of the system may be involved in biochemical processes of many kinds [4,5]. So far, an explicit analysis of the temporal aspects of the transfer problem has been missing; although the fundamental quantum mechanical concepts are well known, treatments susceptible to application are fairly recent [1,6,7]. In this paper, we propose a perturbational analysis of the same problem, leading to a decomposition of Born transfer probabilities into contributions susceptible to different interpretations.

We start from a localized description derived as follows. Let the total Hamiltonian operator be

$$H = T + V_L + V_R + V_{LR} + H^{ext} + V^{int}. \tag{1}$$

The physics of the problem is contained in the four potential-energy terms (T being the usual kinetic energy operator) and in H^{ext}. The potential energies V_L, V_R may be thought of as two single minimum one-dimensional profiles (parabolas, Morse curves, etc.); V_{LR} represents a correction term transforming them into a continuous double-well profile; H^{ext} is the Hamiltonian operator associated to the degrees of freedom not directly involved in the transfer and to the environment; V^{int} is the interaction between the transfer mode and all other degrees of freedom.

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The two local Hamiltonians $T + V_L$ and $T + V_R$ define a subspace spanned by sets $|\chi_L\rangle$, $|\chi_R\rangle$ of (mutually orthogonal) states localized on the left-hand minimum or the right-hand minimum of the given system. A general state $|k(t)\rangle$ can then be expanded as

$$|k(t)\rangle = |\chi_L\rangle L_k + |\chi_R\rangle R_k \tag{2}$$

in terms of time-dependent column vectors L_k and R_k. The composite vector $C_k^+ = (L_k^+, R_k^+)$ obeys the usual Schrödinger equation of motion:

$$\mathrm{d}C_k/\mathrm{d}t = -\mathrm{i}H C_k; \quad C_k = \begin{vmatrix} L_k \\ R_k \end{vmatrix}. \tag{3}$$

Partitioning of the Hamiltonian matrix

$$H = \begin{vmatrix} H_{LL} & H_{LR} \\ H_{RL} & H_{RR} \end{vmatrix} \tag{4}$$

enables one, in analogy to the procedure of Adelmann and Doll [8] and McDowell [9], to derive with the help of Laplace transforms from eq. (3) an equation of motion for L_k,

$$\dot{L}_k = -\mathrm{i}H_{LL}L_k + \int_0^t \mathrm{d}t' M(t-t')L_k + B_k(t), \tag{5}$$

with

$$M(t) = -H_{LR}\exp(-\mathrm{i}H_{RR}t)H_{RL}(0), \tag{6}$$

$$B_k(t) = -\mathrm{i}H_{LR}\exp(-\mathrm{i}H_{RR}t)R_k(0), \tag{7}$$

where the index k points to the fact that the state under study is $|k(t)\rangle$, which was initially $|k(0)\rangle = |k\rangle$. The probability for the particle to move from the right- to the left-hand side is then

$$W_{RL} = \sum_{\substack{k \in \mathcal{H}_R \\ m}} L_{mk}^* p_{kk} L_{mk} = \sum_{k \in \mathcal{H}_R} (L_k^+ L_k) p_{kk}, \tag{8}$$

where k now refers in particular to a state initially localized on the right-hand side, and L_{mk} denotes the mth element of the vector L_k. The p_{kk}'s are the statistical weights of the initial states. The time evolution of W_{RL} is, therefore, essentially determined by $L_k^+ L_k$, and W_{RL} obeys the following equation of motion

$$\dot{W}_{\mathrm{RL}} = \sum_k (\dot{\boldsymbol{L}}_k^+ \boldsymbol{L}_k + \boldsymbol{L}_k^+ \dot{\boldsymbol{L}}_k) p_{kk} = \sum_k [\mathrm{i}\boldsymbol{L}_k^+(t) H_{\mathrm{LL}} \boldsymbol{L}_k(t)$$

$$+ \int_0^t \mathrm{d}t' \boldsymbol{L}_k^+(t') M^+(t-t') \boldsymbol{L}_k(t) + \boldsymbol{B}_k^+(t) \boldsymbol{L}_k(t) - \mathrm{i}\boldsymbol{L}_k^+(t) H_{\mathrm{LL}} \boldsymbol{L}_k(t)$$

$$+ \int_0^t \mathrm{d}t' \boldsymbol{L}_k^+(t') M(t-t') \boldsymbol{L}_k(t) + \boldsymbol{L}_k^+(t) \boldsymbol{B}_k(t)] p_{kk} \,. \tag{9}$$

