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Highly polarized nuclear spin systems and dipolar interactions in NMR/Systèmes de spins nucléaires fortement polarisés et interactions dipolaires en RMN

Moving bases as an alternative to 'interaction representations'

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Abstract

The use of multiple bases moving with respect to each other in quantum dynamics is discussed. This procedure is formally equivalent to the use of interaction pictures, but it leads to an intuitively simpler interpretation of the calculations. A close analogy is shown between the rotating frames of classical NMR theory and the use of moving (rotating) bases in the corresponding quantum presentation, for the traditional basic NMR experiment and for two problems involving Berry's phase. ***To cite this article: J. Jeener, C. R. Physique 5 (2004).***

Résumé

Bases mobiles comme alternative aux « représentations d'interaction ». L'usage de bases multiples, mobiles les unes par rapport aux autres, est discuté en dynamique quantique. Cette technique est formellement équivalente à celle des images d'interactions, mais elle mène à des interpretations intuitives plus simples des calculs. Une forte analogie est montrée entre les référentiels tournants de la théorie classique de la RMN et l'usage de bases mobiles (tournantes) dans la présentation quantique correspondante, pour l'expérience de base traditionnelle de la RMN et dans deux problèmes impliquant la phase de Berry. ***Pour citer cet article : J. Jeener, C. R. Physique 5 (2004).***

Keywords: Quantum dynamics; Moving bases; Rotating frames; Interaction representations; NMR theory; Berry's phase

Mots-clés : Dynamique quantique ; Bases mobiles ; Référentiels tournants ; Images d'interactions ; Théorie de la RMN ; Phase de Berry

1. Introduction

Since its first experimental observations, in molecular beam experiments as well as in more condensed matter, Nuclear Magnetic Resonance (NMR) appeared as distinctly different from most other types of spectroscopy because the use of (strong) coherent irradiation in the spectrometers, combined with long relaxation times, requires an interpretation of the experimental results in terms of explicit spin dynamics (usually quantum dynamics), in contrast to the notion of transition probability which is appropriate for most other standard spectroscopic techniques [1]. Fortunately, the usual difficulty in using intuition and common sense as guides in quantum dynamics is strongly alleviated by the complete analogy between the classical and quantum motion of isolated spins in the presence of classical magnetic fields: the classical motion is easily visualized and calculated by the use of rotating frames of coordinates, and 'interaction pictures' offer a similar simplification of the quantum calculation.

In the *classical procedure*, the state of the spins is always described by the same time dependent magnetization vector (or distribution function) whatever the frame of coordinates used in the discussion, and the same holds true for all other relevant vectors like applied magnetic fields. When seen from a suitable frame rotating at the spectrometer reference frequency, essential

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notions of coherent spectroscopy like the phase of a resonant excitation and the 'rotating frame components' of the spin magnetization (as measured by the acquisition electronics) have a very simple geometrical meaning. Of course, the notion of time derivative of a vector (or distribution function) depends upon the frame of coordinates used, and this offers the welcome possibility to simplify and clarify the equations of motion for the state of the spins by a suitable choice of moving frame.

Usually, a similar simplification is obtained in *quantum mechanical calculations* by the use of 'interaction pictures', but none of the standard quantum mechanical procedures (Schrödinger, Heisenberg or interaction pictures, active or passive view point) offers the same simple intuitive appeal as the classical moving frame scheme. For instance, going from the Schrödinger picture to an interaction picture implies a transformation of the ket or density operator which describes the spins, the relation between laboratory frame and rotating frame components of the magnetization is far from transparent, ... These inconveniences originate in the tacit choice of standard quantum mechanics to define time derivatives of quantum objects always with respect to the basis (in ket space) in which a problem is originally formulated. As a result, this basis appears as intrinsically immobile. However, absolute immobility is not a valid concept in quantum theory any more than in classical theory. All this made it tempting to try and formulate a presentation of quantum dynamics in which reference bases moving with respect to each other can be used at will, while keeping the same abstract quantum objects to describe the spin system and the observables [2,3]. This does not imply any change in the basic principles of quantum mechanics, but requires some additional care in wording and notation. For instance, it is more important than ever to make an explicit distinction between the notions of date and duration (i.e., time interval or delay) which are traditionally called 'time' and denoted by the same symbol t. In the present paper, the notation t is used exclusively for dates, and durations are denoted τ (with the exception of $\mathrm{d}t$ and differences of dates). The notion of immobility (i.e., 'not depending upon the date') of a quantum object is not intrinsic any more but is relative to a basis which must be specified. The same holds true for any comparison of a quantum object taken at different dates, as occurs in the evaluation of time derivatives.

In the present paper, I begin with a brief presentation of such a 'multiple moving bases' scheme for quantum dynamics, suitable for standard NMR theory, hence limited to non-relativistic problems and state spaces of finite dimension. No attempt is made here towards more generality. At the end, I show that this scheme provides the same intuitive convenience at every step of the discussion as the rotating frames of classical NMR theory, for dealing with the motion of a free spin under the action of a classical magnetic field. Section 5 deals with the traditional basic NMR experiment (constant magnetic field with quasi-resonant *rf* irradiation) and Section 6 deals with problems involving Berry's phase (first a spin interacting with a magnetic field of constant intensity and slowly changing orientation, finally a more general case). These two last sections also show how to deal with some of the practical problems that arise when using moving bases.

2. Bases and representations

2.1. Single date

The only deviation from the traditional notation needed here is that all quantum objects (kets, bras, operators) carry date tags. This will be illustrated by a brief recall of some basic elements of quantum engineering. A basis b in ket space is a collection of kets $\{|b_j(t)\rangle\}$ which, at every date t, satisfies the orthonormality condition

$$\langle b_j(t)|b_k(t)\rangle = \delta_{j,k} \tag{1}$$

and the closure relation

$$\sum_j |b_j(t)\rangle\langle b_j(t)| = 1_{op}, \tag{2}$$

where 1_{op} denotes the unit or identity operator (note that this operator is defined for the state space, without reference to any specific basis or date). Using Eq. (2), any ket $|\psi(t)\rangle$, and any operator $A(t)$ involving a single date, can be 'represented' in terms of this basis as

$$|\psi(t)\rangle = 1_{op}|\psi(t)\rangle = \sum_j |b_j(t)\rangle\langle b_j(t)|\psi(t)\rangle, \quad \text{and}$$
$$A(t) = 1_{op}A(t)1_{op} = \sum_{j,k} |b_k(t)\rangle\langle b_j(t)|\langle b_k(t)|A(t)|b_j(t)\rangle, \tag{3}$$

where the date dependent complex numbers $\langle b_j(t)|\psi(t)\rangle$ and $\langle b_k(t)|A(t)|b_j(t)\rangle$ can be evaluated with the aid of any suitable basis.

If a second basis is involved, denoted $\{|c_j(t)\rangle\}$, the relation between the two bases at any date t is described by the single-date unitary operator $W_{[c,b]}(t)$, where the relevant bases are indicated by subscripts between square brackets,

$$W_{[c,b]}(t) = \sum_j \big|c_j(t)\big\rangle\big\langle b_j(t)\big|, \tag{4}$$

such that $|c_k(t)\rangle = W_{[c,b]}(t)|b_k(t)\rangle$. This operator has the expected properties

$$\big(W_{[c,b]}(t)\big)^\dagger = \big(W_{[c,b]}(t)\big)^{-1} = W_{[b,c]}(t) \quad \text{and} \quad W_{[b,b]}(t) = 1_{op}. \tag{5}$$

If more than two bases are involved, Eq. (4) implies that

$$W_{[d,c]}(t)W_{[c,b]}(t) = W_{[d,b]}(t). \tag{6}$$

Whenever a single date is involved, the scalar product of two kets, $|\alpha(t)\rangle$ and $|\beta(t)\rangle$ is easily evaluated using any basis $\{|a_i(t)\rangle\}$ in terms of which the kets are known,

$$\big\langle\alpha(t)|\beta(t)\big\rangle = \big\langle\alpha(t)|1_{op}|\beta(t)\big\rangle = \sum_j \big\langle\alpha(t)|a_j(t)\big\rangle\big\langle a_j(t)|\beta(t)\big\rangle, \tag{7}$$

and the result is independent of the basis chosen. The same traditional technique applies for the evaluation of $\langle\alpha(t)|A(t)|\beta(t)\rangle$ and $\mathrm{Tr}\{A(t)\}$ for any operator $A(t)$ involving a single date. A linear combination of two kets defined at the same date also leads to a well defined object, independent of any choice of basis.

2.2. Multiple dates

Having dropped the convenient (but misleading) fiction that one basis is immobile, we cannot any longer use this privileged basis as a device to "transport a quantum object from one date to another date while keeping the object constant". Obviously, this creates a problem if one undertakes to define a linear combination or a scalar product involving kets defined at different dates. I propose to consider that such operations are meaningless, and to solve the problems which seem to arise by recognizing that changing the date is an important quantum operation in itself, which is easy to incorporate in standard quantum engineering. When this is done, the typography of the equations becomes much more transparent and systematic as far as dates and bases are concerned.

