

APPENDIX B: DENSITY MATRIX FORMALISM

Wave functions and density matrix

The density matrix is a tool used to describe the state of a spin ensemble as well as its evolution in time. It allows the passage from the probabilistic treatment of a *system* of a few spins to the statistical treatment of a large *ensemble* of such systems.

Since we are interested in the magnetization we want to express this observable in terms of the wave function φ of the system. Let us concentrate on one of the nuclei in the system (e.g., nucleus A). The x component of the magnetic moment of nucleus A has the expectation value:

$$\langle \mu_{xA} \rangle = \langle \varphi | \mu_{xA} | \varphi \rangle = \gamma_A \hbar \langle \varphi | I_{xA} | \varphi \rangle \quad (\text{B1})$$

where I_{xA} is the operator of the x -component of the angular momentum of nucleus A in the given system. For instance, in an AX system the I_{xA} matrix is

$$\frac{1}{2} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \quad [\text{see (C12)}]$$

In order to calculate the macroscopic magnetization, we have to take the average (denoted by a bar) over the whole ensemble:

$$M_{xA} = N_o \overline{\langle \mu_{xA} \rangle} = N_o \gamma_A \hbar \overline{\langle \varphi | I_{xA} | \varphi \rangle} \quad (\text{B2})$$

where N_o is the number of systems per unit volume, equal to the number of A spins per unit volume. Similar equations can be written for every component and for every nucleus in the system.

In the Schrödinger representation I_{xA} is a time independent operator, therefore the time dependence of M_{xA} is contained in the wave function φ of each system. This, in turn, may be expressed as a

linear combination of the eigenstates $|n\rangle$ of the system:

$$\varphi = \sum_{n=1}^N c_n |n\rangle$$

N =number of quantum states of the system

Here again we observe that the eigenfunctions $|n\rangle$ are time independent (solutions of the time independent Schrödinger equation), so the time dependence is contained only in the coefficients c_n . In order to introduce these coefficients in the expression (B2), we put

$$\langle\varphi|I_{xA}|\varphi\rangle$$

in matrix form. The "ket" $|\varphi\rangle$ is a column matrix:

$$|\varphi\rangle = \begin{bmatrix} c_1 \\ c_2 \\ \cdot \\ \cdot \\ c_n \end{bmatrix}$$

The "bra" $\langle\varphi|$ is a row matrix

$$\langle\varphi| = [c_1^* \quad c_2^* \quad \cdot \quad \cdot \quad c_n^*]$$

The angular momentum operator I_{xA} is an N by N square matrix.

$$\begin{bmatrix} I_{11} & I_{12} & \cdot & \cdot & I_{1N} \\ I_{21} & I_{22} & \cdot & \cdot & I_{2N} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ I_{N1} & I_{N2} & \cdot & \cdot & I_{NN} \end{bmatrix}$$

The subscript "xA" has been omitted to simplify the writing.

Using the expressions for $\langle\varphi|$, I_{xA} , and $|\varphi\rangle$ on the previous page, we obtain:

$$\langle\varphi|I_{xA}|\varphi\rangle = [c_1^* \quad c_2^* \quad \cdot \quad \cdot \quad c_N^*]$$

$$\begin{aligned}
& \times \begin{bmatrix} I_{11} & I_{12} & \cdot & \cdot & I_{1N} \\ I_{21} & I_{22} & \cdot & \cdot & I_{2N} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ I_{N1} & I_{N2} & \cdot & \cdot & I_{NN} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \\ \cdot \\ \cdot \\ c_N \end{bmatrix} \\
& = \begin{bmatrix} c_1^* & c_2^* & \cdot & \cdot & c_n^* \end{bmatrix} \times \begin{bmatrix} \sum_m I_{1m} c_m \\ \sum_m I_{2m} c_m \\ \cdot \\ \cdot \\ \sum_m I_{Nm} c_m \end{bmatrix} = \sum_n \sum_m c_n^* I_{nm} c_m = \sum_n \sum_m I_{nm} c_m c_n^*
\end{aligned}
\tag{B4}$$