The problem of partitioning the equations of motion can also be approached in a more formal way. From eqs. (3) and (4), we derive

$$\begin{vmatrix} \boldsymbol{L}_k(t) \\ \boldsymbol{R}_k(t) \end{vmatrix} = \exp(-\mathrm{i}Ht) \begin{vmatrix} \boldsymbol{L}_k(0) \\ \boldsymbol{R}_k(0) \end{vmatrix}, \tag{10}$$

i.e.

$$\boldsymbol{L}_k(t) = [\exp(-\mathrm{i}Ht)]_{\mathrm{LL}} \boldsymbol{L}_k(0) + [\exp(-\mathrm{i}Ht)]_{\mathrm{LR}} \boldsymbol{R}_k(0), \tag{11a}$$

$$\boldsymbol{R}_k(t) = [\exp(-\mathrm{i}Ht)]_{\mathrm{RL}} \boldsymbol{L}_k(0) + [\exp(-\mathrm{i}Ht)]_{\mathrm{RR}} \boldsymbol{R}_k(0). \tag{11b}$$

This is a formal solution for $\boldsymbol{C}_k(t)$, but requires calculation of the complete exponential matrix before taking its (LR)- and (LL)-blocks. Calculation of the (LR)-block can be avoided by the formal solution obtained via Laplace transforms [4]. This shows that

$$(\exp(-\mathrm{i}Ht))_{\mathrm{LR}} = \int_0^t (\mathrm{e}^{-\mathrm{i}H(t-t')})_{\mathrm{LL}} H_{\mathrm{LR}} \, \mathrm{e}^{-\mathrm{i}H_{\mathrm{RR}}t'} \mathrm{d}t'. \tag{12}$$

However, the calculation of the (LL)-block still requires that the exponential of the whole matrix should be evaluated. An alternative procedure may be to solve the two differential equations separately (as inhomogeneous equations):

$$\dot{\boldsymbol{L}}_k = -\mathrm{i}H_{\mathrm{LL}} \boldsymbol{L}_k - \mathrm{i}H_{\mathrm{LR}} \boldsymbol{R}_k, \tag{13a}$$

$$\dot{\boldsymbol{R}}_k = -\mathrm{i}H_{\mathrm{RL}} \boldsymbol{L}_k - \mathrm{i}H_{\mathrm{RR}} \boldsymbol{R}_k. \tag{13b}$$

The formal solutions are, as can be easily shown:

$$\boldsymbol{L}_k(t) = \mathrm{e}^{-\mathrm{i}H_{\mathrm{LL}}t} \boldsymbol{L}_k(0) - \mathrm{i} \int_0^t \mathrm{e}^{-\mathrm{i}H_{\mathrm{LL}}(t-t')} H_{\mathrm{LR}} \boldsymbol{R}_k(t') \mathrm{d}t', \tag{14a}$$

$$\boldsymbol{R}_k(t) = \mathrm{e}^{-\mathrm{i}H_{\mathrm{RR}}t} \boldsymbol{R}_k(0) - \mathrm{i} \int_0^t \mathrm{e}^{-\mathrm{i}H_{\mathrm{RR}}(t-t')} H_{\mathrm{RL}} \boldsymbol{L}_k(t') \mathrm{d}t'. \tag{14b}$$

This yields a recursive equation for $\boldsymbol{L}_k$:

$$\boldsymbol{L}_k(t) = \mathrm{e}^{-\mathrm{i}H_{\mathrm{LL}}t}\boldsymbol{L}_k(0) - \mathrm{i}\int_0^t \mathrm{e}^{-\mathrm{i}H_{\mathrm{LL}}(t-t')}H_{\mathrm{LR}}\mathrm{e}^{-\mathrm{i}H_{\mathrm{RR}}t'}\mathrm{d}t'\boldsymbol{R}_k(0)$$

$$-\int_0^t \mathrm{e}^{-\mathrm{i}H_{\mathrm{LL}}(t-t')}H_{\mathrm{LR}}\int_0^{t'}\mathrm{e}^{-\mathrm{i}H_{\mathrm{RR}}(t'-t'')}H_{\mathrm{RL}}\boldsymbol{L}_k(t'')\mathrm{d}t'\mathrm{d}t''. \tag{15}$$