First, I introduce a tool which replaces the standard fiction of immobility of the reference basis. A ket $|\psi(t)\rangle$ will be called *immobile with respect to basis b* if all its projections on this basis are independent of the date t, i.e., $\langle b_j(t_0)|\psi(t_0)\rangle = \langle b_j(t_1)|\psi(t_1)\rangle$ for any j, hence

$$\big|\psi(t_1)\big\rangle = \sum_j \big|b_j(t_1)\big\rangle\big\langle b_j(t_1)|\psi(t_1)\big\rangle = \sum_j \big|b_j(t_1)\big\rangle\big\langle b_j(t_0)|\psi(t_0)\big\rangle = U_{[b]}(t_1,t_0)\big|\psi(t_0)\big\rangle, \tag{8}$$

where the unitary date displacement operator associated with basis b,

$$U_{[b]}(t_1,t_0) = \sum_j \big|b_j(t_1)\big\rangle\big\langle b_j(t_0)\big|, \tag{9}$$

has all the usual properties of evolution operators, including the group property for connected date pairs

$$U_{[b]}(t_2,t_0) = U_{[b]}(t_2,t_1)U_{[b]}(t_1,t_0) \tag{10}$$

and the relations

$$U_{[b]}(t,t) = 1_{op} \quad \text{and} \quad \big(U_{[b]}(t_1,t_0)\big)^\dagger = \big(U_{[b]}(t_1,t_0)\big)^{-1} = U_{[b]}(t_0,t_1). \tag{11}$$

The same discussion that led to Eq. (8) is easily extended to show that, if the single date operator $A(t)$ is immobile in basis b, then all its matrix elements in that basis are date independent, hence

$$A(t_1) = U_b(t_1,t_0)A(t_0)U_b(t_0,t_1). \tag{12}$$

A simple example is that basis kets and bras are immobile as seen from their own basis, hence Eqs. (8), (9) and (11) lead to

$$\big|c_j(t_1)\big\rangle = U_{[c]}(t_1,t_0)\big|c_j(t_0)\big\rangle \quad \text{and} \quad \big\langle b_j(t_1)\big| = \big\langle b_j(t_0)\big|U_{[b]}(t_0,t_1). \tag{13}$$

These relations can be inserted in Eq. (4) to derive the useful transformation rules

$$U_{[c]}(t_1,t_0) = W_{[c,b]}(t_1)U_{[b]}(t_1,t_0)W_{[b,c]}(t_0), \qquad W_{[c,b]}(t_1) = U_{[c]}(t_1,t_0)W_{[c,b]}(t_0)U_{[b]}(t_0,t_1). \tag{14}$$

Consider now the particular case of a basis f which is immobile with respect to basis g, hence $|g_j(t_1)\rangle = U_{[f]}(t_1,t_0)|g_j(t_0)\rangle$. Combining this with the definition (9) of $U_{[f]}(t_1,t_0)$ and the closure relation for basis g, one obtains $U_{[f]}(t_1,t_0) = U_{[g]}(t_1,t_0)$. Bases which are immobile with respect to one another have exactly the same characteristic evolution operator. This leads immediately to $W_{[f,g]}(t_1) = U_{[f]}(t_1,t_0)W_{[f,g]}(t_0)U_{[f]}(t_0,t_1)$, the W operator relating two bases immobile with respect to each other is also immobile in these bases (see Eq. (12)).

As mentioned already at the beginning of the present section, dropping the fiction of an immobile reference basis makes it obvious that, in many cases, comparisons or combinations of quantum objects are meaningful only if certain rules are obeyed by the dates at which the objects are defined. For example, two kets can be equal or enter a linear combination only if they are both defined at the same date, the same holds for the scalar product $\langle\alpha(t)|\beta(t)\rangle$ of the kets $|\alpha(t)\rangle$ and $|\beta(t)\rangle$, but a construction like $|c_j(t_1)\rangle\langle c_j(t_0)|$ is perfectly legitimate although it involves two different dates. All these rules concerning dates can be summarized in a simple way by first associating *date tags* with the various quantum objects in the following way: kets carry their date tag on the left and none on the right, bras carry their date tag on the right and none on the left, single date operators like $A(t)$ carry their date tag t on both sides (operators like 1_{op}, that do not change with the date, behave in the same way but their date tag can be chosen freely), date changing operators like $U_{[b]}(t_1,t_0)$ carry a date tag t_1 on the left and a date tag t_0 on the right (as indicated by the typography), and c-number quantities (which always commute with any quantum object and may be date dependent) carry no date tag and behave as transparent as far as date tags are concerned. Note that the notion of *date tag* introduced in this way is quite different from the ordinary notion of date. With date tags attached, the rules are that (i) at a multiplicative contact in the typography, the date tags must be the same on either side, or be absent on either side (c-numbers are ignored in the discussion), (ii) two quantum objects can be equal or be combined linearly only if both carry the same date tag (or no date tag) on the right and also the same date tag (or no date tag) on the left, possibly with different situations on right and left. It is easy to check that the various equations in this paper manifestly follow these rules. In the standard presentation of quantum dynamics, the equations can also be rewritten to comply manifestly with the date tag rules by using Eq. (11), and by inserting trivial date displacement operators for the 'immobile' reference basis.

3. Time derivatives as seen from different bases

The definition of the time derivative of a vector in classical mechanics requires the specification of the frame of reference in which the derivative is evaluated. For analog reasons, the time derivative of a quantum object must be defined with reference to a quantum mechanical basis. Two equivalent such definitions will now be presented, one in which the time derivative of the quantum object is expressed in terms of time derivatives of its representation in the reference basis (i.e., scalar products or matrix elements which are c-numbers, hence bear no date tag and behave as ordinary functions of the date), and another one in which date tag incompatibilities are resolved by using the characteristic evolution operator of the reference basis.

As a first example, the time derivative of a ket $|\alpha(t)\rangle$ with respect to the basis $\{|b_i(t)\rangle\}$ can be seen in two ways: (i) the j-th component $\langle b_j(t)|(\partial|\alpha(t)\rangle/\partial t)_{[b]}$ of the derivative in basis b is the time derivative $\partial\langle b_j(t)|\alpha(t)\rangle/\partial t$ of the j-th component of $|\alpha(t)\rangle$ in basis b, hence one has, after multiplication of the two expressions above by $|b_j(t)\rangle$ on the left, summation over all j, and use of the closure relation (2)

$$\sum_j \big|b_j(t)\big\rangle\!\big\langle b_j(t)\big|\left(\frac{\partial|\alpha(t)\rangle}{\partial t}\right)_{[b]} = \left(\frac{\partial|\alpha(t)\rangle}{\partial t}\right)_{[b]} = \sum_j \big|b_j(t)\big\rangle\frac{\partial\langle b_j(t)|\alpha(t)\rangle}{\partial t}, \tag{15}$$

and (ii) over an infinitesimal duration Δt, the increment $\Delta t(\partial|\alpha(t)\rangle/\partial t)_{[b]}$ of $|\alpha(t)\rangle$ is the difference between the actual $|\alpha(t+\Delta t)\rangle$ and the result of displacing $|\alpha(t)\rangle$ from t to $t+\Delta t$ locked to basis b, namely $U_{[b]}(t+\Delta t,t)|\alpha(t)\rangle$, hence

$$\left(\frac{\partial|\alpha(t)\rangle}{\partial t}\right)_{[b]} = \lim_{\Delta t\to 0}\frac{|\alpha(t+\Delta t)\rangle - U_{[b]}(t+\Delta t,t)|\alpha(t)\rangle}{\Delta t}. \tag{16}$$

By inserting the closure relation for basis b at date $t+\Delta t$ to the left of $|\alpha(t+\Delta t)\rangle$ in the above equation, and replacing $U_{[b]}(t+\Delta t,t)$ by its definition (9), it becomes clear that the two definitions (i) and (ii) agree.

Following these lines, equivalent explicit definitions, of types (i) and (ii) above, can be given for the time derivative in a given basis of the other usual quantum objects: bra $\langle\beta(t)|$, single date operator $A(t)$, unitary date changing evolution operator $U(t_1,t_0)$. For instance, type (ii) definitions are given by

$$\left(\frac{\partial\langle\beta(t)|}{\partial t}\right)_{[b]} = \lim_{\Delta t\to 0}\frac{\langle\beta(t+\Delta t)| - \langle\beta(t)|U_{[b]}(t,t+\Delta t)}{\Delta t}, \tag{17}$$

$$\left(\frac{\partial A(t)|}{\partial t}\right)_{[b]} = \lim_{\Delta t\to 0}\frac{A(t+\Delta t) - U_{[b]}(t+\Delta t,t)A(t)U_{[b]}(t,t+\Delta t)}{\Delta t}, \tag{18}$$

$$\left(\frac{\partial U(t_1,t_0)}{\partial t_1}\right)_{[b]} = \lim_{\Delta t\to 0}\frac{U(t_1+\Delta t,t_0)-U_{[b]}(t_1+\Delta t,t_1)U(t_1,t_0)}{\Delta t}, \tag{19}$$

$$\left(\frac{\partial U(t_1,t_0)}{\partial t_0}\right)_{[b]} = \lim_{\Delta t\to 0}\frac{U(t_1,t_0+\Delta t)-U(t_1,t_0)U_{[b]}(t_0,t_0+\Delta t)}{\Delta t}. \tag{20}$$

This procedure is easily extended to higher order time derivatives (using the same basis repeatedly) and to Liouville space objects (superbras, superkets, superoperators), but this will not be done here.