We have obtained a compact expression of

$$\langle \varphi | I_{xA} | \varphi \rangle$$

In order to introduce it in the expression (B2) of the magnetization we have to take its average over the whole ensemble of systems. The matrix elements I_{mn} are characteristic for the system. They are identical for all the systems in our macroscopic ensemble. Therefore in (B4) only the product $c_m c_n^*$ has to be averaged over the ensemble and we get

$$M_{xA} = N_o \gamma_A \sum_n \sum_m I_{nm} \overline{c_m c_n^*} \tag{B5}$$

where I_{nm} are the matrix elements of the operator I_{xA} . The only time variable elements in (B5) are the averaged products

$$\overline{c_m c_n^*}.$$

There are N^2 such products which, arranged in a square table, form the density matrix:

$$D = \begin{bmatrix} d_{11} & d_{12} & \cdot & \cdot & d_{1N} \\ d_{21} & d_{22} & \cdot & \cdot & d_{2N} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ d_{N1} & d_{N2} & \cdot & \cdot & d_{NN} \end{bmatrix} \quad (\text{B6})$$

with
$$d_{mn} = \overline{c_m c_n^*} \quad (\text{B7})$$

We notice that $d_{nm} = d_{mn}^*$, i.e., D is a Hermitian matrix.

Density matrix and magnetizations

We rewrite (B5) making use of the expression (B7)

$$M_{xA} = N_o \gamma_A \sum_n \sum_m I_{nm} d_{mn} = N_o \gamma_A \sum_n \sum_m I_{nm} d_{nm}^* \quad (\text{B8})$$

Relation (B8) represents the practical mode of calculating an observable magnetization component (in our case M_{xA}) when the density matrix D is known:

Multiply every matrix element of I_{xA} with the complex conjugate of the corresponding element of D and add all the products. Multiply the sum by $N_o \gamma_A \hbar$.

It is convenient to express the factor $N_o \gamma_A \hbar$ in terms of the equilibrium magnetization M_{oA} :

$$M_{oA} = \frac{N_o \gamma_A^2 \hbar^2 I(I+1) B_o}{3kT} \quad (\text{B9})$$

Note that M_{oA} is always a positive quantity, the absolute value of the equilibrium magnetization for nucleus A. For $I = 1/2$ the expression (B9) becomes:

$$M_{oA} = \frac{N_o \gamma_A^2 \hbar^2 B_o}{4kT} \quad (\text{B10})$$

In (I.3) we have introduced the quantity

$$p = \frac{h\nu_A}{kT} = \frac{\hbar\omega_A}{kT} = \frac{\hbar|\gamma_A|B_o}{kT} \quad (\text{B11})$$

related to the Boltzmann factor of nucleus A. In accordance with our sign convention (negative γ) this can be rewritten as

$$p = -\frac{\hbar\gamma_A B_o}{kT} \quad (\text{B12})$$

and (B10) becomes

$$M_{oA} = -\frac{N_o \gamma_A \hbar p}{4}$$

The factor $N_o \gamma_A \hbar$ in (B8) can now be written in the more convenient form

$$N_o \gamma_A \hbar = -\frac{4}{p} M_{oA} \quad (\text{B13})$$

For nucleus X (see I.4) the factor is

$$N_o \gamma_X \hbar = -\frac{4}{q} M_{oX}$$

Let us apply the "recipe" for finding the magnetization components to the system AX (two spin 1/2 nuclei). The number of states is $N=4$ and the (Hermitian) density matrix has the rank 4:

$$D = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} \\ d_{21} & d_{22} & d_{23} & d_{24} \\ d_{31} & d_{32} & d_{33} & d_{34} \\ d_{41} & d_{42} & d_{43} & d_{44} \end{bmatrix}$$

where $d_{kj} = d_{jk}^*$ and $d_{jj} = \text{real}$ ($d_{jj} = d_{jj}^*$).