Laplace transformation yields

$$\tilde{\boldsymbol{L}}_k(s) = (sI + \mathrm{i}H_{\mathrm{LL}})^{-1}\boldsymbol{L}_k(0) - \mathrm{i}(sI + \mathrm{i}H_{\mathrm{LL}})^{-1}H_{\mathrm{LR}}(sI + \mathrm{i}H_{\mathrm{RR}})^{-1}\boldsymbol{R}_k(0)$$

$$-(sI + \mathrm{i}H_{\mathrm{LL}})^{-1}H_{\mathrm{LR}}(sI + \mathrm{i}H_{\mathrm{RR}})^{-1}H_{\mathrm{RL}}\tilde{\boldsymbol{L}}_k(s), \tag{16}$$

which can be solved for $\tilde{\boldsymbol{L}}_k(s)$:

$$\tilde{\boldsymbol{L}}_k(s)$$

$$= [(sI + \mathrm{i}H_{\mathrm{LL}}) + H_{\mathrm{LR}}(sI + \mathrm{i}H_{\mathrm{RR}})]^{-1}[\boldsymbol{L}_k(0) - \mathrm{i}H_{\mathrm{LR}}(sI + \mathrm{i}H_{\mathrm{RR}})^{-1}\boldsymbol{R}_k(0)]. \tag{17}$$

If $\boldsymbol{L}_k(0) = \boldsymbol{0}$ (initial condition that the system is initially localized on the right-hand side) then:

$$\tilde{\boldsymbol{L}}_k(s)$$

$$= [(sI + \mathrm{i}H_{\mathrm{LL}}) + H_{\mathrm{LR}}(sI + \mathrm{i}H_{\mathrm{RR}})^{-1}H_{\mathrm{RL}}]^{-1}(-\mathrm{i})H_{\mathrm{LR}}(sI + \mathrm{i}H_{\mathrm{RR}})^{-1}\boldsymbol{R}_k(0). \tag{18}$$

(This result would, of course, also have been obtained had eqs. (11a,b) been Laplace transformed and solved for $\tilde{\boldsymbol{L}}_k(s)$.)

Let us introduce the notation

$$M = \begin{vmatrix} sI + \mathrm{i}H_{\mathrm{LL}} & H_{\mathrm{LR}} \\ H_{\mathrm{RL}} & sI + \mathrm{i}H_{\mathrm{RR}} \end{vmatrix} \equiv \begin{vmatrix} W & V^+ \\ V & U \end{vmatrix}. \tag{19}$$

Then

$$\tilde{\boldsymbol{L}}_k(s) = -\mathrm{i}[W + V^+U^{-1}V]^{-1}V^+U^{-1}\boldsymbol{R}_k(0). \tag{20}$$

As a check for this result, one can assume all four blocks of M to be diagonal (this would describe a set of two-level systems). Naming $\varepsilon_m^{\mathrm{L}}$ and $\varepsilon_m^{\mathrm{R}}$ the diagonal elements of H_{LL} and H_{RR}, respectively, and V_m the diagonal elements of V, eq. (20) gives, for the mth element of $\boldsymbol{L}_k$:

$$\tilde{L}_{mk}(t) = -\mathrm{i}\frac{V_m^*}{U_m W_m + |V_m|^2} R_{mk}(0) = -\mathrm{i}\frac{V_m^*}{(s+\mathrm{i}\varepsilon_m^{\mathrm{R}})(s+\mathrm{i}\varepsilon_m^{\mathrm{L}}) + |V_m|^2} R_{mk}(0). \quad (21)$$

Taking the inverse transform yields (by partial fraction decomposition)

$$\tilde{L}_{mk}(t) = -\frac{\mathrm{i}V_m^* R_{mk}(0)}{\Omega_m} \mathrm{e}^{-\mathrm{i}\Sigma_m t} \sin \Omega_m t, \quad (22)$$

with

$$\Omega_m = \sqrt{\Delta_m^2 + |V_m|^2}, \ \Sigma_m = \frac{\varepsilon_m^{\mathrm{R}} + \varepsilon_m^{\mathrm{L}}}{2}, \ \Delta_m = \frac{\varepsilon_m^{\mathrm{R}} - \varepsilon_m^{\mathrm{L}}}{2}. \quad (23)$$

In the general case of noncommuting matrices, it is possible to proceed along the same lines by partitioning V into a diagonal part V^0 proportional to the unit matrix and a perturbation V', and bringing eq. (20) to a form similar to eq. (21):

$$\tilde{\boldsymbol{L}}_k(s) = -\mathrm{i}[U W + \tilde{V}^+ V]^{-1} \tilde{V}^+ \boldsymbol{R}_k(0), \quad (24)$$

with

$$\tilde{V} = V^0 + U^{-1^+} V' U^+. \quad (25)$$

The results of eq. (20) can now be applied by introducing a new matrix Y,

$$Y = \tilde{V}^+ V - V^{0^+} V^0, \quad (26)$$

i.e.