When time derivatives are known, useful expressions are provided by limited Taylor series expansions in powers of (short) time intervals. Assume, for instance, that the operator $A(t)$ and its low order time derivatives in basis b are known at date t_0. In the traditional formalism, in which the only basis used is basis b, treated as immobile, the Taylor expansion would be written as $A(t_0+\tau)=A(t_0)+\tau(\partial A(t_0)/\partial t_0)_{[b]}+(\tau^2/2!)(\partial^2 A(t_0)/\partial t_0^2)_{[b]}+\cdots$. However, this expression obviously does not obey the date tags rule: the l.h.s. is at date $t_0+\tau$ whereas the r.h.s. is at date t_0 (and no limit process is involved which would make τ go to zero). Repeating the discussion which led to Eq. (12), the Taylor expansion can be written in a satisfactory way as

$$A(t_0+\tau)=U_{[b]}(t_0+\tau,t_0)\left\{A(t_0)+\tau\left(\frac{\partial A(t_0)}{\partial t_0}\right)_{[b]}+\frac{\tau^2}{2!}\left(\frac{\partial^2 A(t_0)}{\partial t_0^2}\right)_{[b]}+\cdots\right\}U_{[b]}(t_0,t_0+\tau). \tag{21}$$

As a preparation for the discussion of the relation between time derivatives evaluated in different bases, it is convenient to introduce, for any pair of bases b and c, the operator $D_{[c,b]}(t)$ defined by

$$-\frac{1}{\mathrm{i}\hbar}D_{[c,b]}(t)=\lim_{\Delta t\to 0}\frac{U_{[b]}(t+\Delta t,t)-U_{[c]}(t+\Delta t,t)}{\Delta t}. \tag{22}$$

The limit in the r.h.s. of this expression is reminiscent of the usual definition of a time derivative. However, a close examination shows that it does *not* involve any comparison (i.e., difference) of quantum objects with different sets of date tags, hence no reference basis is required to transport objects from one date to another (see the discussion between Eqs. (15) and (16)), hence any basis can be chosen to evaluate the limit and the results provide equivalent expressions for $D_{[c,b]}(t)$. Before proceeding with such calculations, it is useful to note that the simple structure of Eq. (22) immediately implies the following relations,

$$D_{[b,b]}(t)=0,\quad D_{[c,b]}(t)=-D_{[b,c]}(t)\quad\text{and}\quad D_{[d,b]}(t)=D_{[d,c]}(t)+D_{[c,b]}(t). \tag{23}$$

The r.h.s. of Eq. (22) can now be evaluated with reference to basis b by the following steps: (i) use Eq. (14) to express $U_{[c]}(t+\Delta t,t)$ in terms of $U_{[b]}(t+\Delta t,t)$; (ii) replace $W_{[c,b]}(t+\Delta t)$ introduced in the previous step by its first order Taylor expansion (21) around t, namely $U_{[b]}(t+\Delta t,t)\{W_{[c,b]}(t)+\Delta t(\partial W_{[c,b]}(t)/\partial t)_{[b]}+\mathrm{O}((\Delta t)^2)\}U_{[b]}(t,t+\Delta t)$, where $\mathrm{O}((\Delta t)^2)$ stands for 'of order $(\Delta t)^2$'; (iii) use Eqs. (5), (6), (10) and (11) for simplifications to obtain

$$\begin{aligned}-\frac{1}{\mathrm{i}\hbar}D_{[c,b]}(t)&=\lim_{\Delta t\to 0}\left\{-U_{[b]}(t+\Delta t,t)\left(\frac{\partial W_{[c,b]}(t)}{\partial t}\right)_{[b]}W_{[b,c]}(t)-\frac{U_{[b]}(t+\Delta t,t)\mathrm{O}((\Delta t)^2)W_{[b,c]}(t)}{\Delta t}\right\}\\&=-\left(\frac{\partial W_{[c,b]}(t)}{\partial t}\right)_{[b]}W_{[b,c]}(t).\end{aligned} \tag{24}$$

A similar evaluation using basis c leads to

$$-\frac{1}{\mathrm{i}\hbar}D_{[c,b]}(t)=+\left(\frac{\partial W_{[b,c]}(t)}{\partial t}\right)_{[c]}W_{[c,b]}(t). \tag{25}$$

Other useful relations are obtained by noting that $1_{op}=W_{[c,b]}(t)W_{[b,c]}(t)$ and that the time derivative of 1_{op} is zero in any basis a, hence

$$0=\left(\frac{\partial W_{[c,b]}(t)}{\partial t}\right)_{[a]}W_{[b,c]}(t)+W_{[c,b]}(t)\left(\frac{\partial W_{[b,c]}(t)}{\partial t}\right)_{[a]}. \tag{26}$$

The operator $D_{[c,b]}(t)$ has the dimension of energy, and is Hermitian because $W_{[c,b]}(t)$ is unitary. By noting that a basis ket is always immobile in its own basis, one also shows easily that the operator $D_{[c,b]}(t)/\hbar$ is the generator of the motion of basis c with respect to basis b, in the sense that the motion of any basis ket $|c_j(t)\rangle$ is governed by

$$\mathrm{i}\hbar\left(\frac{\partial|c_k(t)\rangle}{\partial t}\right)_{[b]}=D_{[c,b]}(t)\big|c_k(t)\big\rangle, \tag{27}$$

just in the same way that, in the Schrödinger equation, $H(t)/\hbar$ is the generator of the motion of any state $|\psi(t)\rangle$ of the relevant physical system with respect to an *immobile* basis (denoted b here),

$$\mathrm{i}\hbar\left(\frac{\partial|\psi(t)\rangle}{\partial t}\right)_{[b]}=H(t)\big|\psi(t)\big\rangle. \tag{28}$$

Eqs. (16) to (20) can now be combined with Eq. (22) to relate the time derivatives in two different bases for various quantum objects:

$$\left(\frac{\partial|\alpha(t)\rangle}{\partial t}\right)_{[c]} - \left(\frac{\partial|\alpha(t)\rangle}{\partial t}\right)_{[b]} = \lim_{\Delta t\to 0}\frac{\{U_{[b]}(t+\Delta t,t) - U_{[c]}(t+\Delta t,t)\}|\alpha(t)\rangle}{\Delta t} = -\frac{1}{\mathrm{i}\hbar}D_{[c,b]}(t)\big|\alpha(t)\big\rangle, \tag{29}$$

$$\left(\frac{\partial\langle\beta(t)|}{\partial t}\right)_{[c]} - \left(\frac{\partial\langle\beta(t)|}{\partial t}\right)_{[b]} = \lim_{\Delta t\to 0}\frac{\langle\beta(t)|\{U_{[b]}(t,t+\Delta t) - U_{[c]}(t,t+\Delta t)\}}{\Delta t} = +\frac{1}{\mathrm{i}\hbar}\big\langle\beta(t)\big|D_{[c,b]}(t), \tag{30}$$

$$\begin{aligned}\left(\frac{\partial A(t)}{\partial t}\right)_{[c]} - \left(\frac{\partial A(t)}{\partial t}\right)_{[b]} &= \lim_{\Delta t\to 0}\frac{U_{[b]}(t+\Delta t,t)A(t)U_{[b]}(t,t+\Delta t) - U_{[c]}(t+\Delta t,t)A(t)U_{[c]}(t,t+\Delta t)}{\Delta t}\\ &= \lim_{\Delta t\to 0}\left\{\frac{U_{[b]}(t+\Delta t,t) - U_{[c]}(t+\Delta t,t)}{\Delta t}A(t)U_{[b]}(t,t+\Delta t)\right.\\ &\qquad \left. - U_{[c]}(t+\Delta t,t)A(t)\frac{U_{[c]}(t,t+\Delta t) - U_{[b]}(t,t+\Delta t)}{\Delta t}\right\}\\ &= -\frac{1}{\mathrm{i}\hbar}\big[D_{[c,b]}(t),A(t)\big],\end{aligned} \tag{31}$$

$$\begin{aligned}\left(\frac{\partial U(t_1,t_0)}{\partial t_1}\right)_{[c]} - \left(\frac{\partial U(t_1,t_0)}{\partial t_1}\right)_{[b]} &= \lim_{\Delta t\to 0}\frac{\{U_{[b]}(t_1+\Delta t,t_1) - U_{[c]}(t_1+\Delta t,t_1)\}U(t_1,t_0)}{\Delta t}\\ &= -\frac{1}{\mathrm{i}\hbar}D_{[c,b]}(t_1)U(t_1,t_0),\end{aligned} \tag{32}$$

$$\begin{aligned}\left(\frac{\partial U(t_1,t_0)}{\partial t_0}\right)_{[c]} - \left(\frac{\partial U(t_1,t_0)}{\partial t_0}\right)_{[b]} &= \lim_{\Delta t\to 0}\frac{U(t_1,t_0)\{U_{[b]}(t_0,t_0+\Delta t) - U_{[c]}(t_0,t_0+\Delta t)\}}{\Delta t}\\ &= +\frac{1}{\mathrm{i}\hbar}U(t_1,t_0)D_{[c,b]}(t_0),\end{aligned} \tag{33}$$

where $U(t_1,t_0)$ stands for any unitary date displacement operator ('evolution operator').

4. Quantum dynamics seen from different bases

In this section, I shall recall some of the standard techniques of quantum dynamics, as used in NMR, in a multiple moving bases presentation. In the conventional reference basis, denoted b here, the equation of motion for the density operator $\rho(t)$, which describes the state of the physical system under discussion, is the usual von Neumann equation of motion

$$\mathrm{i}\hbar\left(\frac{\partial}{\partial t}\right)_{[b]}\rho(t) = \big[H(t),\rho(t)\big], \tag{34}$$

where the Hermitian operator $H(t)$ is the Hamiltonian of the system, i.e., the *observable* associated with the total energy (the quantity which enters in thermodynamical discussions).

The classical Liouville equation analog of Eq. (34) is formulated with time derivatives in an inertial reference frame. For the same reasons, the validity of Eq. (34) requires that the basis b, used to evaluate the time derivative, must be an inertial basis. This means that there exists an inertial frame of classical coordinates such that each classical observable of this inertial frame (e.g., the Cartesian components of position, momentum, or angular momentum) is associated with a corresponding quantum observable which is *immobile* in basis b in the sense of Eq. (12). Of course, any practical direct use of Eq. (34) implies that $H(t)$ and all other relevant observables are well known in terms of their action on the basis kets $|b_j(t)\rangle$ of basis b.