The angular momentum components for the AX system are given in (C12) through (C15). We have for instance

$$I_{zA} = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \quad (\text{B14})$$

in which only four matrix elements out of 16 are nonvanishing.

Using (B8) and (B14) in this particular case we get:

$$\begin{aligned} M_{zA} &= -\frac{4}{p} M_{oA} \left(\frac{d_{11}}{2} - \frac{d_{22}}{2} + \frac{d_{33}}{2} - \frac{d_{44}}{2} \right) \\ &= -\frac{2}{p} M_{oA} (d_{11} - d_{22} + d_{33} - d_{44}) \end{aligned} \quad (\text{B15})$$

In the x direction

$$I_{xA} = \frac{1}{2} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \quad (\text{B16})$$

and the "recipe" leads to

$$M_{xA} = -\frac{2}{p} M_{oA} (d_{12}^* + d_{21}^* + d_{34}^* + d_{43}^*) \quad (\text{B17})$$

In the same way we obtain

$$M_{yA} = \frac{2i}{p} M_{oA} (d_{12}^* - d_{21}^* + d_{34}^* - d_{43}^*) \quad (\text{B18})$$

It is always convenient to combine M_x and M_y in one complex quantity, the transverse magnetization

$$M_T = M_x + iM_y \quad (\text{B19})$$

This leads to the simplified form

$$M_{TA} = -\frac{4}{p} M_{oA} (d_{12}^* + d_{34}^*) \quad (\text{B20})$$

The magnetization components for the other nucleus of the system, nucleus X, are given by

$$M_{zX} = -\frac{2}{q} M_{oX} (d_{11} + d_{22} - d_{33} - d_{44}) \quad (\text{B21})$$

$$M_{TX} = -\frac{4}{q} M_{oX} (d_{13}^* + d_{24}^*) \quad (\text{B22})$$

This is equivalent to calculating the trace (sum of diagonal elements) of the product $I \times D$:

$$\sum_n \sum_m I_{nm} d_{mn} = \text{Tr}(I \times D) \quad (\text{B23})$$

The density matrix at thermal equilibrium

At equilibrium the nondiagonal elements are null because of the random phase distribution of the complex coefficients c_m . We denote with ϕ_m the phase of the complex quantity c_m :

$$c_m = |c_m| \exp(i\phi_m) \quad (\text{B24})$$

A nondiagonal matrix element is

$$d_{mn} = \overline{c_m c_n^*} = |c_m| \cdot |c_n| \exp[i(\phi_m - \phi_n)] \quad (\text{B25})$$

The phase difference $\phi_m - \phi_n$ can have any value within 0 and 2π with equal probability. The complex number $\exp[i(\phi_m - \phi_n)]$, described as a vector in the complex plane, may be oriented in any direction. The average of a multitude of such vectors is null.

The diagonal elements are not null since $\phi_m - \phi_m = 0$.

$$d_{mm} = \overline{c_m c_m^*} = |c_m|^2 \quad (\text{B26})$$

In quantum mechanics $|c_m|^2$ is the probability of finding the system in the state $|m\rangle$; therefore $d_{mm} = P_m$ is the population of this state. The density matrix at equilibrium is

$$D = \begin{bmatrix} P_1 & 0 & \cdot & \cdot & 0 \\ 0 & P_2 & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & \cdot & \cdot & P_N \end{bmatrix} \quad (\text{B27})$$

where $\sum P_n = 1$ (normalized populations).