$$Y = V^{0^+} V' + U^{-1^+} V'^+ U^{-1^+} V \quad (27)$$

and

$$Y_{mn} = \left(V_{mm} + \frac{U_{mm}}{U_{nn}}\right) V_{mn} + \sum_{\gamma \neq m,n} \frac{U_{\gamma\gamma}}{U_{mm}} V_{\gamma n} V_{\gamma m}. \quad (28)$$

(In some cases, it may be possible to extract an s-independent diagonal term from Y and add it to the first term.) Note now that U and W can be assumed to be diagonal without any loss of generality, because they represent the Hamiltonian matrices associated to the left-hand and right-hand states, respectively. Then, using the first-order binomial expansion $(1 + x)^{-1} \cong 1 - x$, we can write:

$$\tilde{\boldsymbol{L}}_k(s) \approx -\mathrm{i}[U W + V^{0^+} V^0]^{-1} \tilde{F} \boldsymbol{R}_k(0), \quad (29)$$

with

$$\tilde{F} = [I - Y(UW + V^{0+}V^{0})^{-1}]\tilde{V}^{+}$$

$$= [I - (V^{0+}V' + U^{-1+}V'^{+}U^{+}V)(UW + V^{0+}V^{0})^{-1}]\tilde{V}^{+}. \tag{30}$$

The elements of the inverse transform will be

$$L_{mk}(t) = \sum_{n} \int f_m(t-t') F_{mn}(t')\,\mathrm{d}t' R_{nk}(0), \tag{31}$$

where $F_{mn}(t')$ is the inverse Laplace transform of $\tilde{F}_{mn}(s)$ and

$$f_m(t) = -\frac{\mathrm{i}\mathrm{e}^{-\mathrm{i}\Sigma_m t}}{\Omega_m} \sin(\Omega_m t), \tag{32}$$

with Σ_m and Ω_m as defined in eq. (23). (Note that the strong-coupling limit consists of taking only $n = m$ in eq. (31).) The evaluation of the matrix elements of $\tilde{F}$ to first order in V yields

$$\tilde{F}_{mn}(s) = \delta_{mn} V_{mn} + (1 - \delta_{mn}) \frac{U_{mm}}{U_{nn}} V_{mn}$$

$$= \delta_{mn} V_{nn} + (1 - \delta_{mn}) \frac{s + \mathrm{i}\varepsilon_m^{\mathrm{R}}}{s + \mathrm{i}\varepsilon_n^{\mathrm{R}}} V_{mn}. \tag{33}$$

The inverse transform is

$$F_{mn}(t) = \delta_{mn} V_{nn}\, \delta(t) + (1 - \delta_{mn}) V_{mn} (\delta(t) + \mathrm{i}(\varepsilon_m^{\mathrm{R}} - \varepsilon_n^{\mathrm{R}}) \times \mathrm{e}^{-\mathrm{i}\varepsilon_n^{\mathrm{R}} t})$$

$$= V_{mn}\, \delta(t) + (1 - \delta_{mn}) V_{mn} (\varepsilon_m^{\mathrm{R}} - \varepsilon_n^{\mathrm{R}}) \mathrm{e}^{-\mathrm{i}\varepsilon_n^{\mathrm{R}} t}. \tag{34}$$

Then, from eq. (31),

$$L_{mk}(t) = \sum_{n} f_m(t) V_{mn} R_{nk}(0) + \sum_{n} [(1 - \delta_{mn}) V_{mn}\, \mathrm{i}(\varepsilon_m^{\mathrm{R}} - \varepsilon_n^{\mathrm{R}})$$

$$\times \int_0^t f_m(t-t') \mathrm{e}^{-\mathrm{i}\varepsilon_n^{\mathrm{R}} t'} \mathrm{d}t' R_{nk}(0)]. \tag{35}$$