For problems in which the Hamiltonian $H(t)$ can be separated in a (usually large and simple) part $H_0(t)$ and a (usually small and possibly complicated) part $V(t)$, it is often useful to go over to a new basis c, such that $D_{[c,b]}(t) = H_0(t)$, in which the generator of the motion is only $V(t)/\hbar$ (see Eq. (31))

$$\mathrm{i}\hbar\left(\frac{\partial}{\partial t}\right)_{[c]}\rho(t) = \big[\big\{H(t) - D_{[c,b]}(t)\big\},\rho(t)\big] = \big[V(t),\rho(t)\big]. \tag{35}$$

With this choice of basis c, $H_0(t)/\hbar$ is the generator of the motion of basis c with respect to basis b (see Eq. (27)), hence it is not surprizing that the fast motion (with respect to basis b) due to $H_0(t)$ is not felt any more in basis c. The new basis c is related to the original basis b by an operator $W_{[c,b]}(t)$ such that

$$\mathrm{i}\hbar\left(\frac{\partial}{\partial t}\right)_{[b]}W_{[c,b]}(t) = H_0(t)W_{[c,b]}(t), \tag{36}$$

where $W_{[c,b]}(t)$ is required to be unitary at some initial date, and remains unitary because $H_0(t)$ is Hermitian. It is important to note that, in spite of the analogy between Eqs. (34) and (35), $V(t)$ in Eq. (35) is *not* the total energy of the system, and that the inclusion of its average value in thermodynamic discussions requires utmost care and may be misleading [4].

The unitary operator $W_{[c,b]}(t)$ used here is essentially the same which is used in the 'interaction picture' transformation for the same problem, hence the two procedures are very closely related (see Subsection 5.3 for detailed comparison on a simple example).

Another useful tool is that of series expansions valid for 'short' time intervals. Taking Eq. (35) as an example, the first step is to re-write it as an integral equation starting at date t_0,

$$\rho(t_1) = U_{[c]}(t_1,t_0)\rho(t_0)U_{[c]}(t_0,t_1) + \frac{1}{\mathrm{i}\hbar}\int_{t_2=t_0}^{t_2=t_1} \mathrm{d}t_2\, U_{[c]}(t_1,t_2)\big[V(t_2),\rho(t_2)\big]U_{[c]}(t_2,t_1), \tag{37}$$

and to iterate this procedure on the last occurrence of $\rho(\cdots)$, leading to

$$\begin{aligned}\rho(t_1) = {} & U_{[c]}(t_1,t_0)\rho(t_0)U_{[c]}(t_0,t_1) + \frac{1}{\mathrm{i}\hbar}\int_{t_2=t_0}^{t_2=t_1} \mathrm{d}t_2\, U_{[c]}(t_1,t_2)\big[V(t_2), U_{[c]}(t_2,t_0)\rho(t_0)U_{[c]}(t_0,t_2)\big]U_{[c]}(t_2,t_1) \\ & + \left(\frac{1}{\mathrm{i}\hbar}\right)^2 \int_{t_2=t_0}^{t_2=t_1} \mathrm{d}t_2 \int_{t_3=t_0}^{t_3=t_2} \mathrm{d}t_3\, U_{[c]}(t_1,t_2)\big[V(t_2), U_{[c]}(t_2,t_3) \\ & \quad \times \big[V(t_3), U_{[c]}(t_3,t_0)\rho(t_0)U_{[c]}(t_0,t_3)\big]\big]U_{[c]}(t_3,t_1) + \cdots.\end{aligned} \tag{38}$$

If one uses this expression in the basis in which the time derivative was evaluated originally in Eq. (35), namely basis c, then the operators $U_{[c]}(\cdot)$ appear as trivial identity operators (see Eq. (13)) and the expression just looks like a pedantically decorated version of its standard counterpart. However, this 'decoration' indicates explicitly how to evaluate the expression using any other basis if this proves more convenient.

5. The basic NMR experiment

The model discussed here consists in a free spin interacting with a classical magnetic field composed of a (large) field $\boldsymbol{B}_0(t)$, immobile in the laboratory frame, and a (small) quasi-resonant *rf* field $\boldsymbol{B}_1(t)$ perpendicular to $\boldsymbol{B}_0(t)$.

5.1. Classical presentation: rotating frame

For a free spin acted upon by the classical magnetic field $\boldsymbol{B}(t)$, the equation of motion for the average spin magnetization $\boldsymbol{M}(t)$ is

$$\left(\frac{\partial \boldsymbol{M}(t)}{\partial t}\right)_{lab} = \boldsymbol{M}(t)\times\gamma\boldsymbol{B}(t), \tag{39}$$

where the time derivative is evaluated in an inertial frame of reference, conventionally called the 'laboratory frame' (*lab*). Assuming that the magnetic field $\boldsymbol{B}(t)$ is dominated by a large component $\boldsymbol{B}_0(t)$ immobile in the laboratory frame, it is convenient to choose the Z direction of that frame parallel to the large field, hence $\boldsymbol{B}_0(t) = B_0\widehat{\boldsymbol{Z}}_{lab}(t)$, where the hat $\widehat{\ }$ indicates a unit vector.

The discussion of experiments performed with a coherent NMR spectrometer is considerably simplified by the use of an auxiliary frame of coordinates (*rot*) which rotates with respect to the laboratory frame around the $\widehat{\boldsymbol{Z}}_{lab}(t)$ direction, at an angular velocity $\boldsymbol{\omega}_{rot,lab}(t) = \omega_{rf}\widehat{\boldsymbol{Z}}_{lab}(t)$ such that this rotating frame roughly accompanies the spin in its motion due to $\boldsymbol{B}_0(t)$, and that $|\omega_{rf}|/2\pi$ is exactly the (positive) frequency of the reference oscillator of the spectrometer used to specify the phase of *rf* irradiations and the phase of the detected signals (see Fig. 1):

$$\begin{aligned}\widehat{\boldsymbol{X}}_{rot}(t) &= +\widehat{\boldsymbol{X}}_{lab}(t)\cos\big(\omega_{rf}\{t-t_*\}\big) + \widehat{\boldsymbol{Y}}_{lab}(t)\sin\big(\omega_{rf}\{t-t_*\}\big), \\ \widehat{\boldsymbol{Y}}_{rot}(t) &= -\widehat{\boldsymbol{X}}_{lab}(t)\sin\big(\omega_{rf}\{t-t_*\}\big) + \widehat{\boldsymbol{Y}}_{lab}(t)\cos\big(\omega_{rf}\{t-t_*\}\big), \\ \widehat{\boldsymbol{Z}}_{rot}(t) &= \widehat{\boldsymbol{Z}}_{lab}(t),\end{aligned} \tag{40}$$

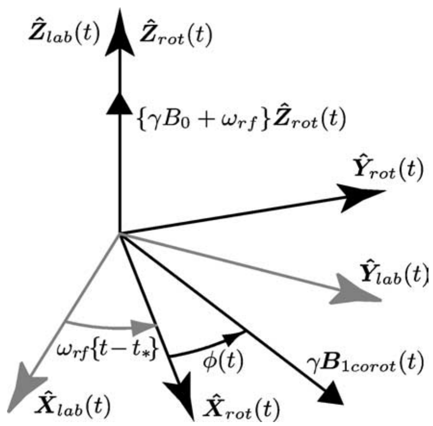

Fig. 1. A number of vectors used in the discussion, as seen at the date t by a third observer that is not necessarily immobile with respect to the *laboratory* or *rotating* frames. The figure is drawn assuming that γ and $b_1(t)$ are both positive.

in which t_* is an arbitrary reference date at which both frames coincide. The time derivatives of classical vectors in the *lab* and *rot* frames are related as follows,

$$\left(\frac{\partial \boldsymbol{M}(t)}{\partial t}\right)_{rot}=\left(\frac{\partial \boldsymbol{M}(t)}{\partial t}\right)_{lab}+\boldsymbol{M}(t)\times\boldsymbol{\omega}_{rot,lab}(t)=\left(\frac{\partial \boldsymbol{M}(t)}{\partial t}\right)_{lab}+\boldsymbol{M}(t)\times\omega_{rf}\widehat{\boldsymbol{Z}}_{lab}(t). \tag{41}$$

For the present discussion, the magnetic field $\boldsymbol{B}(t)$ will be the sum of the (large) field $\boldsymbol{B}_0(t)$ mentioned above and a (usually much smaller) 'radio frequency' field $\boldsymbol{B}_1(t)$, linearly polarized in the direction $\widehat{\boldsymbol{X}}_{lab}(t)$ of the axis of the *rf* coil. The amplitude $b_1(t)$ and the phase $\phi(t)$[1] of this *rf* field are controlled by the spectrometer electronics, and vary slowly on the time scale of the *rf* period $2\pi/\omega_{rf}$. The decomposition of $\boldsymbol{B}_1(t)$ in *corotating* and *counterrotating* parts is the starting point of the traditional approximation, valid for *rf* fields much smaller than the constant field, in which the *counterrotating* part is usually ignored in further calculations:

$$\boldsymbol{B}(t)=\boldsymbol{B}_0(t)+\boldsymbol{B}_1(t),$$

where

$$\boldsymbol{B}_0(t)=B_0\widehat{\boldsymbol{Z}}_{lab}(t)\quad\text{and}\quad\boldsymbol{B}_1(t)=2b_1(t)\cos\bigl[\omega_{rf}\{t-t_*\}+\phi(t)\bigr]\widehat{\boldsymbol{X}}_{lab}(t)=\boldsymbol{B}_{1corot}(t)+\boldsymbol{B}_{1counter}(t), \tag{42}$$

where

$$\boldsymbol{B}_{1corot}(t)=b_1(t)\bigl(\widehat{\boldsymbol{X}}_{rot}(t)\cos\bigl[\phi(t)\bigr]+\widehat{\boldsymbol{Y}}_{rot}(t)\sin\bigl[\phi(t)\bigr]\bigr) \tag{43}$$

and

$$\boldsymbol{B}_{1counter}(t)=b_1(t)\bigl(\widehat{\boldsymbol{X}}_{rot}(t)\cos\bigl[2\omega_{rf}\{t-t_*\}+\phi(t)\bigr]-\widehat{\boldsymbol{Y}}_{rot}(t)\sin\bigl[2\omega_{rf}\{t-t_*\}+\phi(t)\bigr]\bigr). \tag{44}$$

