

Common Approximations for Density Operators May Lead to Imaginary Entropy

KARL LENDI* and MANOEL ROTHIER DO AMARAL JR.

Instituto de Física, Universidade Federal do Rio de Janeiro, Caixa Postal 68528, Rio de Janeiro, 21944, RJ, Brasil.

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Abstract We illustrate the meaning and validity of usual second order approximations for density operators with the help of a simple exactly soluble two-level model in which all relevant quantities can easily be controlled. This leads to exact upper bound error estimates which help to select more precisely permissible correlation times as frequently introduced if stochastic potentials are present. A final consideration of information entropy reveals clearly the limitations of this kind of approximation procedures.

1. INTRODUCTION

Most of the common approximations for density operators^{1,2} involve so many simplifying assumptions that it is difficult to know anything about the reliability of the final result. However, adjustable phenomenological parameters help to bring theoretical solutions into agreement with experimental data. This situation is unsatisfactory.

One of the basic approximations in solving the equation of motion

$$\dot{\rho}(t) = -i[\bar{H}(t), \rho(t)] \quad (1.1)$$

for density operator ρ , with hamiltonian

$$H = H_0 + H_1(t) \quad (1.2)$$

is to keep only terms up to second order in the perturbation $H_1(t)$ which may or may not depend explicitly on time. In many cases, it is taken to be a time dependent stochastic potential. The second order approximation restricts the validity of the solution to a definite time interval $\tau^{(2)}$. Any further approximations such as, e.g., statistical averaging under the assumptions of simple line shapes for two-point autocorrelation functions for H_1 and corresponding correlations times, "coarse graining" procedures, etc., have to be chosen with respect to $\tau^{(2)}$. In general, it

* Present address: Institute of Physical Chemistry, The University of Zurich, CH-8057 Zurich, Switzerland (Suíça)

may be quite difficult to give reasonable quantitative estimates for $\tau^{(2)}$ and it would be desirable to have a simple model where all quantities of interest can be controlled. Therefore, we consider the exactly solvable case of a two-level system and inquire about the relative error A between exact and second order solutions as a function of time. This analysis is by no means only of academic character because many processes may appropriately be described by such a model as, e.g. problems of magnetic resonance^{1,2}, photo-physical processes³, chemically induced polarization phenomena⁴, geminate radical recombination⁵ and delayed fluorescence in magnetic fields⁶, etc.

The following section 2 contains a brief summary of general formulas which will be evaluated explicitly for our model in section 3. The relevance of the results is discussed in the Final section 4.

2. GENERAL

In order to give upper bounds of error estimates for A , the relative difference between the exact and second order solution of eq. (1.1), it is most convenient to choose a time-independent perturbation H_1 in such a way that any explicitly time-dependent operator $H_1(t)$ is maximized through

$$\|H_1(t)\| \leq \|H_1\|, \quad (2.1)$$

for all times, where $\|\dots\|$ denotes the ordinary operator norm. Unitary transformations for time evolution are defined by

$$U_0(t) = \exp[-iH_0 t], \quad (2.2)$$

$$U(t) = \exp[-iH t]. \quad (2.3)$$

The formal solution of eq. (1.1) is then

$$\rho(t) = U(t)\rho(0)U^\dagger(t) \quad (2.4)$$

The approximate solution is most conveniently derived in terms of the interaction representation,

$$\tilde{\rho}(t) = U_0^\dagger(t)\rho(t)U_0(t), \quad (2.5)$$

$$\tilde{H}_1(t) = U_0^\dagger(t)H_1U_0(t), \quad (2.6)$$

for ρ and H_1 , respectively. The corresponding equation of motion in integral form, up to second order, reads

$$\hat{\rho}^{(2)}(t) = -i[\hat{H}_1(t), \hat{\rho}(0)] - [\hat{H}_1(t), [\hat{J}_1(t), \hat{\rho}(0)]] , \quad (2.7)$$

where we have abbreviated

$$\hat{J}_1(t) = \int_0^t ds \hat{H}_1(s) \quad (2.8)$$

A further common step is the statistical averaging $\langle \dots \rangle$ of (2.7) under assumptions like, e.g.,