Evolution of the density matrix between pulses

In the absence of the r.f. excitation the Hamiltonian H accepts the kets $|n\rangle$ as eigenfunctions:

$$H|n\rangle = E_n|n\rangle \quad (\text{B28})$$

and the Schrödinger equation

$$\frac{-\hbar}{i} \cdot \frac{\partial \varphi}{\partial t} = H\varphi$$

becomes:

$$\frac{-\hbar}{i} \sum \frac{dc_n}{dt} \cdot |n\rangle = \sum c_n E_n |n\rangle \quad (\text{B29})$$

Rearranging (B29) gives

$$\sum \left[\left(c_n E_n + \frac{\hbar}{i} \cdot \frac{dc_n}{dt} \right) \cdot |n\rangle \right] = 0 \quad (\text{B30})$$

Due to the orthogonality of the eigenfunctions, (B30) is satisfied only if each term of the sum is null:

$$c_n E_n + \frac{\hbar}{i} \cdot \frac{dc_n}{dt} = 0 \quad (\text{B31})$$

Hence

$$\frac{1}{c_n} \cdot \frac{dc_n}{dt} = \frac{-iE_n}{\hbar} \quad (\text{B32})$$

or

$$\frac{d}{dt}(\ln c_n) = \frac{-iE_n}{\hbar} \quad (\text{B33})$$

Integrating (B33) yields:

$$\ln c_n = -\frac{iE_n}{\hbar}t + C \quad (\text{B34})$$

$$c_n = \exp\left(\frac{-iE_n}{\hbar}t\right) \cdot \exp(C) \quad (\text{B35})$$

The integration constant C may be related to the value of c_n at time $t = 0$. This gives $c_n(0) = \exp(C)$ and (B35) becomes

$$c_n = c_n(0) \cdot \exp\left(\frac{-iE_n}{\hbar}t\right) \quad (\text{B36})$$

Knowing the evolution of all c_n coefficients will allow us to predict the time variation of the density matrix, hence that of the magnetization:

$$\begin{aligned} d_{mn} &= \overline{c_m c_n^*} = \overline{c_m(0) \cdot c_n^*(0)} \cdot \exp\left(\frac{-i(E_m - E_n)}{\hbar}t\right) \\ &= d_{mn}(0) \cdot \exp(-i\omega_{mn}t) \end{aligned} \quad (\text{B37})$$

We have demonstrated here the relation (I.13) used in the density matrix treatment to describe the evolution between pulses. The populations are invariable because $E_m - E_m = 0$ (relaxation processes are neglected throughout this book).

Effects of radiofrequency pulses

We have to find the time evolution of the density matrix under a given Hamiltonian, as we did in the previous section, but there are two things that make the problem more complicated.

First, the Hamiltonian is now time-dependent (radiofrequency magnetic field). This problem can be circumvented by describing the evolution of the system in a rotating frame, in which the rotating magnetic field appears as an immobile vector B_1 , while the main magnetic field B_0 is replaced by

$$\Delta B = B_0 - \omega_{tr} / |\gamma|$$

The resultant of B_1 and ΔB is the effective field B_{eff} (Figure B.1).

The field B_1 is usually much larger than ΔB and the effective field practically is B_1 . The Hamiltonian in the rotating frame is then

$$H = |\gamma| \hbar B_1 I_x \quad (\text{B38})$$

as we have assumed that B_1 is applied along the x axis of the rotating frame. For comparison, in the absence of the r.f. field, the Hamiltonian in the rotating frame is

$$H = |\gamma| \hbar \Delta B I_z \quad (\text{B39})$$

while in the laboratory frame it has the expression

$$H = |\gamma| \hbar B_0 I_z \quad (\text{B40})$$

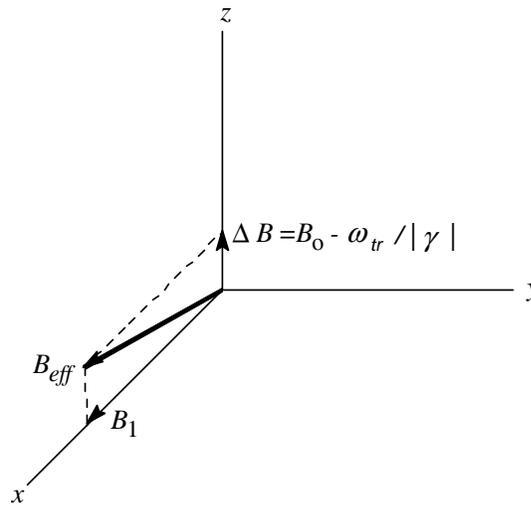


Figure B.1. The effective magnetic field B_{eff} in the rotating frame. Ox, Oy = axes of the rotating frame ; ω_{tr} = angular frequency of r.f. transmitter (angular velocity of the rotating frame)