With this notation, and ignoring $\boldsymbol{B}_{1counter}(t)$, the equation of motion for $\boldsymbol{M}(t)$ becomes

$$\left(\frac{\partial \boldsymbol{M}(t)}{\partial t}\right)_{rot}=\boldsymbol{M}(t)\times\bigl(\{\gamma B_0+\omega_{rf}\}\widehat{\boldsymbol{Z}}_{rot}(t)+\gamma b_1(t)\bigl\{\widehat{\boldsymbol{X}}_{rot}(t)\cos\bigl[\phi(t)\bigr]+\widehat{\boldsymbol{Y}}_{rot}(t)\sin\bigl[\phi(t)\bigr]\bigr\}\bigr). \tag{45}$$

This describes a rotation of $\boldsymbol{M}(t)$ at the (small) angular velocity given by the large brace at the right of the vectorial product $(\times)$ in Eq. (45). In the absence of irradiation or during a simple irradiation with constant $b_1(t)$ and $\phi(t)$, the motion of $\boldsymbol{M}(t)$ is very easy to visualize and to calculate in the rotating frame.

The direct measurement of $\boldsymbol{M}(t)$ occurs by means of the same *rf* coil, immobile in the *lab* frame, which is also used to generate the *rf* field $\boldsymbol{B}_1(t)$. For this, the relevant component of $\boldsymbol{M}(t)$ is its X component in the *lab* frame, easily evaluated from information in any frame as $M_{Xlab}(t)=\boldsymbol{M}(t)\cdot\widehat{\boldsymbol{X}}_{lab}(t)$. The *rf* signal induced in the coil is processed by a set of two orthogonal phase sensitive detectors and fed into the acquisition system. The 'real' and 'imaginary' parts of the acquired signal are directly related to the X and Y components of $\boldsymbol{M}(t)$ in the *rot* frame, easily evaluated as $M_{Xrot}(t)=\boldsymbol{M}(t)\cdot\widehat{\boldsymbol{X}}_{rot}(t)$ and $M_{Yrot}(t)=\boldsymbol{M}(t)\cdot\widehat{\boldsymbol{Y}}_{rot}(t)$.

[1] See [5] and [6] for a detailed discussion of issues of sign which appear between the phases as defined here and the electrical engineering phases in the spectrometer.

5.2. Quantum presentation: moving bases

The role of the classical equation of motion (39) in the *lab* frame will be played here by the von Neumann equation of motion in the *lab* basis,

$$\mathrm{i}\hbar\left(\frac{\partial\rho(t)}{\partial t}\right)_{[lab]} = \left[\left\{-\hbar\boldsymbol{I}(t)\cdot\gamma\boldsymbol{B}(t)\right\}, \rho(t)\right], \tag{46}$$

with the same time dependent classical magnetic field $\boldsymbol{B}(t)$, and $\gamma\hbar\boldsymbol{I}(t)$ standing for the spin magnetic moment. The *lab* basis $\{|lab_j(t)\rangle\}$ is the basis traditionally used to formulate such problems, in which the quantum observables I_X, I_Y, and I_Z are immobile. For the sake of uniformity, these observables will be denoted (and defined) here as

$$I_{Xlab}(t) = \boldsymbol{I}(t)\cdot\widehat{\boldsymbol{X}}_{lab}(t), \qquad I_{Ylab}(t) = \boldsymbol{I}(t)\cdot\widehat{\boldsymbol{Y}}_{lab}(t), \qquad I_{Zlab}(t) = \boldsymbol{I}(t)\cdot\widehat{\boldsymbol{Z}}_{lab}(t). \tag{47}$$

The simplification provided by the classical rotating frame formulation (see Eqs. (40)–(45)) has a direct quantum analog in the use of a corresponding rotating basis $\{|rot_j(t)\rangle\}$ such that the operator $D_{rot,lab}(t) = \hbar\omega_{rf}I_{Zlab}(t)$ essentially compensates the part $-\gamma\hbar B_0 I_{Zlab}$ of the Hamiltonian caused by the large constant field. In this *rot* basis, Eq. (46) takes the form

$$\mathrm{i}\hbar\left(\frac{\partial\rho(t)}{\partial t}\right)_{[rot]} = \left[\left(-\hbar I_{Zlab}(t)\{\gamma B_0+\omega_{rf}\} - \hbar\boldsymbol{I}(t)\cdot\gamma\boldsymbol{B}_1(t)\right), \rho(t)\right], \tag{48}$$

which is easy to manipulate only if the quantum objects are expressed in terms of simple observables immobile in the *rot* basis, and if the operator $W_{[rot,lab]}(t)$ is known explicitly. This operator is easily obtained from the value $\hbar\omega_{rf}I_{Zlab}(t)$ chosen for $D_{[rot,lab]}(t)$ and the choice that the two bases coincide at the date t_*, hence $W_{[rot,lab]}(t_*) = 1_{op}$ (see Eq. (24)):

$$W_{[rot,lab]}(t) = \exp\left(-\mathrm{i}\omega_{rf}\{t-t_*\}I_{Zlab}(t)\right). \tag{49}$$

The relations between Cartesian components of $\boldsymbol{I}(t)$ in the two bases can be obtained in various ways: for instance, (i) express, e.g., $I_{Xrot}(t)$ as $\boldsymbol{I}(t)\cdot\widehat{\boldsymbol{X}}_{rot}(t)$, and use Eqs. (40) and (47) to get

$$I_{Xrot}(t) = \boldsymbol{I}(t)\cdot\widehat{\boldsymbol{X}}_{rot}(t) = +I_{Xlab}(t)\cos\left(\omega_{rf}\{t-t_*\}\right) + I_{Ylab}(t)\sin\left(\omega_{rf}\{t-t_*\}\right), \tag{50}$$

$$I_{Yrot}(t) = \boldsymbol{I}(t)\cdot\widehat{\boldsymbol{Y}}_{rot}(t) = -I_{Xlab}(t)\sin\left(\omega_{rf}\{t-t_*\}\right) + I_{Ylab}(t)\cos\left(\omega_{rf}\{t-t_*\}\right), \tag{51}$$

$$I_{Zrot}(t) = \boldsymbol{I}(t)\cdot\widehat{\boldsymbol{Z}}_{rot}(t) = I_{Zlab}(t), \tag{52}$$

or (ii) require that, e.g., $I_{Xrot}(t)$ is immobile in basis *rot* (just like $I_{Xlab}(t)$ is immobile in basis *lab*) with the additional condition that $I_{Xrot}(t_*) = I_{Xlab}(t_*)$ at the date t_* where both frames coincide (and also both bases). Using Eqs. (12), (14), and (49), this leads to the relations

$$I_{Xrot}(t) = W_{[rot,lab]}(t)I_{Xlab}(t)W_{[lab,rot]}(t), \qquad I_{Yrot}(t) = W_{[rot,lab]}(t)I_{Ylab}(t)W_{[lab,rot]}(t), \tag{53}$$

$$I_{Zrot}(t) = W_{[rot,lab]}(t)I_{Zlab}(t)W_{[lab,rot]}(t) = I_{Zlab}(t). \tag{54}$$

In the present very simple context, relations (52) and (54) between $I_{Zrot}(t)$ and $I_{Zlab}(t)$ are the same, and relations (50), (51) and (53) are directly equivalent to the useful relations

$$I_{+rot}(t) = \exp\left(-\mathrm{i}\omega_{rf}\{t-t_*\}\right)I_{+lab}(t) \quad \text{and} \quad I_{-rot}(t) = \exp\left(\mathrm{i}\omega_{rf}\{t-t_*\}\right)I_{-lab}(t), \quad \text{where}$$
$$I_{\pm lab}(t) = I_{Xlab}(t) \pm \mathrm{i}I_{Ylab}(t) \quad \text{and} \quad I_{\pm rot}(t) = I_{Xrot}(t) \pm \mathrm{i}I_{Yrot}(t), \tag{55}$$

hence the two approaches (i) and (ii) above are equivalent.

The von Neumann equation of motion (48) can now be written explicitly under a form suitable for further calculations in the *rot* basis (again neglecting $\boldsymbol{B}_{1counter}(t)$) as

$$\mathrm{i}\hbar\left(\frac{\partial\rho(t)}{\partial t}\right)_{[rot]} = \left[\left(-\hbar I_{Zrot}(t)\{\gamma B_0+\omega_{rf}\} - \gamma\hbar b_1(t)\left\{I_{Xrot}(t)\cos\left[\phi(t)\right] + I_{Yrot}(t)\sin\left[\phi(t)\right]\right\}\right), \rho(t)\right]. \tag{56}$$

When $\rho(t)$ is known in terms of basic operators immobile in the *rot* basis, the rotating frame components of the average spin magnetization $\boldsymbol{M}(t)$ are easily evaluated as, e.g.,

$$M_{Xrot}(t) = \langle\gamma\hbar I_{Xrot}\rangle(t) = \gamma\hbar\,\mathrm{Tr}\left\{I_{Xrot}(t)\rho(t)\right\} \quad \text{or} \quad M_{Xrot}(t) + \mathrm{i}M_{Yrot}(t) = \gamma\hbar\,\mathrm{Tr}\left\{I_{+rot}(t)\rho(t)\right\}, \tag{57}$$

and the laboratory frame components as, e.g.,

$$M_{Xlab}(t) + \mathrm{i}M_{Ylab}(t) = \gamma\hbar\,\mathrm{Tr}\left\{I_{+lab}(t)\rho(t)\right\} = \gamma\hbar\exp\left(\mathrm{i}\omega_{rf}\{t-t_*\}\right)\mathrm{Tr}\left\{I_{+rot}(t)\rho(t)\right\}. \tag{58}$$

This quantum rotating basis procedure, from Eq. (56) to Eq. (58), is directly analogous to the classical rotating frame procedure of Eq. (45) in the sense that both procedures relate only time derivatives and Cartesian components that are all in the *rot* frame or all in the *rot* basis.