$$\langle \hat{H}_1(t) \rangle = 0 , \quad (2.9)$$

$$\langle \hat{H}_1(t) \hat{\rho}(0) \rangle = 0 , \quad (2.10)$$

$$\langle \hat{H}_1(t) \hat{H}_1(s) \hat{\rho}(0) \rangle = \langle \hat{H}_1(t) \hat{H}_1(s) \rangle \hat{\rho}(0) , \quad (2.11)$$

$$\langle \hat{H}_1(t) \hat{H}_1(t-s) \rangle = G(s) , \quad (2.12)$$

where this last equation defines a correlation function G of a stationary random process¹ with corresponding correlation time τ_c , say. Any matrix element $G_{ik}(s)$ is assumed to be a positive, monotonically decreasing function of $|s|$ with infinite limes zero. In view of these assumptions it is enough to postulate for our extremal error estimates

$$G_{ik}(s) = \begin{cases} G_{ik}(0) , & |s| < \tau_c \\ 0 & |s| \geq \tau_c \end{cases} \quad (2.13)$$

For quantities of direct physical significance like, e.g., the diagonal elements of the density operator, the relative error of interest to us may be defined through

$$\Delta_{kk}(t) = |\hat{\rho}_{kk}(t) - \hat{\rho}_{kk}^{(2)}(t)| / \hat{\rho}_{kk}(t) \quad (2.14)$$

The foregoing general formulas are going to be used in the analysis of a two-level model.

3. THE TWO-LEVEL CASE

We work directly in a matrix representation in which the Pauli-matrix σ_0 is diagonal and introduce the four elements

$$\begin{aligned} \sigma_0 &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} , & \sigma_1 &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \sigma_2 &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} , & \sigma_3 &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} , \end{aligned} \quad (3.1)$$

which form a complete basis for any hermitian (2x2)-matrix. Then, a general two-level system may be characterized by

$$H_0 = \begin{pmatrix} \varepsilon & 0 \\ 0 & -\varepsilon \end{pmatrix} = \varepsilon \sigma_3, \quad (3.2)$$

$$H_1 = \begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix} = \lambda \sigma_1, \quad (3.3)$$

where H_1 does not depend explicitly on time (see eq. (2.1)), and for the subsequent considerations the weak condition $\lambda < \varepsilon$ will be sufficient.

The exponential forms in (2.2) and (2.3) can be reduced to

$$U_0(\pm t) = a_{\pm} \cos(\varepsilon t) \pm \frac{i}{\varepsilon} H_0 \sin(\varepsilon t), \quad (3.4)$$

$$U(\pm t) = \sigma_0 \cos(\phi t) \pm \frac{\lambda}{\phi} H \sin(\phi t), \quad (3.5)$$

$$\phi = (\varepsilon^2 + \lambda^2)^{1/2} \quad (3.6)$$

With the help of these relations the solution (2.4) of (1.1) is found to be

$$\begin{aligned} \rho(t) = & \rho(0) \cos^2(\phi t) + \frac{i}{\phi} [\rho(0), H] \sin(\phi t) \cos(\phi t) \\ & + \frac{1}{\phi^2} (H \rho(0) H) \sin^2(\phi t), \end{aligned} \quad (3.7)$$

For the second order approximation in the interaction representation we need the explicit form of (2.8)

$$\hat{J}_1(t) = \frac{1}{\varepsilon} H_1 \sin(\varepsilon t) \cos(\varepsilon t) - \frac{\lambda}{\varepsilon} \sigma_2 \sin^2(\varepsilon t), \quad (3.8)$$

$$\begin{aligned} \hat{\rho}^{(2)}(t) = & \rho(0) - \frac{i}{2\varepsilon} [H_1, \rho(0)] \sin(2\varepsilon t) \\ & + \frac{i\lambda}{2\varepsilon} [\sigma_2, \rho(0)] (1 - \cos(2\varepsilon t)) \\ & + \frac{1}{16\varepsilon^2} [H_1, [H_1, \rho(0)]] (\cos(4\varepsilon t) - 1) \\ & + \frac{\lambda}{16\varepsilon^2} [H_1, [\sigma_2, \rho(0)]] (4\sin(2\varepsilon t) - \sin(4\varepsilon t) - 4\varepsilon t) \\ & + \frac{\lambda}{16\varepsilon^2} [\sigma_2, [H_1, \rho(0)]] (4\varepsilon t - \sin(4\varepsilon t)) \\ & - \frac{\lambda^2}{16\varepsilon^2} [\sigma_2, [\sigma_2, \rho(0)]] (\cos(4\varepsilon t) - 4\cos(2\varepsilon t) + 3). \end{aligned} \quad (3.9)$$