Now we come to the second difficulty which prevents us from using the same approach as in the previous section: the new Hamiltonian (B38) does not have the kets $|n\rangle$ as eigenfunctions because we have passed from B_0 to B_1 . We have to use a more general equation which describes the evolution of D under any Hamiltonian:

$$\frac{dD}{dt} = \frac{i}{\hbar}(DH - HD) \quad (\text{B41})$$

the demonstration of which is given separately in the following section. The solution of (B41) is:

$$D(t) = \exp(-iHt/\hbar)D(0)\exp(iHt/\hbar) \quad (\text{B42})$$

This can be verified by calculating the time derivative of (B42):

$$\begin{aligned} \frac{dD}{dt} &= \left[\frac{d}{dt} \exp(-iHt/\hbar) \right] D(0) \exp(iHt/\hbar) \\ &\quad + \exp(-iHt/\hbar) \left[\frac{dD(0)}{dt} \right] \exp(iHt/\hbar) \\ &\quad + \exp(-iHt/\hbar) D(0) \left[\frac{d}{dt} \exp(iHt/\hbar) \right] \\ &= \frac{-iH}{\hbar} \exp(-iHt/\hbar) D(0) \exp(iHt/\hbar) + 0 \\ &\quad + \exp(-iHt/\hbar) D(0) \frac{iH}{\hbar} \exp(iHt/\hbar) \\ &= (-iH/\hbar)D + D(iH/\hbar) = i/\hbar(DH - HD) \end{aligned}$$

In the particular case of a strong r.f. field B_1 applied along the x axis of the rotating frame we have, according to (B38):

$$iHt/\hbar = i|\gamma|B_1I_x t = i\alpha I_x \quad (\text{B43})$$

where $\alpha = |\gamma|B_1 t$ is the rotation angle of the magnetization around B_1 in the time t (pulse duration). Relation (B42) becomes

$$D = \exp(-iI_x \alpha) D(0) \exp(-iI_x \alpha)$$

$$= R^{-1}D(0)R \quad (\text{B44})$$

where R is the rotation operator [cf (A6)-(A7)]; $D(0)$ and D denote the density matrix before and after the pulse. We have thus demonstrated the relation (I.8).

In order to get an explicit matrix expression for R we have to calculate

$$R_{\alpha x} = \exp(i\alpha I_x) \quad (\text{B45})$$

using a series expansion of the exponential [see(A11)],

$$R_{\alpha x} = 1 + i\alpha I_x + \frac{(i\alpha)^2 I_x^2}{2!} + \frac{(i\alpha)^3 I_x^3}{3!} + \dots \quad (\text{B46})$$

The powers of I_x may easily be calculated if one notices that

$$I_x^2 = \left(\frac{1}{4}\right) \cdot [\mathbf{1}] \quad (\text{B47})$$

$$I_x = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$I_x^2 = \frac{1}{4} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \left(\frac{1}{4}\right) [\mathbf{1}]$$

$$I_x^3 = \frac{1}{4} I_x = \frac{1}{8} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \left(\frac{1}{8}\right) 2I_x$$

$$I_x^4 = \frac{1}{16} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \left(\frac{1}{16}\right) [\mathbf{1}]$$

In general, for $n = \text{even}$ we have:

$$I_x^n = \frac{1}{2^n} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \left(\frac{1}{2^n}\right) \cdot [\mathbf{1}] \quad (\text{B48})$$

and for $n = \text{odd}$

$$I_x^n = \frac{1}{2^n} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \left(\frac{1}{2^n}\right) \cdot 2I_x \quad (\text{B49})$$

By using (C12) and (C14) one can verify that (B48) and (B49) are also true for I_{xA} and I_{xX} in a two spin system with $I=1/2$.