5.3. Quantum presentation: interaction picture

In the traditional interaction picture procedure followed in this Subsection, only the *lab* basis and Cartesian components in the *lab* frame are used, so that basis tags are superfluous in the calculations. However, comparisons between the two quantum procedures will be clarified by keeping these basis tags here. The interaction picture version of any single date operator $A(t)$ is given by $\tilde{A}(t) = W^{\dagger}(t)A(t)W(t)$, where $W(t)$ is a unitary operator which can be chosen to suit the problem at hand. With this notation, if

$$\mathrm{i}\hbar\left(\frac{\partial\rho(t)}{\partial t}\right)_{[lab]} = \big[H(t),\rho(t)\big],\quad \text{then}\quad \mathrm{i}\hbar\left(\frac{\partial\tilde{\rho}(t)}{\partial t}\right)_{[lab]} = \left[\left\{\widetilde{H}(t) + \mathrm{i}\hbar\left(\frac{\partial W^{\dagger}(t)}{\partial t}\right)_{[lab]} W(t)\right\},\tilde{\rho}(t)\right]. \tag{59}$$

The starting point here will be the same as for the discussion of the moving bases procedure, namely the von Neumann equation (46) in the *lab* basis. If we require that the interaction picture procedure provides the same simplification of the equation of motion as the use of the *rot* basis, then the term added to $\widetilde{H}(t)$ in Eq. (59) must be equal to $-\hbar\omega_{rf} I_{Zlab}(t)$, and this is exactly what happens if we set $W^{\dagger}(t) = W_{lab,rot}(t)$ as given by Eq. (49). With this choice, the interaction picture version of single date operators becomes

$$\tilde{A}(t) = W_{[lab,rot]}(t)A(t)W_{[rot,lab]}(t) \quad \text{and} \quad \tilde{\rho}(t) = W_{[lab,rot]}(t)\rho(t)W_{[rot,lab]}(t). \tag{60}$$

A pictorial description of this transformation may consist, at each date t, to (i) lock the relevant ket, bra or single date operator to the basis vectors of the *rot* basis, (ii) rotate the *rot* basis so that it coincides with the *lab* basis, and (iii) define the rotated objects as the interaction picture version of the original objects.

The von Neumann equation in the interaction picture is (written as required in the *lab* basis and in terms of Cartesian components in the *lab* frame, again neglecting $\boldsymbol{B}_{1counter}(t)$)

$$\mathrm{i}\hbar\left(\frac{\partial\tilde{\rho}(t)}{\partial t}\right)_{[lab]} = \big[\big(-\hbar I_{Zlab}(t)\{\gamma B_0 + \omega_{rf}\} - \gamma\hbar b_1(t)\big\{I_{Xlab}(t)\cos\big[\phi(t)\big] + I_{Ylab}(t)\sin\big[\phi(t)\big]\big\}\big),\tilde{\rho}(t)\big]. \tag{61}$$

When $\tilde{\rho}(t)$ is known, the average values of, e.g., the *lab* frame Cartesian components $I_{Xlab}(t)$ can be evaluated by starting from $\langle I_{Xlab}(t)\rangle(t) = \mathrm{Tr}\{I_{Xlab}(t)\rho(t)\}$, inserting $1_{op} = W_{[rot,lab]}(t)W_{[lab,rot]}(t)$ twice in the trace and using the invariance of the trace for cyclic permutations and Eq. (60) to obtain

$$\big\langle I_{Xlab}(t)\big\rangle(t) = \mathrm{Tr}\big\{I_{Xlab}(t)\rho(t)\big\} = \mathrm{Tr}\big\{\tilde{I}_{Xlab}(t)\tilde{\rho}(t)\big\}, \tag{62}$$

where $\tilde{I}_{Xlab}(t)$ still has to be expressed in terms of $I_{Xlab}(t)$ and $I_{Ylab}(t)$. In the case of *rot* frame components, a similar procedure can be followed, leading to

$$\big\langle I_{Xrot}(t)\big\rangle(t) = \mathrm{Tr}\big\{I_{Xrot}(t)\rho(t)\big\} = \mathrm{Tr}\big\{\tilde{I}_{Xrot}(t)\tilde{\rho}(t)\big\} = \mathrm{Tr}\big\{I_{Xlab}(t)\tilde{\rho}(t)\big\}. \tag{63}$$

The formal analogy between Eqs. (56) and (61) is complete, with the roles of *tilde* ˜ and *lab* in (61) played by *no tilde* and *rot* in (56), hence exactly the same problems of calculation are encountered in solving either equation and evaluating average values. However, Eq. (61) does not offer the same simple intuitive interpretation as its moving bases counterpart (56), in terms of the convenient classical rotating frame concepts.

It is easy to check that the exact equivalence discussed above is a general feature of the relation between the two quantum procedures, and that the moving basis scheme usually leads to simpler intuitive interpretations of the various equations.

6. Problems involving Berry's phase

The simple model discussed in Subsections 6.1 and 6.2 consists in a free spin interacting with a classical magnetic field $\boldsymbol{B}_0(t)$ of constant intensity $B_0 = |\boldsymbol{B}_0(t)|$, slowly changing direction in the laboratory frame. In Subsection 6.3, I show how Berry's original introduction of the geometrical phase can be reproduced with the use of moving bases.

6.1. Simple example, classical presentation using rotating frames

A first rotating frame, denoted *slo*, is used to follow $\boldsymbol{B}_0(t)$ in its changes in *direction* with respect to the *lab* frame. For this, the angular velocity $\boldsymbol{\omega}_{slo,lab}(t)$ of the *slo* frame with respect to the *lab* frame must be such that the unit vector $\widehat{\boldsymbol{B}}_0(t)$ is immobile in the *slo* frame, hence (see Eq. (41))

$$0=\left(\frac{\partial\widehat{\boldsymbol{B}}_0(t)}{\partial t}\right)_{slo}=\left(\frac{\partial\widehat{\boldsymbol{B}}_0(t)}{\partial t}\right)_{lab}+\widehat{\boldsymbol{B}}_0(t)\times\boldsymbol{\omega}_{slo,lab}(t). \tag{64}$$

Eq. (64) specifies only the components of $\boldsymbol{\omega}_{slo,lab}(t)$ perpendicular to $\widehat{\boldsymbol{B}}_0(t)$ and leaves open the possibility of rotation about the direction of $\widehat{\boldsymbol{B}}_0(t)$, i.e., the component of $\boldsymbol{\omega}_{slo,lab}(t)$ parallel to $\widehat{\boldsymbol{B}}_0(t)$. It will prove useful later to choose a value of zero for this parallel component, such that $\boldsymbol{\omega}_{slo,lab}(t)$ appears as a purely nonsecular perturbation in Eq. (66), and this leads to

$$\boldsymbol{\omega}_{slo,lab}(t)=\widehat{\boldsymbol{B}}_0(t)\times\left(\frac{\partial\widehat{\boldsymbol{B}}_0(t)}{\partial t}\right)_{lab}. \tag{65}$$

Starting now from the general equation of motion (39) for the average spin magnetization $\boldsymbol{M}(t)$, with $\boldsymbol{B}_0(t)$ playing here the role of $\boldsymbol{B}(t)$, the equation of motion in the *slo* frame becomes

$$\left(\frac{\partial\boldsymbol{M}(t)}{\partial t}\right)_{slo}=\left(\frac{\partial\boldsymbol{M}(t)}{\partial t}\right)_{lab}+\boldsymbol{M}(t)\times\boldsymbol{\omega}_{slo,lab}(t)=\boldsymbol{M}(t)\times\big(\gamma\boldsymbol{B}_0(t)+\boldsymbol{\omega}_{slo,lab}(t)\big), \tag{66}$$

where the angular velocity $-\gamma\boldsymbol{B}_0(t)$ points in a fixed direction in the *slo* frame and the additional term $\boldsymbol{\omega}_{slo,lab}(t)$ is perpendicular to $\boldsymbol{B}_0(t)$.

Specific discussions will be clarified by the choice of an inertial *lab* frame with its Z axis parallel to $\boldsymbol{B}_0$ at an 'initial' date t_0, hence $\widehat{\boldsymbol{Z}}_{lab}(t_0)=\widehat{\boldsymbol{B}}_0(t_0)$, and by the choice of a *slo* frame with axes coincident with those of the *lab* frame at the same date t_0. Fig. 2 illustrates these choices. Analogous choices for the *sr* frame introduced later also help clarify the corresponding discussions.