We proceed to evaluate the formulas (3.7) and (3.9), without loss of generality, by choosing as initial condition the pure state

$$\rho(0) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad (3.10)$$

and considering, for simplicity, the (22)-elements

$$\hat{\rho}_{22}(t) = \left(\frac{\lambda}{\phi}\right)^2 \sin^2(\epsilon t), \quad (3.11)$$

$$\hat{\rho}_{22}^{(2)}(t) = \left(\frac{\lambda}{\epsilon}\right)^2 \sin^2(\epsilon t). \quad (3.12)$$

This yields for (2.14)

$$\Delta_{22}(t) = \left| 1 - \left\{ 1 + \left(\frac{\lambda}{\epsilon}\right)^2 \right\} \frac{\sin^2(\epsilon t)}{\sin^2(\phi t)} \right|, \quad (3.13)$$

and we have obtained a simple analytical formula for the relative error between exact and second order solutions of (1.?) as a function of time. For times which are short compared to $2\pi/\phi$, the following expansion of (3.13) may be used,

$$\Delta_{22}(t) \approx \left(\frac{\lambda^2}{3}\right)t^2 + \frac{\lambda^2}{45}(\epsilon^2 + 3\lambda^2)t^4. \quad (3.14)$$

4. DISCUSSION

One can easily verify that, in the range of validity of formula (3.14), the error is extremely small, e.g. for $t_1 \leq 1/10\epsilon$, one would find $\Delta_{22} \leq 33$ ppm for $\epsilon = 101$. For longer times one preferably uses (3.13) and gets, e.g.,

$$\Delta_{22} \approx 0.36\% \text{ for } t_2 = 1/\epsilon, \epsilon = 10\lambda,$$

$$\Delta_{22} \approx 9.9\% \text{ for } t = 9\pi/10\phi, \epsilon = 10\lambda.$$

Equivalently, one may say that for a given error tolerance f ($= \Delta_{22}$) the time interval $\tau^{(2)}$, mentioned in the introduction, is given by

$$\tau^{(2)} \approx (3f)^{1/2}/\lambda, \quad (4.1a)$$

or, corresponding to the full expression (3.14),

$$\tau^{(2)} \equiv \left\{ \frac{15}{2(\varepsilon^2 + 3\lambda^2)} \left[\left\{ 1 + \frac{4}{5} \left[3 + \left(\frac{\varepsilon}{\lambda} \right)^2 \right] \right\}^{1/2} - 1 \right] \right\}^{1/2} \quad (4.1b)$$

if $\tau^{(2)} \ll 2\pi/\phi$, whereas for the other cases the transcendental equation (3.13) has to be solved on the computer in order to find $\tau^{(2)}$.

More realistic shapes for the correlation function (2.13) tend to reduce the values of A and, therefore, $\tau^{(2)}$ represents an absolute upper bound for permissible correlation times τ_c in those cases where one can use equations of motion with constant transition rates. This is usually done in the Bloch-Wangsness-Redfield approach² where a coarse graining time Δt is introduced, subject to the condition

$$\Delta t \gg \tau_c \quad (4.2)$$

and, simultaneously, Δt has to be much smaller than the inverse of the norm of the Redfield matrix. The present analysis suggests that, for sufficiently small $\tau^{(2)}$, condition (4.2) is too strong, and Δt may even be of the order of τ_c , but, of course, $\Delta t > \tau_c$. Furthermore, particularities of the shape of the correlation function will not be able to play a decisive role in this case, and this is the reason why very simple line forms as, e.g., Lorentzian shapes, have been successful in most applications.

The error introduced in the expectation value \bar{O} ,

$$\bar{O} = \text{Tr}(\rho O) \quad , \quad (4.3)$$

of any observable O depends also on the properties of this operator and must be discussed for every particular case. Within this model, it could be computed exactly, of course.