The solution of the integral yields:

$$L_{mk}(t) = A_{mk} f_m(t) + \sum_{n \neq m} D_{mn}^{(k)} R_{nk}(0), \tag{36}$$

with

$$D_{mn}^{(k)} = \frac{V_{mn}(\varepsilon_m^{\mathrm{R}} - \varepsilon_n^{\mathrm{R}})}{2\Omega_m}\left[\frac{\mathrm{e}^{-\mathrm{i}\varepsilon_n^{\mathrm{R}}t} - \mathrm{e}^{-\mathrm{i}(\Sigma_m - \Omega_m)t}}{\varepsilon_n^{\mathrm{R}} - \Sigma_m + \Omega_m} - \frac{\mathrm{e}^{-\mathrm{i}\varepsilon_n^{\mathrm{R}}t} - \mathrm{e}^{-\mathrm{i}(\Sigma_n + \Omega_n)t}}{\varepsilon_n^{\mathrm{R}} - \Sigma_m - \Omega_m}\right]. \tag{38}$$

The first term describes a two-level system modulated by a factor depending on the instantaneous coupling of $|m\rangle$ to the other states, and the second term contains the corrections to the approximation.

Let us consider explicitly the dependence of $\boldsymbol{L}_k$ on the initial condition, which is expressed by the subscript k. In particular, let

$$L_{mk}(0) = 0, \quad R_{mk} = \delta_{mk}. \tag{39}$$

Then,

$$L_{mk}(t) = V_{mk} f_m(t) + D_{mk}^{(k)}(1 - \delta_{mk}). \tag{40}$$

The transition probability of eq. (8) can now be written:

$$\begin{aligned} W_{\mathrm{RL}} = & \sum_{m,k} p_k |V_{mk}|^2 |f_m(t)|^2 \\ & + \sum_{\substack{m,k \\ m \neq k}} p_k (V_{mk}^* f_m^*(t) D_{mk}^{(k)}(t) + V_{mk} f_m(t) D_{mk}^{(k)}(t)) \\ & + \sum_{\substack{m,k \\ m \neq k}} p_k |D_{mk}^{(k)}(t)|^2 . \end{aligned} \tag{41}$$

Equations (40) and (41) only take into account the effect of direct (forward) coupling of initial states $|k\rangle$ to each given final state $|m\rangle$. This limitation to direct coupling is due to the truncation to first order in V' in eq. (33).

The "feedback" effect, which amounts to the dependence of the probability of finding $|m\rangle$ at time t in $|k(t)\rangle$, which was initially $|k\rangle$, on the coupling of $|m\rangle$ to initial states $|n\rangle$ other than $|k\rangle$ requires a second-order treatment. With $Z = (UW + V^{0+}V)^{-1}$, the elements of F can be written (again assuming U and W to be diagonal by the choice of the basis functions):

$$\begin{aligned} \tilde{F}_{mn} = & (1 - \frac{Z_{mm}}{U_{mm}} \sum_{\gamma \neq m} U_{\gamma\gamma} |V_{\gamma m}|^2) \tilde{V}_{nm} \\ & + \sum_{\alpha \neq k} \left[(V_{mm} + \frac{U_{\alpha\alpha}}{U_{mm}} V_{\alpha\alpha}) \times V_{\alpha m} Z_{\alpha\alpha} V_{\alpha m} \frac{U_{nn}}{U_{\alpha\alpha}} \right] \\ & - \sum_{\substack{\alpha(\neq n) \\ \gamma \neq (m,\alpha)}} \frac{U_{\gamma\gamma}}{U_{mm}} V_{\gamma n} V_{\gamma m} Z_{\alpha\alpha} V_{n\alpha} \frac{U_{nn}}{U_{\alpha\alpha}} . \end{aligned} \tag{42}$$

Truncation to second order in V' yields

$$\tilde{F}_{mn} = \tilde{V}_{nm} - \frac{Z_{mm}}{U_{mm}} \sum_{\gamma \neq m} U_{\gamma\gamma} |V_{\gamma m}|^2 V_{mm} \delta_{nm}$$

$$- \sum_{\alpha(\neq n)} \left(\frac{U_{nn}}{U_{\alpha\alpha}} V_{mm} - \frac{U_{nn}}{U_{mm}} V_{\alpha\alpha} \right) V_{\alpha m} Z_{\alpha\alpha} V_{n\alpha} \,. \tag{43}$$

From this expression, it is evident that the coupling of $|m\rangle$ to initial states $|\alpha\rangle$ and $|\gamma\rangle$ other than $|k\rangle$ is now taken into account.

Insertion of eq. (43) into eqs. (29) and (31) provides the expression of the probability taking into account "feedback" effects. An assessment of the scope of this second-order expansion can only be obtained by ad hoc numerical tests which may involve some approximations. Work along these lines is in progress, with application to the formamide dimer in particular.

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