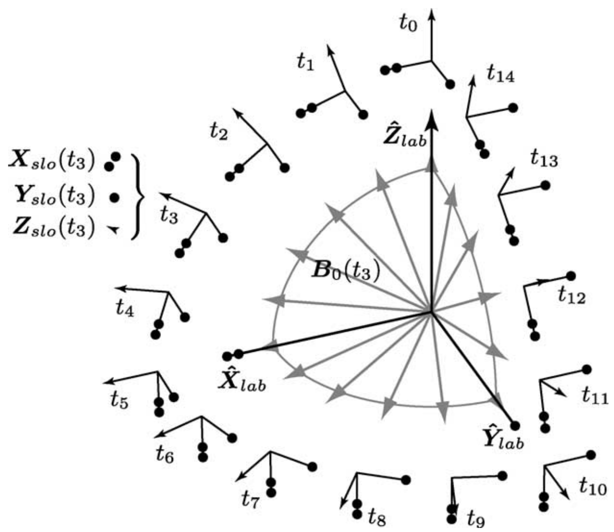

Fig. 2. Various vectors as seen by an observer that is immobile with respect to the laboratory frame. The vectors drawn in grey in the center of the figure show a magnetic field $\boldsymbol{B}_0(t)$ that rotates smoothly from the Z_{lab} direction at date t_0, first in the $Z_{lab}X_{lab}$ plane until it reaches the X_{lab} direction at date t_5, then in the $X_{lab}Y_{lab}$ plane until it reaches the Y_{lab} direction at date t_{10}, and finally in the $Y_{lab}Z_{lab}$ plane until it comes back to the Z_{lab} direction at date t_{15} (not shown). The (small) frames of coordinates in the outer part of the figure show the orientation of the *slo* frame at each discrete date at which $\boldsymbol{B}_0(t)$ is also shown. The direction of $\widehat{\boldsymbol{Z}}_{slo}(t)$ follows that of $\boldsymbol{B}_0(t)$, and the direction of $\widehat{\boldsymbol{X}}_{slo}(t)$ is chosen such that the angular velocity $\boldsymbol{\omega}_{slo,lab}(t)$ of the *slo* frame relative to the *lab* frame is perpendicular to $\boldsymbol{B}_0(t)$. In the simple example shown here, the *slo* frame executes smooth rotations of $\pi/2$ with respect to the *lab* frame, successively about $\widehat{\boldsymbol{Y}}_{lab}$, $\widehat{\boldsymbol{Z}}_{lab}$, and $\widehat{\boldsymbol{X}}_{lab}$. The interesting feature illustrated by this figure is that, when $\boldsymbol{B}_0(t)$ comes back at t_{15} to its original direction at t_0, the *slo* frame has rotated by $\phi=\pi/2$ about $\widehat{\boldsymbol{Z}}_{lab}$ compared to its original orientation at t_0. This 'geometrical phase' ϕ can be evaluated easily as the solid angle enclosed by the closed motion of $\boldsymbol{B}_0(t)$ as seen in the *lab* frame.

The perspective of interest here is that of (slow) *quasi-adiabatic* changes of the orientation of $\boldsymbol{B}_0(t)$ in the *lab* frame, in which $\boldsymbol{B}_0(t) = \boldsymbol{B}_0(t + \tau_{slo})$ is a periodic function of t with period τ_{slo}. The condition of *quasi-adiabaticity* is

$$k = \left[\frac{|\boldsymbol{\omega}_{slo,lab}(t)|}{|\gamma \boldsymbol{B}_0(t)|}\right]_{max} \ll 1. \tag{67}$$

If the same trajectory is followed by the orientation of $\boldsymbol{B}_0(t)$, but at a slower pace, k decreases by the same factor, τ_{slo} increases proportional to $1/k$, and $\boldsymbol{\omega}_{slo,lab}(t)$ decreases proportional to k.

Further discussions will be clarified by the introduction of a third frame of reference, labeled *sr*, that rotates with respect to the *slo* frame at the (large) angular velocity $\boldsymbol{\omega}_{sr,slo}(t) = -\gamma \boldsymbol{B}_0(t)$. The equation of motion of $\boldsymbol{M}(t)$ in the *sr* frame is

$$\left(\frac{\partial \boldsymbol{M}(t)}{\partial t}\right)_{sr} = \left(\frac{\partial \boldsymbol{M}(t)}{\partial t}\right)_{slo} + \boldsymbol{M}(t) \times \boldsymbol{\omega}_{sr,slo}(t) = \boldsymbol{M}(t) \times \boldsymbol{\omega}_{slo,lab}(t), \tag{68}$$

where $\boldsymbol{\omega}_{slo,lab}(t)$ appears in the *sr* frame as a (small) vector, perpendicular to the fixed direction of $\boldsymbol{B}_0(t)$, with a motion that combines its slow evolution in the *slo* frame with a fast rotation at the constant angular velocity $\gamma \boldsymbol{B}_0(t)$. Under these conditions, the motion of $\boldsymbol{M}(t)$ in the *sr* frame is a fast angular oscillation with a small amplitude of order k, superimposed on a very slow angular drift at a rate of order $1/k^2$ (this last conclusion is easily obtained with the help of the classical version of the Magnus expansion). Over one period τ_{slo} of the slow reorientation of $\boldsymbol{B}_0(t)$ in the *lab* frame, both the fast oscillation and the drift cause rotations of $\boldsymbol{M}(t)$ of order k in the *sr* frame. Hence $\boldsymbol{M}(t)$ remains immobile in the *sr* frame in the *quasi-adiabatic* approximation ($k \to 0$), just the same as if $\boldsymbol{B}_0(t)$ was immobile in the *lab* frame. It follows directly that, still in the *quasi-adiabatic* approximation and for durations of the order of τ_{slo}, the motion of $\boldsymbol{M}(t)$ in the *slo* frame is a simple rotation at the constant angular velocity $-\gamma \boldsymbol{B}_0(t)$, also completely ignorant of the slow reorientation of $\boldsymbol{B}_0(t)$ with respect to the *lab* frame.

All this may suggest that adiabatic changes in a simple (classical) Hamiltonian do not generate experimentally observable effects besides the trivially expected oscillations with period τ_{slo}. However, measurements are usually performed by instruments fixed in the *lab* frame, and the simple example illustrated in Fig. 2 shows that cyclic adiabatic changes in the (classical) Hamiltonian systematically rotate the *slo* and *sr* frames with respect to the *lab* frame by Berry's geometrical phase ϕ [7,8] for each period τ_{slo} of the slow evolution of the (classical) Hamiltonian. In the simple case of stroboscopic measurements after successive delays τ_{slo}, this results in a shift of the apparent precession frequency of the spins by ϕ/τ_{slo}.

6.2. Simple example, elementary quantum presentation using moving bases

It is well known that, for the present simple model of a free spin acted upon by a classical magnetic field, the classical and quantum predictions for the motion of $\boldsymbol{M}(t) = \langle \gamma \hbar \boldsymbol{I} \rangle(t)$ are exactly the same; hence a quantum treatment of the problem just discussed above will not lead to new conclusions. I shall, however, briefly proceed with such a treatment as a further example of the close analogy between the use of moving bases and that of moving frames.

The role of the classical equation of motion (39) in the *lab* frame will be played here by the von Neumann equation of motion (46) in the *lab* basis, with $\boldsymbol{B}_0(t)$ playing the role of the classical magnetic field. The simplification provided in the classical discussion by the *slo* frame is provided here by the basis $\{|slo_j(t)\rangle\}$ defined essentially by the requirement that it rotates at the angular velocity $\boldsymbol{\omega}_{slo,lab}(t)$ given by Eq. (65) with respect to the *lab* basis, hence

$$D_{[slo,lab]}(t) = \boldsymbol{\omega}_{slo,lab}(t) \cdot \hbar \boldsymbol{I}(t) = \left[\widehat{\boldsymbol{B}}_0(t) \times \left(\frac{\partial \widehat{\boldsymbol{B}}_0(t)}{\partial t}\right)_{lab}\right] \cdot \hbar \boldsymbol{I}(t), \tag{69}$$

and the von Neumann equation of motion in the *slo* basis is

$$\mathrm{i}\hbar \left(\frac{\partial \rho(t)}{\partial t}\right)_{[slo]} = \big[\big\{-\hbar \boldsymbol{I}(t) \cdot \big(\gamma \boldsymbol{B}_0(t) + \boldsymbol{\omega}_{slo,lab}(t)\big)\big\}, \rho(t)\big]. \tag{70}$$

Complete analogy of notation with the classical discussion of the previous subsection is ensured by the convenient 'initial' condition $W_{slo,lab}(t_0) = 1_{op}$. Eq. (70) can be discussed in the usual way, provided that all observables are expressed in terms of simple observables that are immobile in the *slo* basis, here the Cartesian components of $\boldsymbol{I}(t)$ in the *slo* frame. With this point of view, $\boldsymbol{B}_0(t)$ appears as immobile for calculations in the *slo* basis.

The role of the *sr* frame of the classical discussion is played here by the *sr* basis defined essentially by the requirement that it rotates at the angular velocity $-\gamma \boldsymbol{B}_0(t)$ with respect to the *slo* frame, hence

$$D_{[sr,slo]}(t) = -\gamma \boldsymbol{B}_0(t) \cdot \hbar \boldsymbol{I}(t), \tag{71}$$

and the von Neumann equation of motion in the *sr* basis is

$$\mathrm{i}\hbar \left(\frac{\partial \rho(t)}{\partial t}\right)_{[sr]} = \big[-\hbar \boldsymbol{I}(t) \cdot \boldsymbol{\omega}_{slo,lab}(t), \rho(t)\big], \tag{72}$$

where $\boldsymbol{\omega}_{slo,lab}(t)$ now appears, in the *sr* basis as a (small) angular velocity that essentially rotates at the high rate $\gamma \boldsymbol{B}_0(t)$ in a plane perpendicular to $\boldsymbol{B}_0(t)$. Approximate solutions of this equation are easily obtained by the Magnus expansion technique, and confirm the conclusion that no evolution takes place in the *sr* basis or frame, in the *quasi-adiabatic* limit.