Introducing (B48) and (B49) in (B46) and separating the even and odd terms gives:

$$R_{\alpha x} = \left[1 - \frac{(\alpha/2)^2}{2!} + \frac{(\alpha/2)^4}{4!} - \dots \right] \times \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + i \left[\alpha/2 - \frac{(\alpha/2)^3}{3!} + \frac{(\alpha/2)^5}{5!} - \dots \right] \times \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (\text{B50})$$

Recognizing the sine (A12) and cosine (A13) series expansions we can write

$$R_{\alpha x} = \cos \frac{\alpha}{2} \cdot \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + i \sin \frac{\alpha}{2} \cdot \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \cos \frac{\alpha}{2} \cdot [\mathbf{1}] + i \sin \frac{\alpha}{2} \cdot (2I_x) \\ = \begin{bmatrix} \cos \frac{\alpha}{2} & 0 \\ 0 & \cos \frac{\alpha}{2} \end{bmatrix} + \begin{bmatrix} 0 & i \sin \frac{\alpha}{2} \\ i \sin \frac{\alpha}{2} & 0 \end{bmatrix} = \begin{bmatrix} \cos \frac{\alpha}{2} & i \sin \frac{\alpha}{2} \\ i \sin \frac{\alpha}{2} & \cos \frac{\alpha}{2} \end{bmatrix} \quad (\text{B51})$$

For nucleus A in an AX system the rotation operator is

$$R_{\alpha x} = \begin{bmatrix} \cos \frac{\alpha}{2} & i \sin \frac{\alpha}{2} & 0 & 0 \\ i \sin \frac{\alpha}{2} & \cos \frac{\alpha}{2} & 0 & 0 \\ 0 & 0 & \cos \frac{\alpha}{2} & i \sin \frac{\alpha}{2} \\ 0 & 0 & i \sin \frac{\alpha}{2} & \cos \frac{\alpha}{2} \end{bmatrix} \quad (\text{B52})$$

If the pulse is applied along the y axis, relations similar to (B48), (B49) apply:

$$I_y^n = \left(\frac{1}{2^n} \right) \cdot [\mathbf{1}] \quad \text{for n=even} \\ I_y^n = \left(\frac{1}{2^n} \right) \cdot (2I_y) \quad \text{for n=odd} \quad (\text{B53})$$

and we obtain

$$R_{\alpha y} = \exp(i\alpha I_y) = \cos \frac{\alpha}{2} \cdot [\mathbf{1}] + i \sin \frac{\alpha}{2} \cdot (2I_y) \quad (\text{B54})$$

Appendix C contains angular momentum components and rotation operators in matricial form, for a variety of spin systems and pulses. The reader may check some of those results by making $\alpha = 90^\circ$ or $\alpha = 180^\circ$ in the relations above.

If the radiofrequency field B_1 is applied along the $-x$ axis, it has the same effect as a pulse along the $+x$ axis, only the sense of rotation is reversed (left hand instead of right hand rule). The result of such a pulse is therefore a rotation by $-\alpha$ around Ox :

$$R_{\alpha(-x)} = R_{(-\alpha)x} = \exp(-i\alpha I_x) = \cos \frac{\alpha}{2} \cdot [\mathbf{1}] - i \sin \frac{\alpha}{2} \cdot (2I_x) \quad (\text{B55})$$

It is possible to extend the DM treatment to pulses with any phase (not only the four cardinal phases $x, y, -x, -y$) and/or off resonance pulses (B_{eff} does not coincide with B_1). We will not discuss them here because, as shown in the second part of the book, it is more convenient to handle them by means of the Product Operator formalism (see Appendix M).