Apart from the diagonal matrix elements of the density operator there is one more important quantity defined entirely in terms of ρ , namely the information entropy S , given by

$$S(t) = - \text{Tr}(\rho(t) \ln \rho(t)) \quad , \quad (4.4)$$

whose error may be calculated similarly. We note that S is unitarily invariant,

$$S(t) = S(0) \quad , \quad (4.5)$$

for the exact ρ , at least as long as we do not perform any kind of statistical averaging like, e.g., in eqs. (2.9) to (2.12). Any time-

-dependent change in entropy is therefore entirely due to the second order approximation and has no physical meaning. For a general initial condition,

$$\rho(0) = \sum_{i=0}^3 \alpha_i \sigma_i, \quad (4.6)$$

the exact result for S in terms of

$$\alpha = \left(\sum_{i=1}^3 \alpha_i^2 \right)^{1/2} \quad (4.7)$$

is found to be

$$S = \ln 2 - \frac{1}{2} (1+2\alpha) \ln(1+2\alpha) - \frac{1}{2} (1-2\alpha) \ln(1-2\alpha). \quad (4.8)$$

Because of the spectral condition for the density operator,

$$\frac{1}{2} \leq ||\rho|| \leq 1 \quad (4.9)$$

we find the possible values of α in the closed interval

$$0 \leq \alpha \leq \frac{1}{2}, \quad (4.10)$$

and, consequently, the entropy varies monotonically between zero and $\ln 2$. To illustrate the problems arising in the second order approximation it suffices to choose, for simplicity, a somewhat more special initial condition of the form

$$\rho^{(0)} = \begin{pmatrix} x & 0 \\ 0 & y \end{pmatrix} \quad (4.11)$$

and the error may be expressed in terms of the occupation probability difference

$$\Delta = y - x \quad (4.12)$$

One finds from (3.12) the closed representation

$$\hat{\rho}^{(2)}(t) = \sum_{i=0}^3 b_i(t) \sigma_i, \quad (4.13)$$

where the coefficients are given by

$$\begin{aligned} b_0 &= \frac{1}{2}, \quad b_1(t) = \Delta \frac{\lambda}{E} \sin^2(\epsilon t), \\ b_2(t) &= \Delta \frac{\lambda}{E} \sin(\epsilon t) \cos(\epsilon t), \\ b_3(t) &= \Delta \left(\frac{\lambda^2}{E^2} \sin^2(\epsilon t) - \frac{1}{2} \right) \end{aligned} \quad (4.14)$$

Condition (4.9) and the normalization of $\hat{\rho}^{(2)}(t)$ impose a restriction on the initial conditions,

$$0 \leq |\Delta| < 1 - \frac{2\lambda^4}{\varepsilon^4} \sin^4 \varepsilon \tau^{(2)}, \quad (4.15)$$

where $\tau^{(2)} \ll 2\pi/\phi$, as before. This means that it is possible to calculate a relative error in entropy,

$$\delta S \equiv \left| \frac{S(t) - S^{(2)}(t)}{S(t)} \right| = \left| \frac{S(0) - S^{(2)}(t)}{S(0)} \right|. \quad (4.16)$$

After some algebra, we find

$$\delta S \approx |\Delta| \left| \frac{\ln(y/x)}{\ln(x^x y^y)} \right| \left[\frac{\lambda}{\varepsilon} \sin(\varepsilon \tau^{(2)}) \right]^4 \quad (4.17)$$

For a pure state as initial condition, $|\Delta| = 1$, and one discovers the strange result that the entropy calculated for $\hat{\rho}^{(2)}(t)$ becomes complex. This shows how this kind of approximations can be stressed ad absurdum. It is therefore a necessity to base reasonable approximation procedures on exact Master equations^{8,9} and to maintain always the normalization - and spectral conditions for the density operator. For a certain class of stationary problems this has been done by one of the authors¹⁰, and work on time-dependent problems is in progress.

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Resumo

Nós esclarecemos o significado e a validade da aproximação usual de segunda ordem para operadores de densidade com a ajuda de um modelo simples a duas dimensões, resolvível exatamente, em que todas as quantidades relevantes podem ser facilmente controladas. Isso permite uma avaliação exata do limite máximo de erro, o que nos ajuda a selecionar mais precisamente os tempos de correlação permissíveis, que são frequentemente introduzidos se potenciais estocásticos estão presentes. Uma consideração final sobre a informação entropia revela claramente as limitações desse tipo de aproximação.