Coming back to the *slo* basis and, eventually, to the *lab* basis, it is clear that the only non-trivial observable effects of a quasi-adiabatic change of the direction of $\boldsymbol{B}_0(t)$ in the *lab* frame are due to the geometrical phase ϕ.

In the quantum treatment of the simple model discussed here, ϕ appears as the angle of rotation of the reference directions defined by the basis *slo* with respect to those of the inertial basis *lab*, over a time interval τ_{slo}, in complete analogy with the corresponding classical discussion. Inspection easily shows that ϕ is also the additional phase difference between successive eigenstates of the Hamiltonian $H(t) = -\gamma\hbar \boldsymbol{I} \cdot \boldsymbol{B}_0(t)$ caused by the reorientation of $\boldsymbol{B}_0(t)$ over a delay τ_{slo}, as usually emphasized in discussions about Berry's phase.

6.3. A more general quantum presentation

In this subsection, I show how Berry's original derivation of the geometrical phase [7] can be presented using moving bases along the lines of the two previous subsections.

Let the Hamiltonian $H(\boldsymbol{R})$ depend upon the set of (slowly time dependent) parameters denoted $\boldsymbol{R}$. This is a laboratory frame description, which means that the Hamiltonian can be written as a linear combination of operators that are immobile in the inertial $\{|lab_j(t)\rangle\}$ basis, with coefficients that depend upon $\boldsymbol{R}$ and are time dependent through the time dependence of $\boldsymbol{R}$ only. The eigenvalue spectrum of $H(\boldsymbol{R})$ is assumed to be nondegenerate over the whole relevant range of $\boldsymbol{R}$. The equation of motion of the density operator $\rho(t)$ in the *lab* basis is

$$\mathrm{i}\hbar\left(\frac{\mathrm{d}\rho(t)}{\mathrm{d}t}\right)_{[lab]} = \big[H(\boldsymbol{R}), \rho(t)\big]. \tag{73}$$

In analogy with the *slo* basis of the previous subsection, an *h* basis will now be constructed, that follows the slow time dependence of the Hamiltonian. The basis vectors of *h* are the normalized eigenvectors of $H(\boldsymbol{R})$, denoted $|h_j(\boldsymbol{R},t)\rangle$, in which an explicit dependence upon the date t allows the presence of a phase factor $\exp(i\alpha_j(t))$ that cannot be expressed as a function of $\boldsymbol{R}$,

$$H(\boldsymbol{R})\big|h_j(\boldsymbol{R},t)\big\rangle = E_j(\boldsymbol{R})\big|h_j(\boldsymbol{R},t)\big\rangle, \quad \text{where } \big|h_j(\boldsymbol{R},t)\big\rangle = \exp\big(\mathrm{i}\alpha_j(t)\big)\big|h_j(\boldsymbol{R},t_0)\big\rangle. \tag{74}$$

t_0 is a reference date, the phases $\alpha_j(t)$ are real, $E_j(\boldsymbol{R})$ are the eigenvalues of $H(\boldsymbol{R})$, and $|h_j(\boldsymbol{R},t_0)\rangle$ is a linear combination of kets that are immobile in the *lab* basis with coefficients that depend only on $\boldsymbol{R}$ and j. The operators $W_{[h,lab]}(\boldsymbol{R},t)$ and $D_{[h,lab]}(\boldsymbol{R},t)$ used in the change of basis between *lab* and *h* are given by

$$W_{[h,lab]}(\boldsymbol{R},t) = \sum_j \big|h_j(\boldsymbol{R},t)\big\rangle\big\langle lab_j(t)\big| \quad \text{and} \quad D_{[h,lab]}(\boldsymbol{R},t) = \mathrm{i}\hbar\left(\frac{\mathrm{d}W_{[h,lab]}(\boldsymbol{R},t)}{\mathrm{d}t}\right)_{[lab]} W_{[lab,h]}(\boldsymbol{R},t), \tag{75}$$

where the total time derivative $\mathrm{d}/\mathrm{d}t$ includes the effects of the explicit variable t and of the implicit time dependence of $\boldsymbol{R}$. As an example, we have

$$\begin{aligned}\left(\frac{\mathrm{d}|h_j(\boldsymbol{R},t)\rangle}{\mathrm{d}t}\right)_{[lab]} &= \left(\frac{\partial|h_j(\boldsymbol{R},t)\rangle}{\partial t}\right)_{[lab]} + \left(\frac{\mathrm{d}\boldsymbol{R}}{\mathrm{d}t}\right)\cdot\big(\nabla_{\boldsymbol{R}}\cdot\big|h_j(\boldsymbol{R},t)\big\rangle\big)\\ &= \mathrm{i}\frac{\partial\alpha_j(t)}{\partial t}\big|h_j(\boldsymbol{R},t)\big\rangle + \left(\frac{\mathrm{d}\boldsymbol{R}}{\mathrm{d}t}\right)\cdot\big(\nabla_{\boldsymbol{R}}\cdot\big|h_j(\boldsymbol{R},t)\big\rangle\big).\end{aligned} \tag{76}$$

Using Eq. (31), the equation of motion (73) can be written in the *h* basis as

$$\mathrm{i}\hbar\left(\frac{\mathrm{d}\rho(t)}{\mathrm{d}t}\right)_{[h]} = \big[\big\{H(\boldsymbol{R}) - D_{[h,lab]}(\boldsymbol{R},t)\big\}, \rho(t)\big]. \tag{77}$$

Further distinction between the dynamical and geometrical contributions to the phases will be simplified if the phases of the basis kets $|h_j(\boldsymbol{R},t)\rangle$ are chosen in such a way that $D_{[h,lab]}(\boldsymbol{R},t)$ appears as a non-secular perturbation in Eq. (77). For this, the diagonal matrix elements of $D_{[h,lab]}(\boldsymbol{R},t)$, in a basis of eigenkets of $H(\boldsymbol{R})$, must all be equal to zero, hence, using Eqs. (74)–(76) and (13),

$$\begin{aligned}0 &= \frac{1}{\mathrm{i}\hbar}\big\langle h_j(\boldsymbol{R},t)\big|D_{[h,lab]}(\boldsymbol{R},t)\big|h_j(\boldsymbol{R},t)\big\rangle = \big\langle h_j(\boldsymbol{R},t)\big|\left(\frac{\partial|h_j(\boldsymbol{R},t)\rangle}{\partial t}\right)_{[lab]} + \left(\frac{\mathrm{d}\boldsymbol{R}}{\mathrm{d}t}\right)\cdot\big\{\big\langle h_j(\boldsymbol{R},t)\big|\big(\nabla_{\boldsymbol{R}}\cdot\big|h_j(\boldsymbol{R},t)\big\rangle\big)\big\}\\ &= \mathrm{i}\frac{\partial\alpha_j(t)}{\partial t} + \left(\frac{\mathrm{d}\boldsymbol{R}}{\mathrm{d}t}\right)\cdot\big\{\big\langle h_j(\boldsymbol{R},t)\big|\big(\nabla_{\boldsymbol{R}}\cdot\big|h_j(\boldsymbol{R},t)\big\rangle\big)\big\} \quad \text{for all } j.\end{aligned} \tag{78}$$

If the pace at which $\boldsymbol{R}$ evolves in time is changed by a factor k, specifically if the function $\boldsymbol{R}(t)$ is replaced by the function $\boldsymbol{R}(t_0 + k\{t - t_0\})$, then the adiabatic limit corresponds to $k \to 0$, the operator $D_{[h,lab]}(\boldsymbol{R}, t)$ is a small quantity of order k, and the delay τ after which $\boldsymbol{R}$ returns to its initial value at t_0 increases as $1/k$. Furthermore, when $D_{[h,lab]}(\boldsymbol{R}, t)$ is expressed in terms of operators that are immobile in basis h, it appears as evolving at a slow pace of order k.

Further discussions of dynamics in the adiabatic limit will be simplified by the use of a third basis *fas* whose motion with respect to the *h* basis is generated by $H(\boldsymbol{R}, t)$, hence $D_{[fas,h]}(\boldsymbol{R}, t) = H(\boldsymbol{R}, t)$ and

$$\mathrm{i}\hbar \left(\frac{\mathrm{d}\rho(t)}{\mathrm{d}t} \right)_{[fas]} = \left[-D_{[h,lab]}(\boldsymbol{R}, t), \rho(t) \right]. \tag{79}$$

When seen in the *fas* basis, $D_{[h,lab]}(\boldsymbol{R}, t)$ still appears as a small operator of order k, but evolving at fast paces governed by the differences between the eigenvalues of $H(\boldsymbol{R})$. The condition (78) ensures that no component of $D_{[h,lab]}(\boldsymbol{R}, t)$ escapes this fast time dependence in the *fas* basis. As a consequence, the motion of $\rho(t)$ in the *fas* basis is the superposition of a fast oscillation of amplitude of order k superimposed on a slow drift at a rate of order k^2. Over the duration τ (of order $1/k$) of a closed loop in parameter space, the total change of $\rho(t)$ with respect to the *fas* basis is of order k, hence negligible in the adiabatic limit $k \to 0$.

Coming back to the *h* basis, the motion of $\rho(t)$ in the adiabatic limit appears as governed by $H(\boldsymbol{R})$, completely unaffected by the slow time evolution of $\boldsymbol{R}$. However, at the last step, going from the *h* basis back to the *lab* basis, a significant phase effect shows up, given by Eq. (78) and related to the trajectory of $\boldsymbol{R}$ in parameter space. Inspection easily shows that this is exactly the geometrical phase introduced by Berry in Eq. (4) of [7], derived here in a slightly different way.

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