Demonstration of (B41)

In order to demonstrate that

$$\frac{dD}{dt} = \frac{i}{\hbar} (DH - HD)$$

we follow the procedure used by Slichter (see Suggested Readings). We start with the (time dependent) Schrödinger equation

$$\frac{-\hbar}{i} \cdot \frac{\partial \varphi}{\partial t} = H\varphi$$

where

$$\varphi = \sum_{n=1}^N c_n |n\rangle$$

with the observation that $|n\rangle$ are not assumed to be eigenfunctions of H . Combining the last two equations gives

$$\frac{-\hbar}{i} \sum_{n=1}^N \frac{dc_n}{dt} \cdot |n\rangle = \sum_{n=1}^N c_n \mathbf{H} |n\rangle \quad (\text{B56})$$

If we premultiply this equation with the bra $\langle m |$ we get

$$\frac{-\hbar}{i} \sum_{n=1}^N \frac{dc_n}{dt} \langle m | n \rangle = \sum_{n=1}^N c_n \langle m | \mathbf{H} | n \rangle \quad (\text{B57})$$

The choice of normalized and orthogonal functions for the basis set $|n\rangle$ implies

$$\begin{aligned} \langle m | n \rangle &= 0 && \text{for } m \neq n \\ \langle m | n \rangle &= 1 && \text{for } m = n \end{aligned} \quad (\text{B58})$$

On the other hand $\langle m | \mathbf{H} | n \rangle$ is the matrix element H_{mn} in the matrix representation of the Hamiltonian, so (B57) becomes

$$\frac{-\hbar}{i} \frac{dc_n}{dt} = \sum_{n=1}^N c_n H_{mn} \quad (\text{B59})$$

If we consider now the product

$$p_{jk} = c_j c_k^* \quad (\text{B60})$$

its time derivative will be

$$\begin{aligned} \frac{dp_{jk}}{dt} &= \frac{dc_j}{dt} c_k^* + c_j \frac{dc_k^*}{dt} \\ &= \frac{dc_j}{dt} c_k^* + c_j \left(\frac{dc_k}{dt} \right)^* \\ &= \frac{-i}{\hbar} \left(\sum_{n=1}^N c_n H_{jn} \right) c_k^* + c_j \left[\frac{-i}{\hbar} \left(\sum_{n=1}^N c_n H_{kn} \right) \right]^* \\ &= \frac{i}{\hbar} \left(\sum_{n=1}^N c_j c_n^* H_{kn}^* - \sum_{n=1}^N c_n c_k^* H_{jn} \right) \end{aligned}$$

The change of sign comes from $(-i)^* = i$.

If we take into account that \mathbf{H} is Hermitian ($H_{kn}^* = H_{nk}$) we get

$$\frac{dp_{jk}}{dt} = \frac{i}{\hbar} \left(\sum_{n=1}^N p_{jn} H_{nk} - \sum_{n=1}^N H_{jn} p_{nk} \right) \quad (\text{B61})$$

The density matrix element d_{jk} is nothing other than the product p_{jk} averaged over the whole ensemble:

$$d_{jk} = \overline{p_{jk}}$$

On the other hand the Hamiltonian and its matrix elements are the same for all the systems within the ensemble, they are not affected by the operation of averaging. Taking the average on both sides of (B61) yields

$$\frac{dd_{jk}}{dt} = \frac{i}{\hbar} \left(\sum_{n=1}^N d_{jn} H_{nk} - \sum_{n=1}^N H_{jn} d_{nk} \right) \quad (\text{B62})$$

According to the matrix multiplication rule (see Appendix A) the sums in (B62) represent matrix elements of the products DH and HD , so (B62) can be written as

$$\left(\frac{dD}{dt} \right)_{jk} = \frac{i}{\hbar} \left[(DH)_{jk} - (HD)_{jk} \right] = \frac{i}{\hbar} (DH - HD)_{jk}$$

This demonstrates (B41) since the time derivative of a matrix is performed by taking the derivative of each element.